UNIT - I
THERMODYNAMICS - I

THERMODYNAMICS-I

Thermo – Energy Dynamics – Pattern of changes. The study of changes in energy associated with physical and chemical reaction is called as thermodynamics. In general, it is the study of effect of work, heat and energy on a system. When changes in energy are studied from the view of chemistry it is called as chemical thermodynamics.

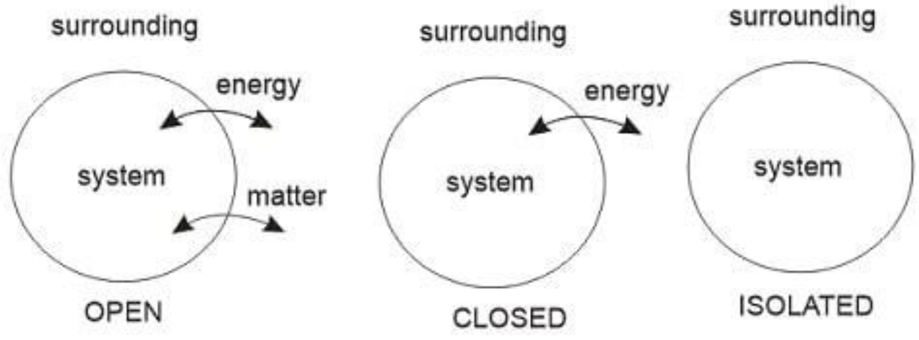
The study of changes in energy and chemical reaction are based on the basis of principles called as laws of thermodynamics. These are known as zeroth, first, second and third law of thermodynamics. Thermodynamics is a branch of physics that deals with heat and temperature, and their relation to energy, work, radiation, and properties of matter. The behavior of these quantities is governed by the four laws of thermodynamics which convey a quantitative description using measurable macroscopic physical quantities, but may be explained in terms of microscopic constituents by statistical mechanics. Thermodynamics applies to a wide variety of topics in science and engineering, especially physical chemistry, chemical engineering and mechanical engineering, but also in fields as complex as meteorology.

Historically, thermodynamics developed out of a desire to increase the efficiency of early steam engines, particularly through the work of French physicist Nicolas Léonard Sadi Carnot (1824) who believed that engine efficiency was the key that could help France win the Napoleonic Wars.

In thermodynamics, it is imperative to define a system and its surroundings because that concept becomes the basis for many types of descriptions and calculations.

A primary goal of the study of thermochemistry is to determine the quantity of heat exchanged between a system and its surroundings. The **system** is the part of the universe being studied, while the **surroundings** are the rest of the universe that interacts with the system. A system and its surroundings can be as large as the rain forests in South America or as small as the contents of a beaker in a chemistry laboratory. The type of system one is dealing with can have very important implications in chemistry because the type of system dictates certain conditions and laws of thermodynamics associated with that system.

Types of system



Open System

An open system is a system that freely exchanges *energy* and *matter* with its surroundings. For instance, when you are boiling soup in an open saucepan on a stove, energy and matter are being transferred to the surroundings through steam. The saucepan is an open system because it allows for the transfer of matter (for example adding spices in the saucepan) and for the transfer of energy (for example heating the saucepan and allowing steam to leave the saucepan).

Matters and energy can exchange in a open system. Matter can be exchanged rather easily: by adding matter (i.e spices) or removing matter (i.e tasting what is being cooked). Energy exchange is more complicated than matter exchange. There are a couple of ways that energy can be exchanged: through heat and through work (a more in-depth discussion of heat and work has been included below). Energy induced through heat can be demonstrated by bringing the system close to an object that dissipates heat (i.e. Bunsen burner, stove, etc.). By doing so, one is able to change the temperature of the system and therefore, induce energy through heat. Another way to increase the energy is through work. An example of inducing work is by taking a stirrer and then mixing the coffee in the cup with the stirrer. By mixing coffee, work is done as the coffee is being moved against a force.

Closed System

Putting a lid on the saucepan makes the saucepan a closed system. A **closed system** that exchanges **only energy** with its surroundings, not matter. By putting a lid on the saucepan, matter can no longer transfer because the lid prevents matter from entering the saucepan and leaving the saucepan. Still, the saucepan allows energy transfer. Imagine putting the saucepan on a stove and heating it. The saucepan allows energy transfer up and heats the contents inside it. For example, when a lid is put a beaker, it becomes a closed system. Next, when the contents in the beaker are boiled, the sides of the beaker will start getting foggy and misty. This fog and mist is the steam which covers the sides of the container because it cannot escape the beaker due to the lid. The fact that the beaker is able to produce this steam means that the beaker allows for energy transfer. Thus, even though a closed system cannot allow matter transfer, it can still allow energy transfer.

The methods of energy transfer in a closed system are the same as those described for an open system above.

Isolated System

A thermos is used to keep things either cold or hot. Thus, a thermos does not allow for energy transfer. Additionally, the thermos, like any other closed container, does not allow matter transfer because it has a lid that does not allow anything to enter or leave the container. As a result, the thermos is what we call an isolated system. An **isolated systemdoes not exchange energy or matter** with its surroundings. For example, if soup is poured into an insulated container (as seen below) and closed, there is no exchange of heat or matter. The fact that, in reality, a thermos is not perfect in keeping things warm/cold illustrates the difficulty in creating a truly isolated system. In fact, there are a few, if any, systems that exist in this world that are completely isolated systems.

Extensive Properties

Some properties of matter depend on the size of the sample, while some do not. An **extensive** property is a property that depends on the amount of matter in a sample. The mass of an object is a measure of the amount of matter that an object contains. A small sample of a certain type of matter will have a small mass, while a larger sample will have a greater mass. Another extensive property is volume. The volume of an object is a measure of the space that is occupied by that object.

Examples of extensive properties include:

- amount of substance, n
- energy, E
- enthalpy, H
- entropy, S
- Gibbs energy, G
- heat capacity, C_p
- Helmholtz energy, A or F
- internal energy, U
- mass, m
- volume, V

Intensive Properties

The electrical conductivity of a substance is a property that depends only on the type of substance. Silver, gold, and copper are excellent conductors of electricity, while glass and plastic are poor conductors. A larger or smaller piece of glass will not change this property. An **intensive** property is a property of matter that depends only on the type of matter in a sample and not on the amount. Other intensive properties include color, temperature, density, and solubility. The copper wire shown in the picture above has a certain electrical conductivity. You could cut off the small end sticking out and it would have the same conductivity as the entire long roll of wire shown here. The conductivity is a property of the copper metal itself, not of the length of the wire.

Functions:

Whenever compounds or chemical reactions are discussed, one of the first things mentioned is the state of the specific molecule or compound. "State" refers to temperature, pressure, and the amount and type of substance present. Once the state has been established, state functions can be defined. State functions are values that depend on the state of the substance, and not on how that state was reached. For example, density is a state function, because a substance's density is not affected by how the substance is obtained. Consider a quantity of H_2O: it does not matter whether that H_2O is obtained from the tap, from a well, or from a bottle, because as long as all three are in the same state, they have the same density. When deciding whether a certain property is a state function or not, keep this rule in mind: is this property or value affected by the path or way taken to establish it? If the answer is no, then it is a state function, but if the answer is yes, then it is not a state function.

Mathematics of State Functions

Another way to think of state functions is as integrals. Integrals depend on only three things: the function, the lower limit and the upper limit. Similarly, state functions depend on three things: the property, the initial value, and the final value. In other words, integrals illustrate how state functions depend only on the final and initial value and not on the object's history or the path taken to get from the initial to the final value.

Here is an example of the integral of enthalpy, H, where $t0$ represents the initial state and $t1$ represents the final state.
$\int t1to H(t)dt = H(t1) - H(to)$(1)

This is equivalent to a familiar definition of enthalpy:
$\Delta H = Hfinal - Hinitial$(2)

As represented by the solution to the integral, enthalpy is a state function because it only depends on the initial and final conditions, and not on the path taken to establish these conditions. Therefore, the integral of state functions can be taken using only two values: the final and initial values. On the other hand, multiple integrals and multiple limits of integration are required take the integral of a path function. If an integral of a certain property can be calculated using just the property and it's initial and final value, the property is a state function.

State Functions vs. Path Functions

State functions are defined by comparing them to path functions. As stated before, a state function is a property whose value does not depend on the path taken to reach that specific function or value. In essence, if something is not a path function, it is probably a state function. To better understand state functions, first define path functions and then compare path and state functions.

Path functions are functions that depend on the path taken to reach that specific value. For example, suppose you have $1000 in your savings account. Suppose you want to deposit some money to this account. The amount you deposit is a path function because it is dependent upon the path taken to obtain that money. In other words, the amount of money you will deposit in your savings account is dependent upon the path or way taken to obtain that money. If you work as a CEO of a company for a week versus working at a gas station for a week, you would receive two different amounts of money at the end of the week. Thus, a path function is a property or value that is dependent on the path taken to establish that value.

State functions do not depend on the path taken. Using the same example, suppose you have $1000 in your savings account. You withdraw $500 from your savings account. It does not matter whether you withdraw the $500 in one shot or whether you do so at a rate of $50. At the end when you receive your monthly statement, you will notice a net withdrawal of $500 and will see your resulting balance as $500. Thus, the bank balance is a state function because it does not depend on the path or way taken to withdraw or deposit money. In the end whether you do so in one lump or in multiple transactions, your bank balance will stay the same. The figure below illustrates state functions in the form of enthalpy:

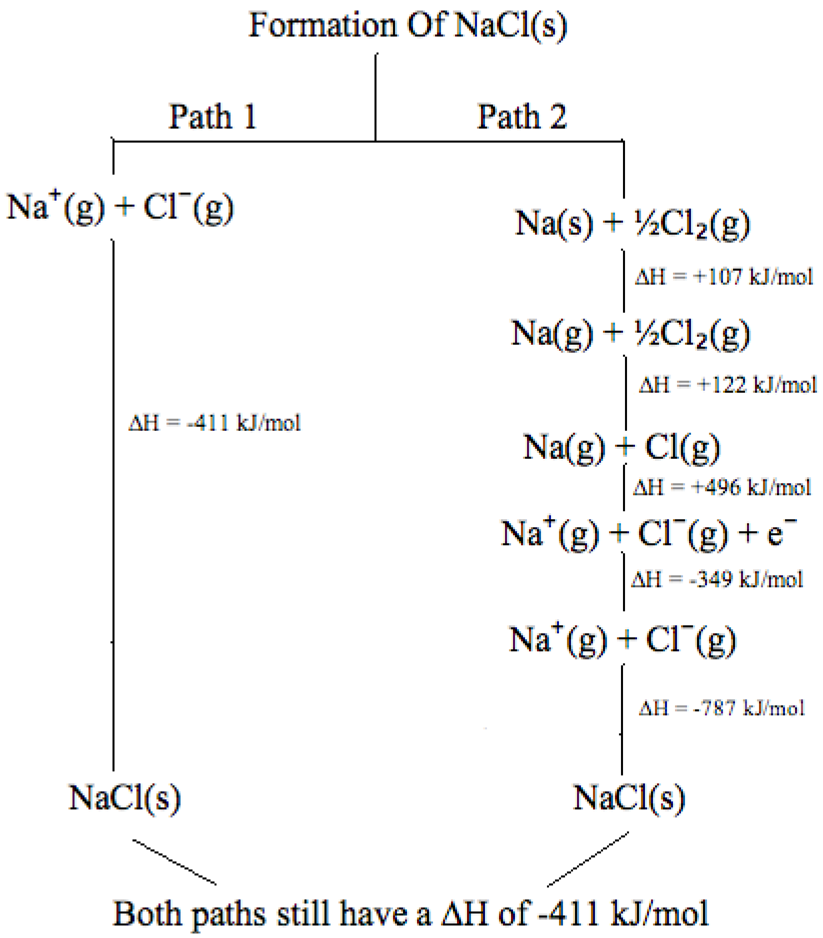


Figure. 1

State vs. Path Functions

A *state function* is a property whose value does not depend on the path taken to reach that specific value. In contrast, functions that depend on the path from two values are call *path functions*. Both path and state functions are often encountered in thermodynamics.

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Path one: The first path takes only a single step with an enthalpy of formation of -411 kJ/mol:
$Na+(g)+Cl-(g) \rightarrow NaCl(s)$(3)

Path two: The second path takes five steps to form $NaCl(s)$
$Na(s)+1/2Cl(g) \rightarrow Na(g)+1/2Cl(g)$(1: sublimation)
$Na(g)+1/2Cl(g) \rightarrow Na(g)+Cl(g)$(2: atomization)
$Na(g)+Cl(g) \rightarrow Na+(g)+Cl(g)$(3: ionization)
$Na+(g)+Cl(g) \rightarrow Na+(g)+Cl-(g)$(4: electron affinity)
$Na+(g)+Cl-(g) \rightarrow NaCl(s)$(5: lattice formation)

When enthalpies of all these steps are added, the enthalpy of formation of $NaCl(s)$ is still -411 kJ/mol. This is a perfect example of a state function: no matter which path is taken to form $NaCl(s)$, it results the same enthalpy of formation of -411 kJ/mol.

Summary of differences between state and path functions	
State Function	**Path Function**
Independent of path taken to establish property or value.	Dependent on path taken to establish property or value.
Can integrate using final and initial values.	Need multiple integrals and limits of integration in order to integrate.
Multiple steps result in same value.	Multiple steps result in different value.
Based on established state of system (temperature, pressure, amount, and identity of system).	Based on how state of system was established.
Normally represented by an uppercase letter.[1]	Normally represented by a lowercase letter.

Thermodynamic process

Classical thermodynamics considers three main kinds of thermodynamic process by change in a system, cycles in a system, and flow processes.

Defined by change in a system, a **thermodynamic process** is a passage of a thermodynamic system from an initial to a final state of thermodynamic equilibrium. The initial and final states are the defining elements of the process. The actual course of the process is not the primary concern, and thus often is ignored. This is the customary default meaning of the term 'thermodynamic process'. In general, during the actual course of a thermodynamic process, the system passes through physical states which are not describable as thermodynamic states, because they are far from internal thermodynamic equilibrium. Such processes are useful for thermodynamic theory.

Defined by a cycle of transfers into and out of a system, a **cyclic process** is described by the quantities transferred in the several stages of the cycle, which recur unchangingly. The descriptions of the staged states of the system are not the primary concern. Cyclic processes were important conceptual devices in the early days of thermodynamical investigation, while the concept of the thermodynamic state variable was being developed.

Defined by flows through a system, a **flow process** is a steady state of flows into and out of a vessel with definite wall properties. The internal state of the vessel contents is not the primary concern. The quantities of primary concern describe the states of the inflow and the outflow materials, and, on the side, the transfers of heat, work, and kinetic and potential energies for the vessel. Flow processes are of interest in engineering.

1) Isothermal process:

When the system undergoes change from one state to the other, but its temperature remains constant, the system is said to have undergone isothermal process. For instance, in our example of hot water in thermos flask, if we remove certain quantity of water from the flask, but keep its temperature constant at 50 degree Celsius, the process is said to be isothermal process.

Another example of isothermal process is latent heat of vaporization of water. When we heat water to 100 degree Celsius, it will not start boiling instantly. It will keep on absorbing heat at constant temperature; this heat is called latent heat of vaporization. Only after absorbing this heat water at constant temperature, water will get converted into steam.

2) Adiabatic process:

The process, during which the heat content of the system or certain quantity of the matter remains constant, is called as adiabatic process. Thus in adiabatic process no transfer of heat between the system and its surroundings takes place. The wall of the system which does not allows the flow of heat through it, is called as adiabatic wall, while the wall which allows the flow of heat is called as diathermic wall.

3) Isochoric process:

The process, during which the volume of the system remains constant, is called as isochoric process. Heating of gas in a closed cylinder is an example of isochoric process.

4) Isobaric process:

The process during which the pressure of the system remains constant is called as isobaric process. Example: Suppose there is a fuel in piston and cylinder arrangement. When this fuel is burnt the pressure of the gases is generated inside the engine and as more fuel burns more pressure is created. But if the gases are allowed to expand by allowing the piston to move outside, the pressure of the system can be kept constant.

The constant pressure and volume processes are very important. The Otto and diesel cycle, which are used in the petrol and diesel engine respectively, have constant volume and constant pressure processes. In practical situations ideal constant pressure and constant pressure processes cannot be achieved.

5) Reversible process:

In simple words the process which can be revered back completely is called a reversible process. This means that the final properties of the system can be perfectly reversed back to the original properties. The process can be perfectly reversible only if the changes in the process are infinitesimally small. In practical situations it is not possible to trace these extremely small changes in extremely small time, hence the reversible process is also an ideal process. The changes which occur during reversible process are in equilibrium with each other.

Exact and inexact differentials

In our investigation of heat and work we have come across various infinitesimal objects such as dE and dW. It is instructive to examine these infinitesimals more closely.

Consider the purely mathematical problem where $F_{(X,Y)}$ is some general function of two independent variables X and Y Consider the change in F in going from the point (x, y) in the x - y plane to the neighbouring point (x+dx, y+dy). This is given by

$$dF = F(x+dx, y+dy) - F(x, y),$$

which can also be written as

$$dF = X(x, y)\,dx + Y(x, y)\,dy,$$

$$X = \partial F/\partial x\, Y = \partial F/\partial y$$

where and. Clearly, dF is simply the infinitesimal difference between two adjacent values of the function F. This type of infinitesimal quantity is termed an *exact differential* to distinguish it from another type to be discussed presently. If we move in the x-y plane from an initial point i=(xi, yi) to a final point then the corresponding change in F is given by

$$\Delta F = F_f - F_i = \int_i^f dF = \int_i^f (X\,dx + Y\,dy).$$

Note that since the difference on the left-hand side depends only on the initial and final points, the integral on the right-hand side can only depend on these points as well. In other words, the value of the integral is independent of the path taken in going from the initial to the final point. This is the distinguishing feature of an exact differential. Consider an integral taken around a closed circuit in the x-y plane. In this case, the initial and final points correspond to the same point, so the difference $F_f - F_i$ is clearly zero. It follows that the integral of an exact differential over a closed circuit is always zero:

$$\oint dF \equiv 0.$$

Of course, not every infinitesimal quantity is an exact differential. Consider the infinitesimal object

$$đG \equiv X'(x, y)\,dx + Y'(x, y)\,dz,$$

where X' and Y' are two general functions of x and y. It is easy to test whether or not an infinitesimal quantity is an exact differential. Consider the expression (136). It is clear that since $X = \partial F/\partial x$ and $Y = \partial F/\partial y$ then

$$\frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x} = \frac{\partial^2 F}{\partial x \partial y}.$$

Thus, if

$$\frac{\partial X'}{\partial y} \neq \frac{\partial Y'}{\partial x}$$

(as is assumed to be the case), then $\text{đ}G$ cannot be an exact differential, and is instead termed an *inexact differential*. The special symbol đ is used to denote an inexact differential. Consider the integral of $\text{đ}G$ over some path in the x-y plane. In general, it is not true that

$$\int_i^f \text{đ}G = \int_i^f (X'\,dx + Y'\,dy)$$

is independent of the path taken between the initial and final points. This is the distinguishing feature of an inexact differential. In particular, the integral of an inexact differential around a closed circuit is not necessarily zero, so

$$\oint \text{đ}G \neq 0.$$

Consider, for the moment, the solution of

$$\text{đ}G = 0,$$

which reduces to the ordinary differential equation

$$\frac{dy}{dx} = -\frac{X'}{Y'}.$$

Since the right-hand side is a known function of x and y, the above equation defines a definite direction (*i.e.*, gradient) at each point in the x-y plane. The solution simply consists of drawing a system of curves in the x-y plane such that at any point the tangent to the curve is as specified in Eq. (145). where c is a labeling parameter. It follows that

$$\frac{d\sigma}{dx} \equiv \frac{\partial \sigma}{\partial x} + \frac{\partial \sigma}{\partial y}\frac{dy}{dx} = 0.$$

$$Y'\,\frac{\partial\sigma}{\partial x} = X'\,\frac{\partial\sigma}{\partial y} = \frac{X'\,Y'}{\tau},$$

where $\tau(x,y)$ is function of x and y. The above equation could equally well be written

$$X' = \tau\,\frac{\partial\sigma}{\partial x}, \qquad Y' = \tau\,\frac{\partial\sigma}{\partial y}.$$

Inserting Eq. (148) into Eq. (139) gives

$$\text{đ}G = \tau\left(\frac{\partial\sigma}{\partial x}\,dx + \frac{\partial\sigma}{\partial y}\,dy\right) = \tau\,d\sigma,$$

However, since the mean energy is just a function of the macrostate under consideration, $\bar{E}_f$ and $\bar{E}_i$ depend only on the initial and final states, respectively. Thus, the integral $\int d\bar{E}$ depends only on the initial and final states, and not on the particular process used to get between them.

Consider, now, the infinitesimal work done by the system in going from some initial macrostate i to some neighbouring final macrostate f. In general, $\text{đ}W = \sum \bar{X}_\alpha\,dx_\alpha$ is *not* the difference between two numbers referring to the properties of two neighboringmacrostates. Instead, it is merely an infinitesimal quantity characteristic of the process of going from state i to state f. In other words, the work $\text{đ}W$ is in general an inexact differential. The total work done by the system in going from any macrostate i to some other macrostate f can be written as

$$W_{if} = \int_i^f \text{đ}W,$$

where the integral represents the sum of the infinitesimal amounts of work $\text{đ}W$ performed at each stage of the process. In general, the value of the integral *does* depend on the particular process used in going from macrostate i to macrostate f.

Recall that in going from macrostate i to macrostate f the change $\Delta\bar{E}$ *does not* depend on the process used whereas the work W, in general, *does*. Thus, it follows from the first law of thermodynamics, Eq. (123), that the heat Q, in general, also depends on the process used. It follows that

$$đQ \equiv d\bar{E} + đW$$

is an inexact differential. However, by analogy with the mathematical example discussed previously, there must exist some integrating factor, T, say, which converts the inexact differential $đQ$ into an exact differential. So,

$$\frac{đQ}{T} \equiv dS.$$

It will be interesting to find out what physical quantities correspond to the functions T and S. Suppose that the system is thermally insulated, so that $Q = 0$. In this case, the first law of thermodynamics implies that

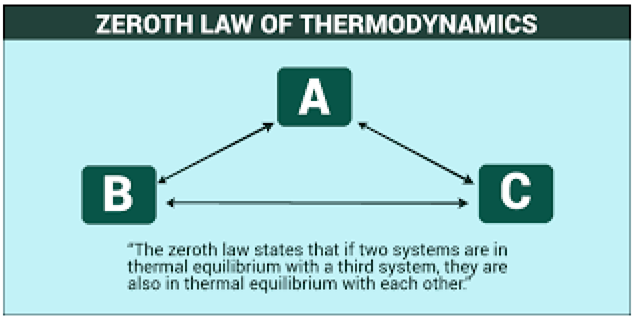
$$W_{if} = -\Delta\bar{E}.$$

Zeroth law of thermodynamics

The **zeroth law of thermodynamics** states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other. Accordingly, thermal equilibrium between systems is a transitive relation.

Two systems are said to be in the relation of thermal equilibrium if they are linked by a wall permeable only to heat and they do not change over time.[1] As a convenience of language, systems are sometimes also said to be in a relation of thermal equilibrium if they are not linked so as to be able to transfer heat to each other, but would still not do so (even) if they were connected by a wall permeable only to heat.

When a body 'A' is in thermal equilibrium with another body 'b', and also separately in thermal equilibrium with a body 'C', then body 'B' and 'C' will also be in thermal equilibrium with each other. This statement defines the zeroth law of thermodynamics. The law is based on temperature measurement.



"The zeroth law states that if two systems are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other."

Zeroth Law of Thermodynamics Example and Applications

This law is mostly used to compare temperatures of different objects.

To measure the accurate temperature, a reference body is required and a certain characteristic of that body which changes with temperature. The change in that characteristic may be taken as an indication of a change of temperature. That selected characteristic is known as thermodynamic property.

Nonetheless, the most common application of the zeroth law of thermodynamics can be seen in thermometers. We can observe the zeroth law in action by taking a very common thermometer having mercury in a tube. As the temperature is increased this mercury expands since the area of the tube is constant. Due to this expansion, the height is increased. Now, the increase in the height of the mercury label shows the changes in temperature and basically helps us to measure it.

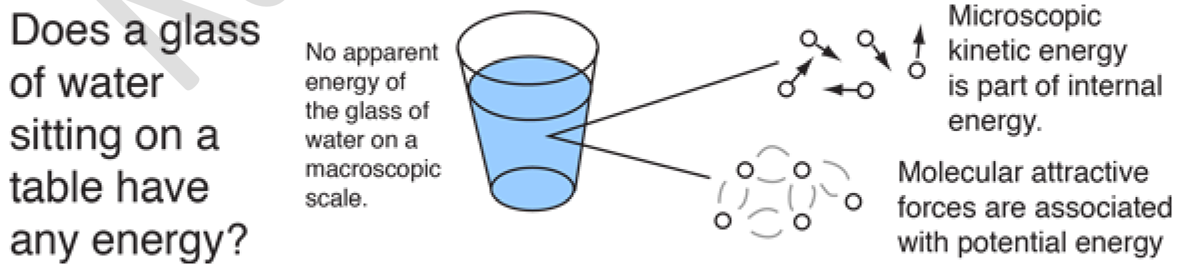
First law of thermodynamics

The First Law of Thermodynamics states that heat is a form of energy, and thermodynamic processes are therefore subject to the principle of conservation of energy. This means that heat energy cannot be created or destroyed. It can, however, be transferred from one location to another and converted to and from other forms of energy.

Mitra continued, "The change in internal energy of a system is the sum of all the energy inputs and outputs to and from the system similarly to how all the deposits and withdrawals you make determine the changes in your bank balance.” This is expressed mathematically as: $\Delta U = Q - W$, where ΔU is the change in the internal energy, Q is the heat added to the system, and W is the work done by the system.

Internal energy

Internal energy is defined as the energy associated with the random, disordered motion of molecules. It is separated in scale from the macroscopic ordered energy associated with moving objects; it refers to the invisible microscopic energy on the atomic and molecular scale. For example, a room temperature glass of water sitting on a table has no apparent energy, either potential or kinetic. But on the microscopic scale it is a seething mass of high speed molecules traveling at hundreds of meters per second. If the water were tossed across the room, this microscopic energy would not necessarily be changed when we superimpose an ordered large scale motion on the water as a whole.



Enthalpy

Enthalpy, a property of a thermodynamic system, is equal to the system's internal energy plus the product of its pressure and volume. In a system enclosed so as to prevent mass transfer, for processes at constant pressure, the heat absorbed or released equals the change in enthalpy.

The unit of measurement for enthalpy in the International System of Units (SI) is the joule.

Enthalpy comprises a system's internal energy, which is the energy required to create the system, plus the amount of work required to make room for it by displacing its environment and establishing its volume and pressure.

Enthalpy is a state function that depends only on the prevailing equilibrium state identified by the system's internal energy, pressure, and volume. It is an extensive quantity.

Change in enthalpy (ΔH) is the preferred expression of system energy change in many chemical, biological, and physical measurements at constant pressure, because it simplifies the description of energy transfer. In a system enclosed so as to prevent matter transfer, at constant pressure, the enthalpy change equals the energy transferred from the environment through heat transfer or work other than expansion work.

The enthalpy of an ideal gas is a function of temperature only, so does not depend on pressure. Real materials at common temperatures and pressures usually closely approximate this behavior, which greatly simplifies enthalpy calculation and use in practical designs and analyses.

Formal definition

The enthalpy of a thermodynamic system is defined as

$H = U + pV$,

where

H is enthalpy,

U is the internal energy of the system,

p is pressure,

V is the volume of the system.

Enthalpy Change Accompanying a Change in State

When a liquid vaporizes the liquid must absorb heat from its surroundings to replace the energy taken by the vaporizing molecules in order for the temperature to remain constant. This heat required to vaporize the liquid is called enthalpy of vaporization (or heat of vaporization). For example, the vaporization of one mole of water the enthalpy is given as:

$\Delta H = 44.0$ kJ at 298 K

When a solid melts, the required energy is similarly called enthalpy of fusion (or heat of fusion). For example, one mole of ice the enthalpy is given as:

$\Delta H = 6.01$ kJ at 273.15 K

$\Delta H = \Delta U + p\Delta V$(5)

According to the second equation, the ΔH will also be greater than zero. On the other hand, an exothermic reaction at constant pressure is when heat is released. This implies that the system gives off heat to the surroundings, so q is less than zero. Furthermore, ΔH will be less than zero.

Effect of Temperature on Enthalpy

When the temperature increases, the amount of molecular interactions also increases. When the number of interactions increase, then the internal energy of the system rises. According to the first equation given, if the internal energy (U) increases then the ΔHincreases as temperature rises. We can use the equation for heat capacity and Equation 2 to derive this relationship.

$C=q\Delta T$(7)

Under constant pressure, substitute Equation 6into Equation 7: $Cp=(\Delta H\Delta T)P$(8)

where the subscript Pindicates the derivative is done under constant pressure.

Heat capacity

Heat capacity, ratio of heat absorbed by a material to the temperature change. It is usually expressed as calories per degree in terms of the actual amount of material being considered, most commonly a mole (the molecular weight in grams). The heat capacity in calories per gram is called specific heat. The definition of the calorie is based on the specific heat of water, defined as one calorie per degree Celsius.

Stefan-Boltzmann law, statement that the total radiant heatpower emitted from a surface is proportional to the fourth power of its absolute temperature. SE is the radiant heat energy emitted from a unit area in one second (that is, the power from a unit area) and T is the absolute temperature (in kelvins), then $E = \sigma T^4$, the Greek letter sigma (σ) representing the constant of proportionality, called the Stefan-Boltzmann constant. This constant has the value $5.670374419 \times 10^{-8}$watt per metre^2 per K^4. The law applies only to blackbodies, theoretical surfaces that absorb all incident heat radiation.

Cp to Cv Ratio γ

Heat-capacity values that apply to a given substance under conditions in which either the temperature (T) or the pressure (P) is held constant throughout the problem. The basic equations $\Delta H = E + P\Delta V$ and $P\Delta V = R\Delta T$.

The latter two equations are another way to express change in enthalpy, ΔH, is:$E + R\Delta T$

Although no derivation is provided here, one way to express the first law of thermodynamics, which applies to closed systems and which may have heard colloquially stated as "Energy is neither created nor destroyed," is:$\Delta E = C_v\Delta T$

The Cp and Cv of Air

The C_p and C_v of air are both important in the study of fluid dynamics because air (consisting of a mixture of mostly nitrogen and oxygen) is the most common gas that humans experience. Both C_p and C_v are temperature-dependent, and not precisely to the same extent; as it happens, C_v rises slightly faster with increasing temperature. This means that the "constant" γ is not in fact constant, but it is surprisingly close across a range of likely temperatures. For example, at 300 degrees Kelvin, or K (equal to 27 C), the value of γ is 1.400;

at a temperature of 400 K, which is 127 C and considerably above the boiling point of water, the value of γ is 1.395.

Heat Capacity at Constant Volume

$Q = nC_V\Delta T$

For an ideal gas, applying the First Law of Thermodynamics tells us that heat is also equal to:

$Q = \Delta E_{int} + W$, although $W = 0$ at constant volume.

For a monatomic ideal gas we showed that $\Delta E_{int} = (3/2)nR\Delta T$

Comparing our two equations

$Q = nC_V\Delta T$ and $Q = (3/2)nR\Delta T$

we see that, for a monatomic ideal gas:

$C_V = (3/2)R$

For diatomic and polyatomic ideal gases we get:

diatomic: $C_V = (5/2)R$

polyatomic: $C_V = 3R$

This is from the extra 2 or 3 contributions to the internal energy from rotations.

Because $Q = \Delta E_{int}$ when the volume is constant, the change in internal energy can always be written:

$\Delta E_{int} = n\ C_V\ \Delta T$

Heat Capacity at Constant Pressure

For an ideal gas at constant pressure, it takes more heat to achieve the same temperature change than it does at constant volume. At constant volume all the heat added goes into raising the temperature. At constant pressure some of the heat goes to doing work.

$Q = nC_P\Delta T$

For an ideal gas, applying the First Law of Thermodynamics tells us that heat is also equal to:

$Q = \Delta E_{int} + W$

At constant pressure $W = P\Delta V = nR\Delta T$

For a monatomic ideal gas, where $\Delta E_{int} = (3/2)nR\Delta T$, we get:

$Q = (3/2)nR\Delta T + nR\Delta T = (5/2)nR\Delta T$

So, for a monatomic ideal gas:

$C_P = (5/2)R$

For diatomic and polyatomic ideal gases we get:

diaatomic: $C_P = (7/2)R$

polyatomic: $C_P = 4R$

The ratio C_P / C_V

It turns out that the ratio of the specific heats is an important number. The symbol we use for the ratio is γ. For a monatomic ideal gas we have:

$\gamma = C_P / C_V = [5R/2] / [3R/2] = 5/3$

Heat capacity and internal energy

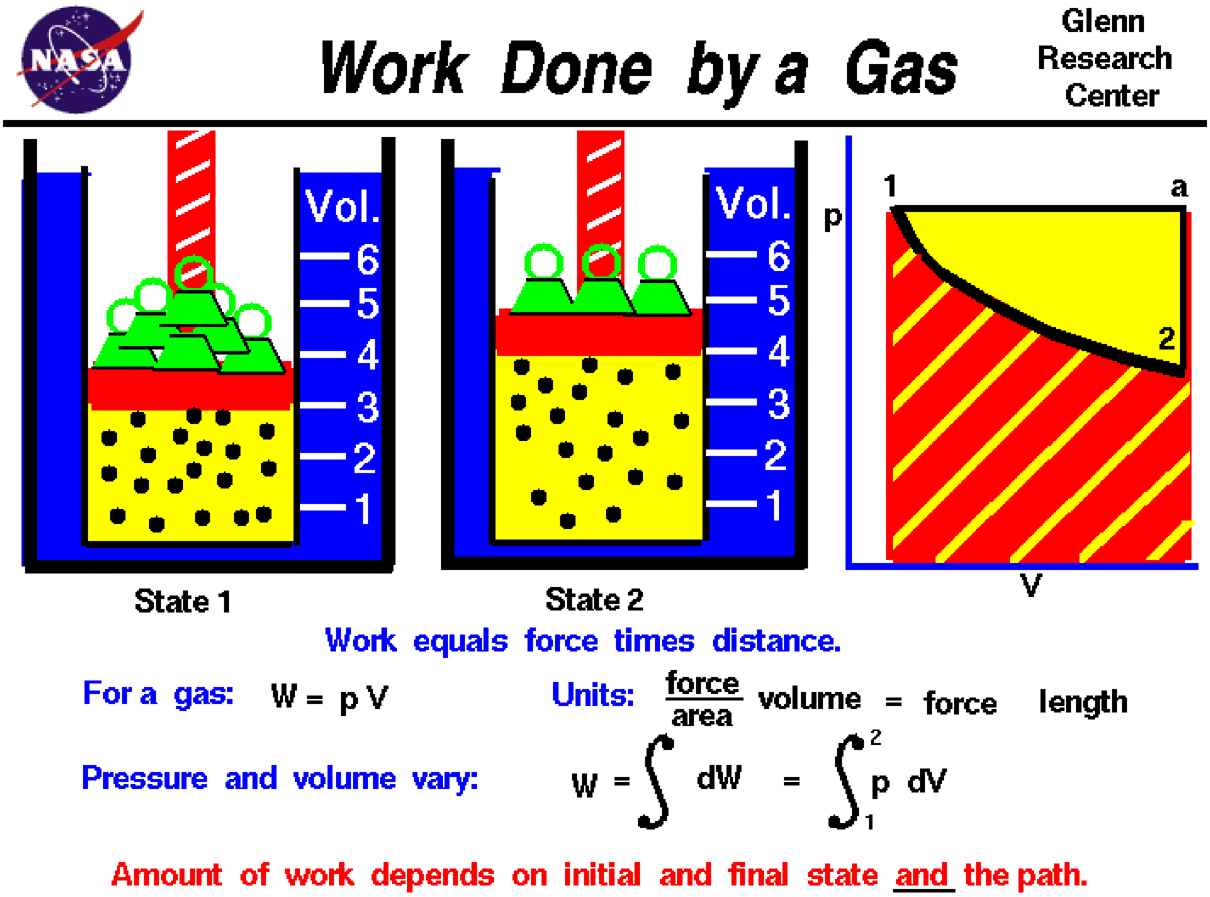
The goal in defining heat capacity is to relate changes in the internal energy to measured changes in the variables that characterize the states of the system. For a system consisting of a single pure substance, the only kind of work it can do is atmospheric work, and so the first law reduces to $dU = d'Q - PdV$. (28)

Suppose now that U is regarded as being a function$U(T, V)$ of the independent pair of variables T and V. The differential quantity dU can always be expanded in terms of its partial derivatives according to $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial T}\right)_T dV$ (29) where the subscripts denote the quantity being held constant when calculating derivatives. Substituting this equation into $dU = d'Q - PdV$ then yields the general expression $d'Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial T}\right)_T\right] dV$ (30) for the path-dependent heat. The path can now be specified in terms of the independent variables T and V. For a temperature change at constant volume, $dV = 0$ and, by definition of heat capacity, $d'Q_V = C_V dT$. (31) The above equation then gives immediately $C_V = \left(\frac{\partial U}{\partial T}\right)_V$(32) for the heat capacity at constant volume, showing that the change in internal energy at constant volume is due entirely to the heat absorbed.

To find a corresponding expression for C_P, one need only change the independent variables to T and P and substitute the expansion $dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$ (33) for dV in equation (28) and correspondingly for dU to obtain $d'Q = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP.$ (34) For a temperature change at constant pressure, $dP = 0$, and, by definition of heat capacity, $d'Q = C_P dT$, resulting in $C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P.$ (35)

The two additional terms beyond C_V have a direct physical meaning. The term $P\left(\frac{\partial V}{\partial T}\right)_P$ represents the additional atmospheric work that the system does as it undergoes thermal expansion at constant pressure, and the second term involving $\left(\frac{\partial U}{\partial V}\right)_T$represents the internal work that must be done to pull the system apart against the forces of attraction between the molecules of the substance (internal stickiness). Because there is no internal stickiness for an ideal gas, this term is zero, and, from the ideal gas law, the remaining partial derivative is $P\left(\frac{\partial V}{\partial T}\right)_P = nR.$ (36) With these substitutions the equation for C_P becomes simply $C_P = C_V + nR$ (37) or $c_P = c_V + R$ (38) for the molar specific heats. For example, for a monatomic ideal gas (such as helium), $c_V = 3R/2$ and $c_P = 5R/2$ to a good approximation. $c_V T$ represents the amount of translational kinetic energy possessed by the atoms of an ideal gas as they bounce around randomly inside their container. Diatomic molecules (such as oxygen) and polyatomic molecules (such as water) have additional rotational motions that also store thermal energy in their kinetic energy of rotation. Each additional degree of freedom contributes an additional amount R to c_V. Because diatomic molecules can rotate about two axes and polyatomic molecules can rotate about three axes, the values of c_V increase to $5R/2$ and $3R$ respectively, and c_P correspondingly increases to $7R/2$ and $4R$. (c_V and c_P increase still further at high temperatures because of vibrational degrees of freedom.) For a real gas such as water vapour, these values are only approximate, but they give the correct order of magnitude. For example, the correct values are c_P = 37.468 joules per K (i.e., 4.5*R*) and $c_P - c_V$ = 9.443 joules per K (i.e., 1.14*R*) for water vapour at 100 °C and 1 atmosphere pressure.

Work is the energy required to move something against a force.The energy of a system can change due to work and other forms of energy transfer such as heat.Gases do expansion or compression work following the equation:Work = −PΔV



Thermodynamics is a branch of physics which deals with the energy and work of a system. Thermodynamics deals only with the large scale response of a system which we can observe and measure in experiments. In aerodynamics, we are most interested in the thermodynamics of high speed flows, and in propulsion systems which produce thrust by accelerating a gas. To understand how thrust is created, it is useful to study the basic thermodynamics of gases.

The state of a gas is determined by the values of certain measurable properties like the pressure,temperature, and volume which the gas occupies. The values of these variables and the state of the gas can be changed. On this figure we show a gas confined in a blue jar in two different states. On the left, in State 1, the gas is at a higher pressure and occupies a smaller volume than in State 2, at the right. We can represent the state of the gas on a graph of pressure versus volume, which is called a p-V diagram as shown at the right. To change the state of the gas from State 1 to State 2, we must change the conditions in the jar, either by heating the gas, or physically changing the volume by moving a piston, or by changing the pressure by adding or removing weights from the piston. In some of these changes, we do work on, or have work done by the gas, in other changes we add, or remove heat. Thermodynamics helps us determine the amount of work and the amount of heat necessary to change the state of the gas. *Notice that in this example we have a fixed* ***mass*** *of gas. We can therefore plot either the physical volume or the specific volume, volume divided by mass, since the change is the same for a constant mass. On the figure, we use physical volume.*

Scientists define work**W** to be the product of force **F** acting through a distance **s** : W = F x s
For a gas, work is the product of the pressure **p** and the volume **V** during a change of volume.
W = p x V

We can do a quick units check to see that pressure **force / area**times volume **area x length** gives units of force times length which are the units of work
W = (force / area) * (area * length) = force * length

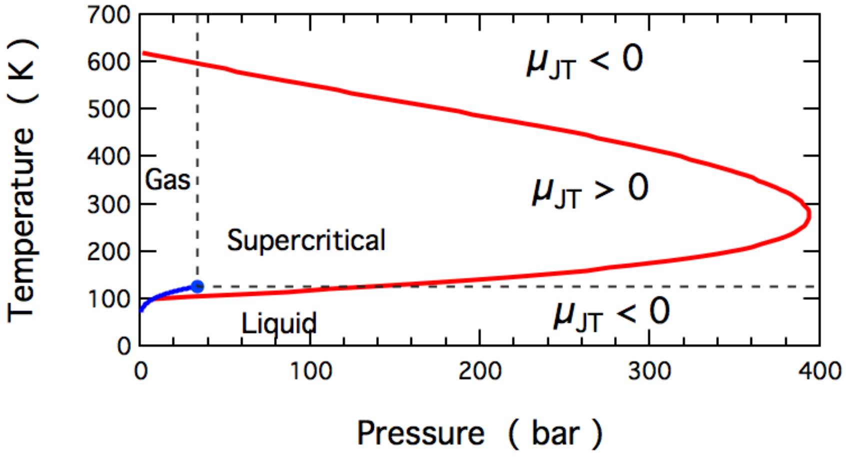
Joule–Thomson effect

In thermodynamics, the **Joule–Thomson effect** (also known as the **Joule–Kelvin effect** or **Kelvin–Joule effect**) describes the temperature change of a *real* gas or liquid (as differentiated from an ideal gas) when it is forced through a valve or porous plug while keeping it insulated so that no heat is exchanged with the environment. This procedure is called a *throttling process* or *Joule–Thomson process*.

joule-thomson coefficient

The *adiabatic* (no heat exchanged) expansion of a gas may be carried out in a number of ways. The change in temperature experienced by the gas during expansion depends not only on the initial and final pressure, but also on the manner in which the expansion is carried out.

- If the expansion process is reversible, meaning that the gas is in thermodynamic equilibrium at all times, it is called an *isentropic* expansion. In this scenario, the gas does positive work during the expansion, and its temperature decreases.
- In a free expansion, on the other hand, the gas does no work and absorbs no heat, so the internal energy is conserved. Expanded in this manner, the temperature of an ideal gas would remain constant, but the temperature of a real gas decreases, except at very high temperature.
- The method of expansion discussed in this article, in which a gas or liquid at pressure P_1 flows into a region of lower pressure P_2 without significant change in kinetic energy, is called the Joule–Thomson expansion. The expansion is inherently irreversible. During this expansion, enthalpy remains unchanged (see proof below). Unlike a free expansion, work is done, causing a change in internal energy. Whether the internal energy increases or decreases is determined by whether work is done on or by the fluid; that is determined by the initial and final states of the expansion and the properties of the fluid.



Sign of the Joule–Thomson coefficient, for N_2. Within the region bounded by the red line, a Joule–Thomson expansion produces cooling outside that region, the expansion produces heating. The gas–liquid coexistence curve is shown by the blue line, terminating at the critical point (the solid blue circle). The dashed lines demarcates the regions where N_2 is neither a supercritical fluid, a liquid, nor a gas.

The temperature change produced during a Joule–Thomson expansion is quantified by the Joule–Thomson coefficient, This coefficient may be either positive (corresponding to cooling) or negative (heating); the regions where each occurs for molecular nitrogen, N_2, are shown in the figure. Note that most conditions in the figure correspond to N_2 being a supercritical fluid, where it has some properties of a gas and some of a liquid, but can not be really described as being either. The coefficient is negative at both very high and very low temperatures; at very high pressure it is negative at all temperatures. The maximum inversion temperature (621 K for N_2) occurs as zero pressure is approached. For N_2 gas at low pressures,

is negative at high temperatures and positive at low temperatures. At temperatures below the gas-liquid coexistence curve, N_2 condenses to form a liquid and the coefficient again becomes negative. Thus, for N_2 gas below 621 K, a Joule–Thomson expansion can be used to cool the gas until liquid N_2 forms.

There are two factors that can change the temperature of a fluid during an adiabatic expansion: a change in internal energy or the conversion between potential and kinetic internal energy. Temperature is the measure of thermal kinetic energy (energy associated with molecular motion); so a change in temperature indicates a change in thermal kinetic energy. The internal energy is the sum of thermal kinetic energy and thermal potential energy. Thus, even if the internal energy does not change, the temperature can change due to conversion between kinetic and potential energy; this is what happens in a free expansion and typically produces a decrease in temperature as the fluid expands. If work is done on or by the fluid as it expands, then the total internal energy changes. This is what happens in a Joule–Thomson expansion and can produce larger heating or cooling than observed in a free expansion.

In a Joule–Thomson expansion the enthalpy remains constant. The enthalpy, is defined as where is internal energy, is pressure, and is volume. Under the conditions of a Joule–thomson expansion, the change in represents the work done by the fluid (see the proof below). If increases, with constant, then must decrease as a result of the fluid doing work on its surroundings. This produces a decrease in temperature and results in a positive Joule–Thomson coefficient. Conversely, a decrease in means that work is done on the fluid and the internal energy increases. If the increase in kinetic energy exceeds the increase in potential energy, there will be an increase in the temperature of the fluid and the Joule–Thomson coefficient will be negative.

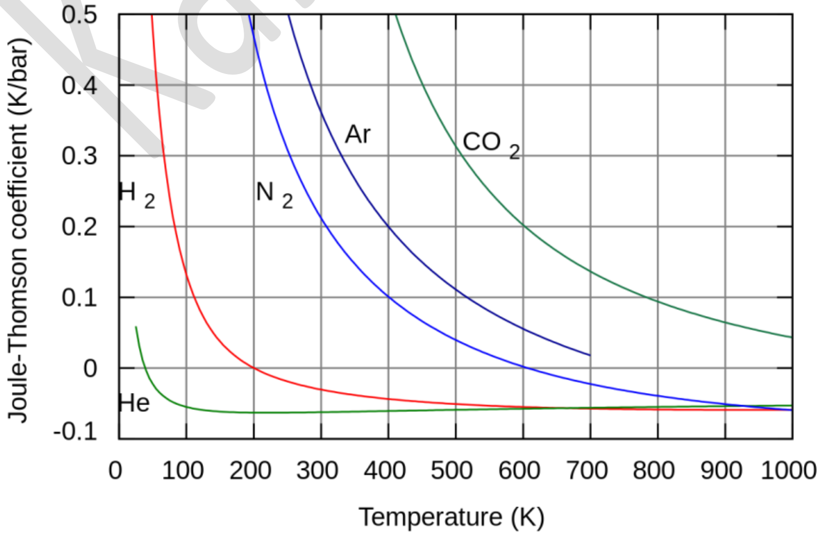
For an ideal gas, does not change during a Joule–Thomson expansion.[14] As a result, there is no change in internal energy; since there is also no change in thermal potential energy, there can be no change in thermal kinetic energy and, therefore, no change in temperature. In real gases, does change.

The ratio of the value of to that expected for an ideal gas at the same temperature is called the compressibility factor, . For a gas, this is typically less than unity at low temperature and greater than unity at high temperature (see the discussion in compressibility factor). At low pressure, the value of always moves towards unity as a gas expands.[15] Thus at low temperature, and will increase as the gas expands, resulting in a positive Joule–Thomson coefficient. At high temperature, and decrease as the gas expands; if the decrease is large enough, the Joule–Thomson coefficient will be negative.

For liquids, and for supercritical fluids under high pressure, increases as pressure increases.[15] This is due to molecules being forced together, so that the volume can barely decrease due to higher pressure. Under such conditions, the Joule–Thomson coefficient is negative, as seen in the figure above.

The physical mechanism associated with the Joule–Thomson effect is closely related to that of a shock wave,[16] although a shock wave differs in that the change in bulk kinetic energy of the gas flow is not negligible.

The rate of change of temperature with respect to pressure in a Joule–Thomson process (that is, at constant enthalpy) is the *Joule–Thomson (Kelvin) coefficient*. This coefficient can be expressed in terms of the gas's volume , its heat capacity at constant pressure, and its coefficient of thermal expansionas



Derivation of Joule-Thomson Co-efficient

H is a state function of the system, for a gaseous system it may be represented as

$$H = f(P, T)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

when, enthalpy is constant i.e., dH = 0

$$\left(\frac{\partial H}{\partial P}\right)_T dP = -\left(\frac{\partial H}{\partial T}\right)_P dT$$

Dividing by dP at constant H, We get

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = C_P \mu_{J.T.} \ldots\ldots\ldots (1)$$

$$C_P \mu_{J.T.} = -\left(\frac{\partial H}{\partial P}\right)_T$$

$$\mu_{J.T.} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \ldots\ldots\ldots\ldots\ldots (2)$$

We Know,

$$H = U + PV$$

$$dH = dU + PdV + VdP = TdS + VdP$$

Dividing by dP at constant T

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \ldots\ldots\ldots\ldots\ldots (3)$$

From Maxwell's relation we get

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Putting the Maxwell's relation on equation (3) weget,

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial S}{\partial P}\right)_T + V \ldots\ldots\ldots\ldots\ldots (4)$$

Equation (4)is called 2nd thermodynamic equation of state. Hence from equation (2) & (4) we get,

$$\mu_{J.T.} = -\frac{1}{C_p}\left[\left[V - T\left(\frac{\partial V}{\partial T}\right)\right]_P\right]$$

$$\mu_{J.T.} = \frac{1}{C_p}\left[\left[T\left(\frac{\partial V}{\partial T}\right)\right]_P - V\right] \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Equation (5) is the general thermodynamic expression for the Joule –Thomson co-efficient of the gas.

For one mole of an ideal gas,

$$PV = RT$$

$$V = \frac{RT}{P}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$\mu_{J.T.} = \frac{1}{C_p}\left[\left[T\left(\frac{\partial V}{\partial T}\right)\right]_P - V\right] = \frac{1}{C_p}\left[\frac{RT}{P} - V\right] = \frac{1}{C_p}[V - V] = 0$$

Thus for an ideal gas, Joule –Thomson co-efficient is zero, i.e., an ideal gas does not exhibit the Joule-Thomson effect.

For one mole of Vander wall's gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2}$$

$$V = \frac{RT}{P} + b - \frac{a}{PV} + \frac{ab}{PV^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The term a/PV & ab/PV^2, we are dividing a small quantity by a large quantity. So replacement of V by RT/P in these two terms does not introduce much error to the result. Thus V appearing in the correction terms a/PV & ab/PV^2 may be replaced by RT/P & equation (6) modifies to

$$V = \frac{RT}{P} + b - \frac{a}{RT} + \frac{abP}{R^2T^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Differentiating this equation with respect to T at constant P

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} - \frac{2abP}{R^2T^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

From equation (7)we find that

$$\frac{R}{P} = \frac{V-b}{T} + \frac{a}{RT^2} - \frac{abP}{R^2T^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Substituting this on equation (8) we get,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{a}{RT^2} - \frac{abP}{R^2T^3} + \frac{a}{RT^2} - \frac{2abP}{R^2T^3}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{2a}{RT^2} - \frac{3abP}{R^2T^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

Hence from Equation (5) and (10) we get,

$$\mu_{J.T.} = \frac{1}{C_p}\left[T\left\{\frac{V-b}{T} + \frac{2a}{RT^2} - \frac{3abP}{R^2T^3}\right\} - V\right] = \frac{1}{C_p}\left[V - b + \frac{2a}{RT} - \frac{3abP}{R^2T^2} - V\right]$$

$$\mu_{J.T.} = \frac{1}{C_P}\left[\frac{2a}{RT} - \frac{3abP}{R^2T^2} - b\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

At low pressure and high temperature $\frac{3abP}{R^2T^2}$ term is very small and in that case

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu_{J.T.} = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

The sign of $\mu_{J.T.}$ depends on the quantity within the square bracket of equation (12) and whether a gas suffers a fall or increase in temperature depends on the sign of $\mu_{J.T.}$. Thus when $\frac{2a}{RT} > b$, then $\mu_{J.T.}$ is +ve and dT is –Ve (since dP is always –Ve) and the gas suffers a fall in temperature. Conversely when $\frac{2a}{RT} < b$ then $\mu_{J.T.}$ is -ve and dT is +Ve (since dP is always –Ve), hence there is a rise of temperature. At high temperature $\frac{2a}{RT} < b$, hence $\mu_{J.T.}$ is –ve and at low temperature $\frac{2a}{RT} > b$, hence $\mu_{J.T.}$ is +ve

But for H_2 and He, "a" is very small and $\frac{2a}{RT} < b$, even at room temperature and therefore show the heating effect at room temperature in the Joule-Thomson expansion although the other gases show the cooling effect at room temperature.

For every gas there is a temperature where $\frac{2a}{RT} = b$ i.e., $\mu_{J.T.}$ = zero, when neither heating nor cooling of the gas would occur due to possing through fine orifice. This is called the inversion temperature, T_i of the gas. Putting, $\mu_{J.T.}$ = zero, at T_i , we get from equation (12).

$$\left[\frac{2a}{RT_i} - b\right] = 0$$

$$T_i = \frac{2a}{Rb} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Under the conditions when the term $\frac{3abP}{R^2T^2}$ is negligibly small the inversion temperature T_i of a gas according to equation (11) should be,

$$\left[\frac{2a}{RT_i} - \frac{3abP}{R^2 T_i^{\,2}} - b\right] = 0$$

$$\left[T_i^{\,2} - \frac{2a}{Rb} T_i + \frac{3aP}{R^2}\right] = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

Equation (14) being a quadratic equation in T_i, should yield two values of T_i, one minimum and other maximum., i.e., two inversion temperature is possible. This has been verified by experiment.

It is clear from the above discussion that in order to cool a gas by the Joule- Thomson expansion, the gas must first through a porous plug from a higher to lower pressure. As the temperature of the experiment decreases the extent of cooling increases.

Kirchhoff's Law

Kirchhoff's Law describes the enthalpy of a reaction's variation with temperature changes. In general, enthalpy of any substance increases with temperature, which means both the products and the reactants' enthalpies increase. The overall enthalpy of the reaction will change if the increase in the enthalpy of products and reactants is different.

At constant pressure, the heat capacity is equal to change in enthalpy divided by the change in temperature. $c_p = \Delta H \Delta T$(1)

Therefore, if the heat capacities do not vary with temperature then the change in enthalpy is a function of the difference in temperature and heat capacities. The amount that the enthalpy changes by is proportional to the product of temperature change and change in heat capacities of products and reactants. A weighted sum is used to calculate the change in heat capacity to incorporate the ratio of the molecules involved since all molecules have different heat capacities at different states.

$H_{T_f}=H_{T_i}+\int_{T_f T_i} c_p dT$(2)

If the heat capacity is temperature independent over the temperature range, then Equation 1can be approximated as$H_{T_f}=H_{T_i}+c_p(T_f-T_i)$(3)
With$c_p$is the (assumed constant) heat capacity and H_{T_i} and $H_{T_f}$are the enthalpy at the respective temperatures.

Equation 3can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. There are many biochemical applications because it allows us to predict enthalpy changes at other temperatures by using standard enthalpy data.

In fluid dynamics, the **Kirchhoff equations**, named after Gustav Kirchhoff, describe the motion of a rigid body in an ideal fluid.

$$\frac{d}{dt}\frac{\partial T}{\partial \vec{\omega}} = \frac{\partial T}{\partial \vec{\omega}} \times \vec{\omega} + \frac{\partial T}{\partial \vec{v}} \times \vec{v} + \vec{Q}_h + \vec{Q},$$

$$\frac{d}{dt}\frac{\partial T}{\partial \vec{v}} = \frac{\partial T}{\partial \vec{v}} \times \vec{\omega} + \vec{F}_h + \vec{F},$$

$$T = \frac{1}{2}\left(\vec{\omega}^T \tilde{I} \vec{\omega} + mv^2\right)$$

$$\vec{Q}_h = -\int p\vec{x} \times \hat{n}\, d\sigma,$$

$$\vec{F}_h = -\int p\hat{n}\, d\sigma$$

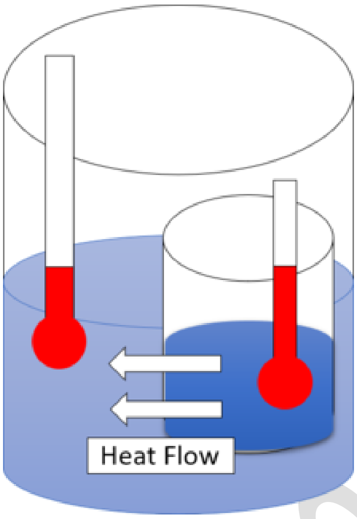
where and the angular and linear velocity vectors at the point , respectively; is the moment of inertia tensor, is the body's mass; is a unit normal to the surface of the body at the point ; is a pressure at this point; are the hydrodynamic torque and force acting on the body, respectively; likewise denote all other torques and forces acting on the body. The integration is performed over the fluid-exposed portion of the body's surface.

If the body is completely submerged body in an infinitely large volume of irrational, incompressible, in viscid fluid, that is at rest at infinity, then the vectors and can be found via explicit integration, and the dynamics of the body is described by the Kirchhoff – Clebsch equations.

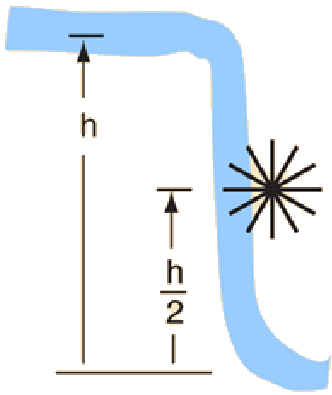
UNIT - II
THERMODYNAMICS - II

The **second law of thermodynamics** states that the total entropy of an isolated system can never decrease over time, and is constant if and only if all processes are reversible.[1] Isolated systems spontaneously evolve towards thermodynamic equilibrium, the state with maximum entropy.

The total entropy of a system and its surroundings can remain constant in ideal cases where the system is in thermodynamic equilibrium, or is undergoing a (fictive) reversible process. In all processes that occur, including spontaneous processes, the total entropy of the system and its surroundings increases and the process is irreversible in the thermodynamic sense. The increase in entropy accounts for the irreversibility of natural processes, and the asymmetry between future and past.

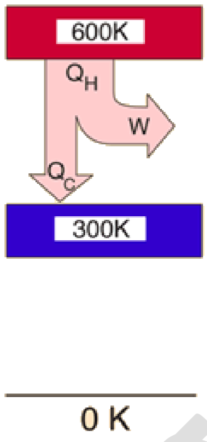


The second law of thermodynamics is a general principle which places constraints upon the direction of heat transfer and the attainable efficiencies of heat engines. In so doing, it goes beyond the limitations imposed by the first law of thermodynamics. Its implications may be visualized in terms of the waterfall analogy.



If you are constrained to put your waterwheel half-way up the waterfall, then you can extract at most half of the available energy.

If a 600K heat engine must exhaust heat at 300K, then it can be at most 50% efficient.



Entropy

Entropy, the measure of a system’s thermal energy per unit temperature that is unavailable for doing useful work. Because work is obtained from ordered molecularmotion, the amount of entropy is also a measure of the molecular disorder, or randomness, of a system. The concept of entropy provides deep insight into the direction of spontaneous change for many everyday phenomena.

Heat never flows spontaneously from cold to hot is equivalent to requiring the net entropy change to be positive for a spontaneous flow of heat. If $T_1 = T_2$, then the reservoirs are in equilibrium, no heat flows, and $\Delta S = 0$.

The condition $\Delta S \geq 0$ determines the maximum possible efficiency of heat engines—that is, systems such as gasoline or steam engines that can do work in a cyclic fashion. Suppose a heat engine absorbs heat Q_1 from R_1 and exhausts heat Q_2 to R_2 for each complete cycle. By conservation of energy, the work done per cycle is $W = Q_1 - Q_2$, and the net entropy change is $\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$. To make W as large as possible, Q_2 should be as small as possible relative to Q_1. However, Q_2 cannot be zero, because this would make ΔS negative and so violate the second law. The smallest possible value of Q_2 corresponds to the condition $\Delta S = 0$, yielding $\left(\frac{Q_2}{Q_1}\right)_{\min} = \frac{T_2}{T_1}$ as the fundamental equation limiting the efficiency of all heat engines. A process for which $\Delta S = 0$ is reversible because an infinitesimal change would be sufficient to make the heat engine run backward as a refrigerator.

Different Statements of The Law

There are two statements on the second law of thermodynamics which are;

1. Kelvin- Plank Statement
2. Clausius Statement

Kelvin-Planck Statement

It is impossible for a heat engine to produce a network in a complete cycle if it exchanges heat only with bodies at a single fixed temperature.

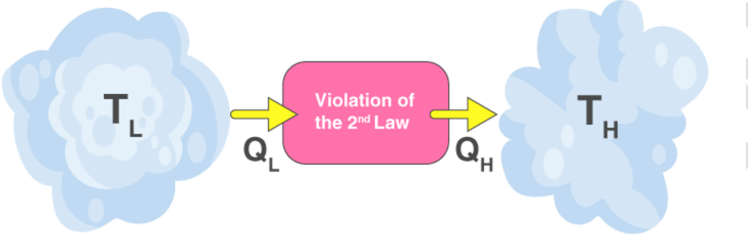
Clausius's Statement

It is impossible to construct a device operating in a cycle that can transfer heat from a colder body to warmer without consuming any work.

In other words, unless the compressor is driven by an external source, the refrigerator won't be able to operate.

Heat pump and Refrigerator works on Clausius's statement.

Both Clausius's and Kelvin's statements are equivalent i.e a device violating Clausius's statement will also violate Kelvin's statement and vice versa.



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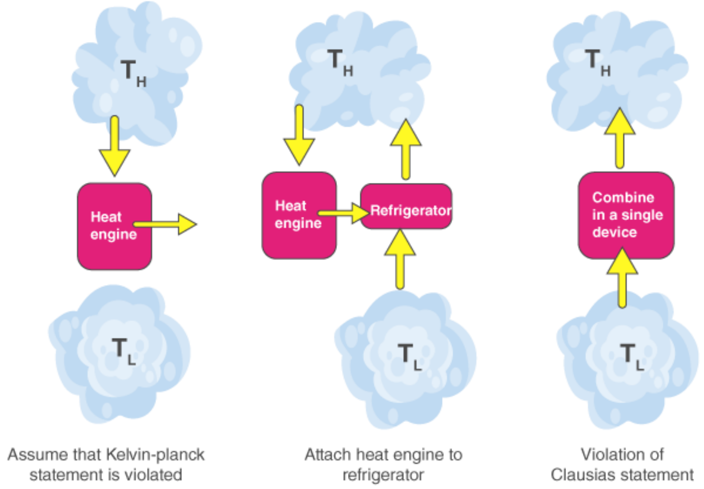

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In addition to these statements, a French physicist named Nicolas Léonard Sadi Carnot also known as"father of thermodynamics," basically introduced the Second Law of Thermodynamics. However, as per his statement, he emphasized the use of caloric theory for the description of the law. Caloric (self repellent fluid) relates to heat and Carnot observed that some caloric was lost in the motion cycle.

As was already stated above, the first law of thermodynamics characterises quantitatively the processes of conversion of energy. The second law of thermodynamics characterises the qualitative side of these processes. The first law provides all that is necessary to compose the energy balance of a process. However, it gives no indications whether this or another process is feasible. Meanwhile, by far not all processes can be practically realized.

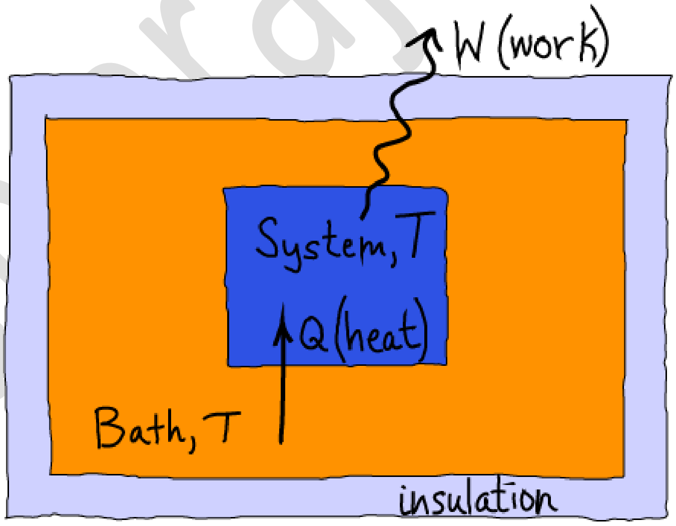
It should be stressed that the second law of thermodynamics, as well as the first, is based on experience.In the most general form the second law of thermodynamics can be stated as follows:

Free energy

Free energy, in thermodynamics, energy-like property or state function of a system in thermodynamic equilibrium. Free energy has the dimensions of energy, and its value is determined by the state of the system and not by its history. Free energy is used to determine how systems change and how much work they can produce. It is expressed in two forms: the Helmholtz free energy$F$, sometimes called the work function, and the Gibbs free energy$G$. If U is the internal energy of a system, PV the pressure-volume product, and TS the temperature-entropy product (T being the temperature above absolute zero), then $F = U - TS$ and $G = U + PV - TS$. The latter equation can also be written in the form $G = H - TS$, where $H = U + PV$ is the enthalpy. Free energy is an extensive property, meaning that its magnitude depends on the amount of a substance in a given thermodynamic state.

Work and free energy functions

The amount of work a system can do is limited by the the change in its free energy. Work is done during spontaneous processes in which the free energy decreases. Spontaneous processes, roughly speaking, amount to systems in non-equilibrium states either relaxing toward equilibrium, or systems "trying" to relax to equilibrium without being able to because of external constraints. An example of external constraints is the continual addition of substrate and removal of product from an enzyme in steady state: the system never reaches the natural equilibrium between substrate and product because of (externally driven) addition/removal processes.



Our derivation will be based on the following **assumptions and notation**, which are explained in most basic physics texts.

- A system is separated from a much larger "bath" in such a way that the system is maintained at the same constant temperature T as the bath.
- Q is the heat transferred from bath to system - could be negative
- W is the work done *by* the system on the environment.
- The entropy and average energy of the system are S_{sys} and $\langle E \rangle_{sys}$.

- The *changes* in these quantities during the spontaneous process are deoted by ΔS_{sys} and $\Delta\langle E\rangle_{sys}$.
- Our derivation will assume the system's volume remains constant and therefore use the Helmholtz free energy $F=\langle E\rangle-TS$ but an analogous result is valid for the Gibbs free energy G.
- The first law of thermodynamics: $Q=\Delta\langle E\rangle_{sys}+W$, which just states that energy is conserved.
- The second law of thermodynamics: $\Delta S_{tot}=\Delta S_{bath}+\Delta S_{sys}>0$, which says that the *total* entropy (of the universe) increases in any spontaneous process.
- $\Delta S_{bath}=-Q/T$ because the only change to the bath is the addition or removal of heat.

The derivation itself starts with the second law:

$$0 < \Delta S_{\text{bath}} + \Delta S_{\text{sys}} = -\frac{Q}{T} + \Delta S_{\text{sys}}, \quad (1)$$

whereΔS_{sys} is unknown because a complex process may be occurring in the system.
Substituting the first law into (1) leads to

$$\Delta E_{\text{sys}} - T\Delta S_{\text{sys}} < -W \quad (2)$$

Now, multiplying both sides by -1 (noting that the direction of inequality therefore switches) and using the definition of F yields

$$W < -\Delta F_{\text{sys}} \quad (3)$$

This is the key result: the work done in a spontaneous process is limited by the change in free energy. The negative sign in front of F reflects that $\Delta F<0$ in a spontaneous process, so that the work can be positive.

Biologically the most important type of work is chemical (i.e., shifting a chemical system further from equilibrium than it was previously) although mechanical work clearly is important for cytoskeletal processes and muscle contraction. Not surprisingly, free energy typically is stored by chemical means, and is naturally quantified using the chemical potential.

General conditions of equilibrium and spontaneity

It is identified that three criteria for whether a given reaction will occur spontaneously: $\Delta S_{univ} > 0$, $\Delta G_{sys} < 0$, and the relative magnitude of the reaction quotient Q versus the equilibrium constant K. Recall that if Q < K, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if Q > K, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If Q = K, then the system is at equilibrium, and no net reaction occurs. Table 18.3 "Criteria for the Spontaneity of a Process as Written" summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes. Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG°) and the equilibrium constant (K).

Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
$Q < K$	$Q = K$	$Q > K$

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude of ΔG° (Equation 18.26), and because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. Using higher math, the general relationship can be shown as follows:

$$\Delta G=V\Delta P-S\Delta T$$

If a reaction is carried out at constant temperature (ΔT = 0), then Equation 18.29 simplifies to

$$\Delta G=V\Delta P$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

If the initial state is the standard state with P_i = 1 atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G-G_{\circ}=nRT\ln P$$

This can be rearranged as follows:

$$G=G_{\circ}+nRT\ln P$$

relate ΔG° and K_p. Any relationship that is true for $K_p$must also be true for K because K_p and $K$are simply different ways of expressing the equilibrium constant using different units.

To consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA+bB\rightleftharpoons cC+dD \quad (18.33)$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\delta G=\sum mG_{products}-\sum nG_{reactants}=(cG_C+dG_D)-(aG_A+bG_B)$$

$$\Delta G=[(cG^{\circ}_C+cRT\ln P_C)+(dG^{\circ}_D+dRT\ln P_D)]-[(aG^{\circ}_A+aRT\ln P_A)+(bG^{\circ}_B+bRT\ln P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G=\Delta G_{\circ}+RT\ln(P_{cC}P_{dD}P_{aA}P_{bB})=\Delta G_{\circ}+RT\ln Q$$

where ΔG° indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q=K_p$,), and as you've learned in this chapter, ΔG = 0 for a system at equilibrium. Therefore, we can describe the relationship between ΔG° and K_p for gases as follows:

$0 = \Delta G° + RT\ln K_p$

$\Delta G° = -RT\ln K_p$

If the products and reactants are in their standard states and $\Delta G° < 0$, then $K_p > 1$, and products are favored over reactants. Conversely, if $\Delta G° > 0$, then $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

Properties of the Gibbs free energy

We have defined the Gibbs free energy *G* and the enthalpy *H* as:

$$G = H - TS$$
$$H = U + pV$$

and hence:

$$dG = dH - TdS - SdT$$
$$dH = dU + pdV + Vdp$$

i.e.: $dG = dU + pdV + Vdp - TdS - SdT$

But for a system doing no non-expansion work, *dU* may be replaced by the fundumental equation of thermodynamics, i.e.:

$$dU = TdS - pdV$$

and hence we have:

$$dG = \left(TdS - pdV\right) + pdV + Vdp - TdS - SdT$$

which simplifies to:

$$dG = Vdp - SdT$$

which since *dG* is an exact differential gives us:

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

and:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

These relationships show that *G* varies with temperature and pressure

(1) The temperature dependence of the Gibbs free energy (The Gibbs-Helmholtz equation.)

The temperature dependence of G is governed by the following relationship:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

This means that because *S* is positive, then *G* decreases when the temperature increases at constant pressure (*G vs T* plot, see fig. 1).

Then **sharpness of the decrease** of *G* decreases with temperature at constant pressure is determined by the entropy of the system. This means that the sharpness of the decrease of the *G vs T* (i.e. the sensitivity of *G* with changes in T, = gradient of *G vs T* plot, see fig. 1) is greatest for a gas, then liquid, then solid.

Let us now derive a relationship between the Gibbs energy and enthalpy (The Gibbs-Helmholzequantion). From the definition of *G* , we have:

$$G = H - TS$$

i.e.:

$$S = \frac{H - G}{T}$$

i.e.:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S = -\left(\frac{H - G}{T}\right) = \frac{G - H}{T}$$

which simplifies to the Gibbs-Helmholtz equation (see proof below):

$$\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = -\frac{H}{T^2}$$

The Gibbs-Helmholtz equation is most useful when applied to changes, including change of phase or chemical reactions at constant pressures. Then since $DG = G_f - G_i$, and since the Gibbs-Helmholtz equation applies to both $G_f$and G_i, we can write:

$$\left(\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right)_p = -\frac{\Delta H}{T^2}$$

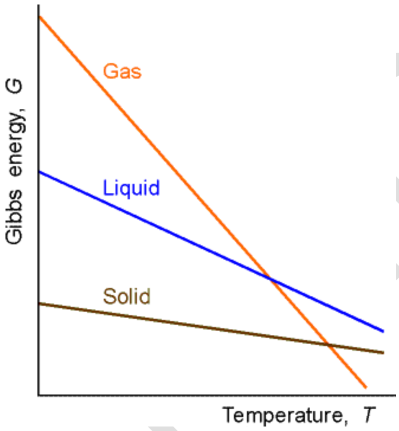


Fig. 1: The variation of the Gibbs energy with the temperature is determined by the entropy.

Aside: Proof of the Gibbs-Helmholtz equation:

$$\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = \left(\frac{\partial}{\partial T}\left[GT^{-1}\right]\right)_p$$

$$= T^{-1}\left(\frac{\partial G}{\partial T}\right)_p + G\left(\frac{d}{dT}T^{-1}\right)$$

$$= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2}$$

$$= \frac{1}{T}\left[\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right]$$

$$= \frac{1}{T}\left[\frac{G-H}{T} - \frac{G}{T}\right]$$

$$= -\frac{H}{T^2}$$

(2) The pressure dependence of the Gibbs free energy

The pressure dependence of *G* is governed by the following relationship:

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

This means that because *V* is positive, then *G* always **increases** when the pressure increases at constant temperature (*G vs p* plot, see fig. 2). Also, since *V* is the gradient of the *G vs p* plot, then the sensitivity of *G* to changes in *p* is greatest for gases and negligible for liquids and solids

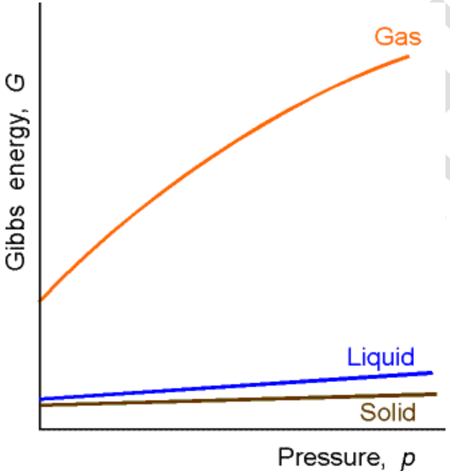


Fig. 2: The variation of the Gibbs energy with the pressure

We can find the change in the Gibb's energy due to a change in pressure at constant temperature through:

$$\Delta G = G(p_f) - G(p_i) = \int_{p_i}^{p_f} V dp$$

For solids and liquids, we then treat *V* as constant, whilst for an ideal gas we use the *pV=nRT* relationship, and we get:

$$G(p_f) = G(p_i) + \int_{p_o}^{p_f} \frac{nrT}{p} dp = G(p_i) + nRT \ln\left(\frac{p_f}{p_i}\right)$$

or if we assume $p_i = p^0$ then we get:

$$G(p_f) = G^0 + nRT \ln\left(\frac{p_f}{p^0}\right)$$

ΔG depends only on the difference in free energy of products and reactants (or final state and initial state). $\Delta G$is independent of the path of the transformation and is unaffected by the mechanism of a reaction.

ΔG

The standard Gibbs energy change ΔG_o

(at which reactants are converted to products at 1 bar) for:

$aA+bB \rightarrow cC+dD$

$\Delta_r G_o = c\Delta_f G_o(C) + d\Delta_f G_o(D) - a\Delta_f G_o(A) - b\Delta_f G_o(B)$

$\Delta_f G_0 = \sum v\Delta_f G_0(\text{products}) - \sum v\Delta_f G_0(\text{reactants})$

The standard-state free energy of reaction (ΔG_o) is defined as the free energy of reaction at standard state conditions:

$\Delta G_o = \Delta H_o - T\Delta S_o$(4.8.9)

At equilibrium, $\Delta G = 0$ and Q=K. Thus the equation can be arranged into:

$\Delta G = \Delta Go + RT\ln[C][D][A][B]$(4.8.34)

with

- ΔGo
- = standard free energy change$R$
- = gas constant = 1.98 * 10^{-3} kcal mol^{-1} deg^{-10}
- T
- = is usually room temperature = 298 K
- $K=[C][D][A][B]$

Gibbs Helmholtz equation

For a mole of ideal gas we can use the gas law to integrate volume over pressure and we get

$\Delta Gmolar = RT\ln(P2P1)$

It is customary to identify one of the pressures (P_1} with the *standard state* of **1 bar** and use the plimsoll to indicate the fact that we are referring to a standard state by writing:

$Gmolar(P) = Gomolar + RT\ln(P1) = Gomolar + RT\ln[P]$

The fact that we are making the function intensive (per mole) is usually indicated by putting a bar over the G

symbol, although this is often omitted for G^o_{molar}

Solids

For solids the volume does not change very much with pressure (the *isothermal compressibility*$\kappa$is small), so can assume it more or less constant:
$G(Pfinal)=G(Pinitial)+\int VdP$(from init to final)$\approx G(Pinitial)+V\int dP$(from init to final)$=G(Pinitial)+V\Delta P$(22.7.3)

The Gibbs-Helmholtz Expression

$GT=HT-S$(22.7.4)
Take the derivative under constant pressure of each side to get
$(\partial G/T\partial T)P=-HT2+1T(\partial H\partial T)P-(\partial S\partial T)P$
We make use of the relationship between Cp
and$H$ and Cp and S
$(\partial G/T\partial T)P=-HT2+CPT$
$-CPT=-HT2$

We said before that $S$is a first order derivative of G. As you can see from this derivation the enthalpy H is also a first order derivative, albeit not of G itself, but of G/T.
$(\partial\Delta G/T\partial T)P=-\triangle HT2$
The last step in the derivation simply takes the step before twice -say for the G
and$H$ at the begin and end of a *process*- and subtracts the two identical equations leading to a Δ symbol. In this differential form the Gibbs-Helmholtz equation can be applied to any process.

UNIT - III

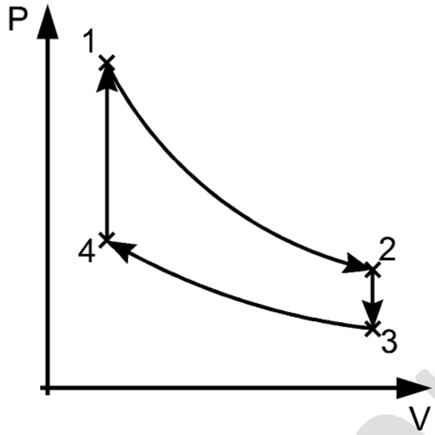
CHEMICAL EQUILIBRIUM

Reversible and irreversible reactions

The reversible process is the ideal process which never occurs, while the irreversible process is the natural process that is commonly found in nature. When we tear a page from our notebooks, we cannot change this and 'un-tear'. This is an irreversible process. Whereas when water evaporates, it can also be condensed in the form of rains. This is a reversible process. Let us study more about them below.

Reversible Process

A thermodynamic process is reversible if the process can return back in such a that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. It means both system and surroundings are returned to their initial states at the end of the reverse process.



In the figure above, the system has undergone a change from state 1 to state 2. The reversible process can reverse completely and there is no trace left to show that the system had undergone thermodynamic change. During the reversible process, all the changes in state that occur in the system are in thermodynamic equilibrium with each other.

Internally reversible process

The process is internally reversible if no irreversibilities occur within the boundaries of the system. In these processes, a system undergoes through a series of equilibrium states, and when the process reverses, the system passes through exactly the same equilibrium states while returning to its initial state.

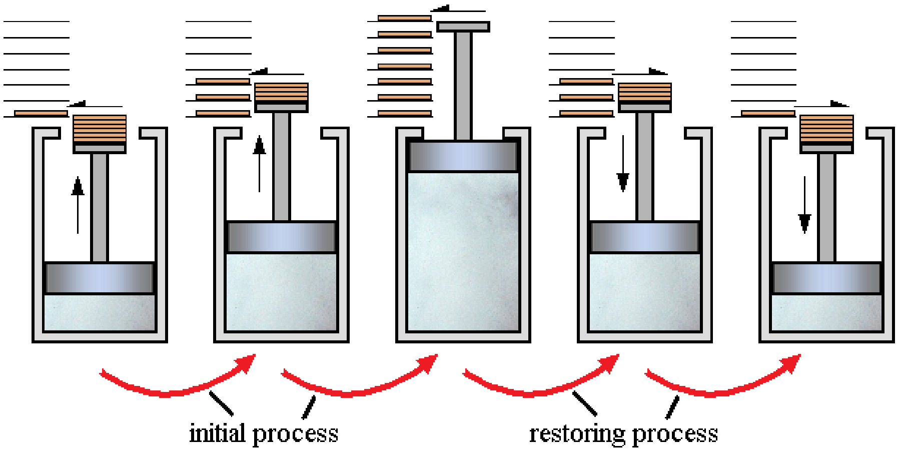
Externally reversible process

In externally reversible process no irreversibilities occur outside the system boundaries during the process. Heat transfer between a reservoir and a system is an externally reversible process if the surface of contact between the system and reservoir is at the same temperature.

A process can be reversible only when its satisfying two conditions

- Dissipative force must be absent.

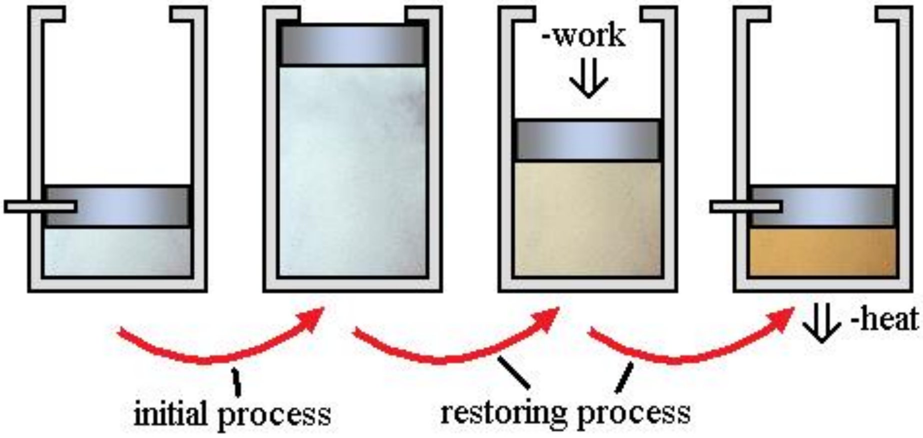
- The process should occur in infinite small time.



In simple words, the process which can reverse back completely is a reversible process. This means that the final properties of the system can perfectly reverse back to the original properties. The process can be perfectly reversible only if the changes in the process are infinitesimally small. In practical situations it is not possible to trace these extremely small changes in extremely small time, hence the reversible process is also an ideal process. The changes that occur during the reversible process are in equilibrium with each other.

Irreversible Process

Irreversible processes are a result of straying away from the curve, therefore decreasing the amount of overall work done. An irreversible process is a thermodynamic process that departs from equilibrium. In terms of pressure and volume, it occurs when the pressure (or the volume) of a system changes dramatically and instantaneously that the volume (or the pressure) do not have the time to reach equilibrium.



A classic example of an irreversible process is allowing a certain volume of gas to release into a vacuum. By releasing pressure on a sample and allowing it to occupy a large space, the system and surroundings are not in equilibrium during the expansion process.

Here little work occurs. However, there is a requirement of significant work, with a corresponding amount of energy dissipation as heat flows to the environment. This is in order to reverse the process.

Nature of chemical equilibrium

For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N2O4) to nitrogen dioxide (NO2). You may recall that NO2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N2O4 (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of NO2 appears (Figure 14.1.1). The reaction can be followed visually because the product (NO2) is colored, whereas the reactant (N2O4) is colorless:

Law of mass action

The law of mass action states that the rate of a reaction is proportional to the product of the concentrations of each reactant.

This law can be used to explain the behavior exhibited by solutions in dynamic equilibria. The law of mass action also suggests that the ratio of the reactant concentration and the product concentration is constant at a state of chemical equilibrium.

$$\mathbf{A + B \rightleftharpoons C + D}$$

A mixture of products and reactants in a state of chemical equilibrium is known as an equilibrium mixture. There exists a relation between the concentration of products and the concentration of reactants for an equilibrium mixture. This relation can be equated as follows.

$$Kc = [C][D]/[A][B]$$

Here, $K_c$is called the equilibrium constant. In this equation, the concentration of A at equilibrium is represented as [A] (similarly for B, C, and D), and the stoichiometric coefficients of the reactants and products are 1. It has been experimentally observed that the equilibrium constant is also dependent on the stoichiometric coefficients of the reactants and products.

Therefore, the law of mass action dictates that the equilibrium constant, at a given constant temperature, is equal to the product of the concentration of products raised to the respective stoichiometric coefficients divided by the product of the reactant concentrations, each raised to the corresponding stoichiometric coefficient.

This is also known as the equilibrium law or the law of chemical equilibrium.

Representation of the Equilibrium Constant

For a balanced reaction of the type,

aA + bB⇌ cC + dD

According to the law of mass action, the constant value obtained by relating equilibrium concentrations of reactants and products is called the equilibrium constant. For the forward reaction, this is given by

$K_c = [C]_c[D]_d / [A]_a[B]_b$

equilibrium constants- Kp, and Kc

Kc and *Kp* are the equilibrium constants of gaseous mixtures. However, the difference between the two constants is that *Kc* is defined by molar concentrations, whereas *Kp* is defined by the partial pressures of the gasses inside a closed system. The equilibrium constants do not include the concentrations of single components such as liquids and solid, and they do not have any units.

Here are some easy steps on writing Gas Equilibrium Constants (this is the same for finding K_c, K_p, K_{sp}, Q and etc.):

In equilibrium equations, even though the arrows point both ways (⇌) we usually associate the left as reactants and the right as products.

The products are on the TOP of the fraction (the numerator).

The reactants are on the BOTTOM of the fraction (the denominator).

The concentrations of the products and reactants are always raised to the power of their coefficient in the balanced chemical equation.

If any of the reactants or products are solids or liquids, their concentrations are equal to one because they are pure substances.

The standard example of writing Gas Equilibrium Constants are:

$aA+bB \rightleftharpoons cC+dD$(Gas Equilibrium Constants.1)

$K_c=[C]_c[D]_d[A]_a[B]_b$(Gas Equilibrium Constants.2)

$K_p=(C)_c(D)_d(A)_a(B)_b$(Gas Equilibrium Constants.3)

Definition of K_c and K_p

K_c is an equilibrium constant in terms of molar **concentrations** and is usually defined as:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \text{Constants.14)}$$

in the general reaction,

$$aA + bB \rightleftharpoons cC + dD \qquad \text{Constants.15)}$$

If a large K_c is formed then there are more products formed. Inversely, a small K_c indicates that the reaction favors the reactants.
K_p is an equilibrium constant in terms of **partial pressures**. and is usually defined as:

$$K_p = \frac{(C)^c(D)^d}{(A)^a(B)^b} \qquad \text{Constants.16)}$$

for the general reaction

$$aA + bB \rightleftharpoons cC + dD \qquad \text{Constants.17)}$$

Homogeneous Equilibria: Reactants/Products all in a single phase. For example:

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)} \quad \text{Constants.18)}$$

Heterogeneous Equilibria: Reactants/Products in more than one phase. For example:

$$A_{(s)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(s)} \quad \text{Constants.19)}$$

The relationship between the two equilibrium constants are:

$$K_p = K_c(RT)^{\Delta n} \qquad \text{Constants.20)}$$

or

$$K_c = \frac{K_p}{(RT)^{\Delta n}} \qquad \text{Constants.21)}$$

where,

- Δn = (Total moles of gas on the products side) - (Total moles of gas on the reactants side).
  Hence \(\Delta = (d + c) - (a + b)\] [The lower case numbers are the exponents]
- R is the gas constant found in the ideal gas law $(0.0821 \frac{Liter\ Atm}{Mole\ Kelvin})$

Relating Gas Equilibrium Constants to Equilibrium (K)

The value of K depends on whether the solution being calculated for is using concentrations or partial pressures. The gas equilibrium constants relate to the equilibrium (K) because they are both derived from the ideal gas law (PV = nRT).

K_c is the concentration of the reaction, it is usually shown as:

$$\frac{c[C]c[D]}{c[A]c[B]} \quad \text{Constants.22)}$$

K_p is the amount of partial pressure in the reaction, usually shown as:

$$\frac{p(C)p(D)}{p(A)p(B)} \quad \text{Constants.23)}$$

As we have seen above, $K_p = K_c (RT)^{\Delta n}$,we can derive this formula from the Ideal Gas Law.

We know that K_c is in terms Molarity $\left(\frac{Moles}{Liters}\right)$,

and we can also arrange the Ideal Gas Law (PV = nRT) as: $\left(\frac{n}{L}\right) = \left(\frac{P}{RT}\right)$.

We know that Partial Pressure is directly proportional to Concentration:

$P = \left(\frac{n}{L}\right) * RT$ Pressure can be in units of: Pascal (Pa), Atmosphere (atm), or Torr.

Therefore we can replace K_c with Molarity: the equation become, $K_p = K_c (RT)^{\Delta n}$

$$(RT)^{\Delta n} = \frac{(RT)^c (RT)^d}{(RT)^a (RT)^b}$$

Also: $\left(\frac{n}{L}\right) = \left(\frac{P}{RT}\right)$, can be shown as $K_c = K_p (RT)$

K is also written the same as K_c and K_p:

$$aA + bB \rightleftharpoons cC + dD.$$

$K_{equ} = k_f/k_b = [C]^c [D]^d/[A]^a [B]^b = K_c$ and $K_{equ} = k_f/k_b = [[pC]^c [pD]^d]/[[pA]^a [pB]^b] = K_p$

Temperature dependence of equilibrium constant

The value of K_p is independent of pressure, although the composition of a system at equilibrium may be very much dependent on pressure. Temperature dependence is another matter. Because the value of ΔG^o_{rxm} is dependent on temperature, the value of K_p is as well. The form of the temperature dependence can be taken from the definition of the Gibbs function. At constant temperature and pressure

Substituting

$$\frac{\Delta G^o_{T_2}}{T_2} - \frac{\Delta G^o_{T_1}}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{9.6.1}$$

$$\Delta G^o = -RT \ln K \tag{9.6.2}$$

For the two values of ΔG^o and using the appropriate temperatures, yields

$$\frac{-RT_2 \ln K_2}{T_2} - \frac{-RT_1 \ln K_1}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{9.6.3}$$

And simplifying the expression so that only terms involving K are on the left and all other terms are on the right results in the **van 't Hoff equation**, which describes the temperature dependence of the equilibrium constant.

$$ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{9.6.4}$$

Because of the assumptions made in the derivation of the Gibbs-Helmholtz equation, this relationship only holds if ΔH^o is independent of temperature over the range being considered. This expression also suggests that a plot of $\ln(K)$ as a function of $1/T$ should produce a straight line with a slope equal to $-\Delta H^o/R$. Such a plot is known as a **van 't Hoff plot**, and can be used to determine the reaction enthalpy.

Pressure dependence of equilibrium constant

Since the equilibrium constant K_p is a function of ΔG^o_{rxn} which is defined for a specific composition (all reactants in their standard states and at unit pressure (or fugacity), changes in pressure have no effect on equilibrium constants for a fixed temperature. However, changes in pressure can have profound effects on the compositions of equilibrium mixtures.

To demonstrate the relationship, one must recall Dalton's law of partial pressures. According to this relationship, the partial pressure of a component of a gas-phase mixture can be expressed

$$p_i = \chi_t p_{tot} \tag{9.4.1}$$

It is the combination of mole fractions that describes the composition of the equilibrium mixture.

Substituting the above expression into the expression for K_p yields

$$K_p = \prod_i (\chi_i p_{tot})^{\nu_i} \tag{9.4.2}$$

This expression can be factored into two pieces – one containing the mole fractions and thus describing the composition, and one containing the total pressure.

$$K_p = \left(\prod_i \chi_i^{\nu_i}\right)\left(\prod_i p_{tot}^{\nu_i}\right) \tag{9.4.3}$$

The second factor is a constant for a given total pressure. If the first term is given the symbol K_x, the expression becomes

$$K_p = K_x (p_{tot})^{\sum_i \nu_i} \tag{9.4.4}$$

In this expression, K_x has the same form as an equilibrium constant

$$K_x = \prod \chi_i^{\sum_i \nu_i} \tag{9.4.5}$$

but is not itself a constant. The value of K_x will vary with varying composition, and will *need* to vary with varying total pressure (in most cases) in order to maintain a constant value of K_p.

Le-Chatelier principle

If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium. If a chemical reaction is at equilibrium and experiences a change in pressure, temperature, or concentration of products or reactants, the equilibrium shifts in the opposite direction to offset the change.

If we mechanically decrease the volume of a container of gases the pressure inside the container will increase. Le Chatelier's principle tells us the reaction will re-achieve equilibrium by shifting to counteract this change. Since the change we made was to increase the pressures the reaction will shift in such a way to decrease the pressures. This can be achieved by moving towards the side of the reaction with fewer gas molecules.

So, if you increase the pressure by decreasing the volume, the partial pressures will increase. Since the reactants have two moles of gas, the pressures of the reactants are squared. This means that the effect will be larger for the reactants. Dividing by a bigger number will make Q smaller and you'll find that after increasing the pressures $Q < K$. Then equilibrium is towards the products side. This is the side with fewer molecules.

Similarly if we mechanically increase the volume of a container, the pressure of the gas inside the container will decrease. Now the system will re-establish equilibrium by shifting to side of the reaction with the greatest number of moles of gas.

If the reaction has the same number of moles of gas in the reactants and products then volume (pressure) will have no effect.

Finally, sometimes the volume is increased by adding an inert gas to the mixture at constant pressure. In this case the total pressure will stay constant, *but the partial pressures of the reactants and products will decrease*. This is because the total pressure now includes the pressure resulting from the inert gas. This has the effect of diluting the mixture and is identical to simply mechanically increasing the volume.

Increasing the pressure by adding an inert gas at constant volume has no effect. This is because what matters for the equilibrium are the partial pressures of the reactants and products. Adding an inert component to a system at constant volume will change the total pressure but not the partial pressures of the compounds of interest.

For reactions in the solution, you can have identical effects by changing the total volume of the solution. Adding water will effectively dilute all the concentrations. The reaction will then shift to counter this by moving toward the side of the reaction with more aqueous species in solution. Conversely concentration the solution lowers the volume and raises the concentrations. This will cause the reaction to shift to the side with fewer aqueous species. It follows the identical reasoning to the Q vs K examples given above except that the mass action quotient has concentrations instead of partial pressures.

UNIT - IV

SOLUTIONS

A solution is a type of homogeneous mixture that is made up of two or more substances. A homogeneous mixture is a type of mixture with a uniform composition. This means that the substances cannot be distinguished easily from one another.

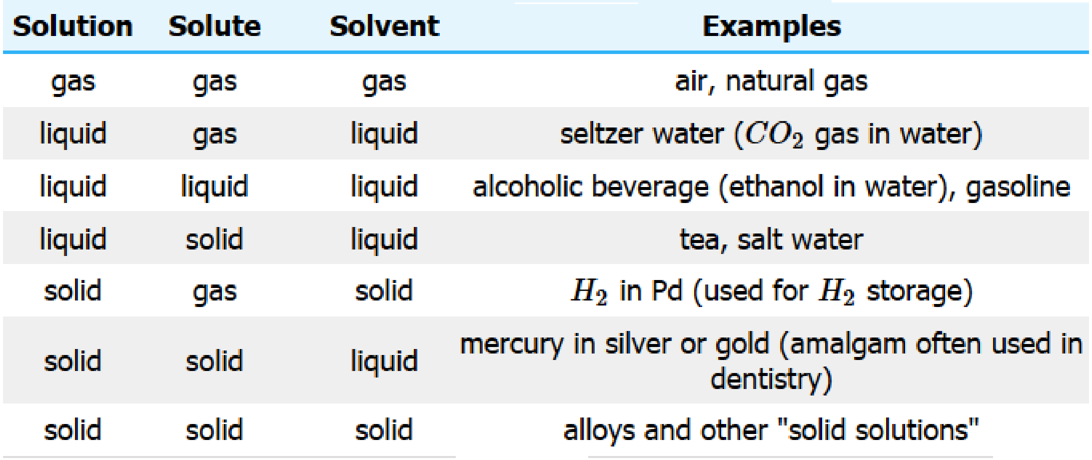
Some examples of solutions are salt water, rubbing alcohol, and sugar dissolved in water. When you look closely, upon mixing salt with water, salt particles cant be seen anymore, making this a homogeneous mixture.

This salt water example to talk about the two main parts of a solution. These are: Solute: this is the substance that makes up the minority of the solution, or this is the part that is dissolved. In our example of salt water, the solute is the salt. Solvent: this is the substance that makes up the majority of the solution. This is the part where the solute is dissolved. In our example of salt water, the solvent is water.

When we think about solutions, the first thing we think about is a substance dissolved in water. This is natural because after all, water is the universal solvent. However, solutions are not limited to the liquid phase. Solutions can exist in the gaseous phase - the air we breathe is a solution that is composed of a mixture of gases. Solutions are also present in the solid phase - brass is a solid solution that is a mixture of copper and zinc. In the next section, we'll discuss what the different types of solutions are in different phases.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table 13.2.1 lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table 13.2.1: Types of Solutions



Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)
solid	solid	solid	alloys and other "solid solutions"

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$Zn(NO3)2(s)+H2O(l)\rightarrow Zn2+(aq)+2NO-3(aq)$

Because $Zn(NO3)2$can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$Zn(s)+2H+(aq)+2Cl-(aq)\rightarrow Zn2+(aq)+2Cl-(aq)+H2(g)(13.2.2)$

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

Molarity:

Molar concentration (also called molarity, amount concentration or substance concentration) is a measure of the concentration of a chemical species, in particular of a solute in a solution, in terms of amount of substance per unit volume of solution. In chemistry, the most commonly used unit for molarity is the number of moles per litre, having the unit symbol mol/L or mol·dm^{-3} in SI unit. A solution with a concentration of 1 mol/L is said to be 1 molar, commonly designated as 1 M. To avoid confusion with SI prefixMega which has the same abbreviation, small capsᴍ or italicized*M* are also used in journals and textbooks.

Definition

Molar concentration or molarity is most commonly expressed in units of moles of solute per litre of solution. For use in broader applications, it is defined as amount of substance of solute per unit volume of solution, or per unit volume available to the species, represented by lowercase *c*.

$$c = \frac{n}{V} = \frac{N}{N_A\,V} = \frac{C}{N_A}.$$

Here, n is the amount of the solute in moles, N is the number of constituent particles present in volume V (in litres) of the solution, and N_A is the Avogadro constant, since 20 May 2019, by definition, exactly 6.022 140 76×10^{23}mol^{-1}. The ratio N/V is the number concentration$C$

Units

In the International System of Units (SI) the base unit for molar concentration is mol/m^3. However, this is impractical for most laboratory purposes and most chemical literature traditionally uses mol/dm^3, which is the same as mol/L. These traditional units are often denoted by the letter M, optionally preceded by an SI prefix as needed to denote sub-multiples, for example:

mol/m^3 = 10^{-3}mol/dm^3 = 10^{-3}mol/L = 10^{-3} M = 1 mmol/L = 1 mM.

	Abbreviation	**Concentration**	
		(mol/L)	**(mol/m³)**
millimolar	mM	10^{-3}	10^{0}
micromolar	µM	10^{-6}	10^{-3}
nanomolar	nM	10^{-9}	10^{-6}
picomolar	pM	10^{-12}	10^{-9}
femtomolar	fM	10^{-15}	10^{-12}
attomolar	aM	10^{-18}	10^{-15}
zeptomolar	zM	10^{-21}	10^{-18}
yoctomolar	yM[5]	10^{-24} (6 particles per 10 L)	10^{-21}

The properties and behavior of many solutions depend not only on the nature of the solute and solvent but also on the concentration of the solute in the solution. Chemists use many different units when expressing concentration; however, one of the most common units is molarity. Molarity (M) is the concentration of a solution expressed as the number of moles of solute per liter of solution:

$$\text{Molarity (M)} = \frac{\text{moles solute}}{\text{liters solution}}$$

For example, a 0.25 M NaOH solution (this is read as 0.25 molar) contains 0.25 moles of sodium hydroxide in every liter of solution. Anytime you see the abbreviation M you should immediately think of it as mol/L.

In order to calculate the molarity of a solution, you need to know the number of moles of solute and the total volume of the solution.

To calculate molarity:

1. Calculate the number of moles of solute present.
2. Calculate the number of liters of solution present.
3. Divide the number of moles of solute by the number of liters of solution.

Instead of calculating the moles of solute and liters of solution present individually, you can also string all the calculations together in one problem:

1. Divide the amount of solute by the volume of solution (regardless of the initial units given).
2. Use dimensional analysis to convert the amount of solute to moles of solute.
3. Use dimensional analysis to convert the volume of solution to liters of solution (if necessary).

The following example will illustrate both methods.

Example: What is the molarity of a solution prepared by dissolving 15.0 g of sodium hydroxide in enough water to make a total of 225 mL of solution?

Method 1:

- Calculate the number of moles of solute present.

$$\text{molNaOH} = 15.0\text{g NaOH} \times \frac{1\text{ molNaOH}}{40.0\text{ g NaOH}}$$

$$\text{molNaOH} = 0.375\text{ molNaOH}$$

- Calculate the number of liters of solution present.

$$\text{L soln} = 225\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} = 0.225\text{ L soln}$$

- Divide the number of moles of solute by the number of liters of solution.

$$M = \frac{0.375\text{ molNaOH}}{0.225\text{ L soln}} = 1.67\text{ M NaOH}$$

Method 2:

- Divide the amount of solute by the volume of solution (regardless of the initial units given).

$$M = \frac{15.0\text{ g NaOH}}{225\text{ mL soln}}$$

- Use dimensional analysis to convert the amount of solute to moles of solute.

$$M = \frac{15.0\text{ g NaOH}}{225\text{ mL soln}} \times \frac{1\text{ molNaOH}}{40.0\text{ g NaOH}}$$

- Use dimensional analysis to convert the volume of solution to liters of solution (if necessary).

$$M = \frac{15.0\text{ g NaOH}}{225\text{ mL soln}} \times \frac{1\text{ molNaOH}}{40.0\text{ g NaOH}} \times \frac{1000\text{ mL soln}}{1\text{ L soln}}$$

$$M = \frac{1.67\text{ molNaOH}}{\text{L soln}} = 1.67\text{ M NaOH}$$

As you can see, both methods give exactly the same result. Choose whichever method is most comfortable for you. Just remember that ultimately your units must be mol/L (= M).

Molality

Molality (m) is defined as the number of **moles** of solute per **kilogramofsolvent**.
molality = moles of solute/kilograms of solvent
Although their spellings are similar, molarity and molality cannot be interchanged. **Molarity** is a measurement of the moles in the total volume of the solution, whereas **molality** is a measurement of the moles in relationship to the mass of the solvent.

When water is the solvent and the concentration of the solution is low, these differences can be negligible (d = 1.00 g/mL). However, when the density of the solvent is significantly different than 1 or the concentration of the solution is high, these changes become much more evident.

Molality Formula

Molality(M)=Number of moles of solute / Mass of solvent in kgs
Molality(M)=g×1000W×m

Example:

Compare the molar and molal volumes of 1 mol of a solute dissolved in CCl_4 (d = 1.59/mL).
For a **1 Molar** solution, 1 mol of solute is dissolved in CCl_4 until the final volume of solution is 1 L.
For a **1 molal** solution, 1 mol of solute is dissolved in 1 kg of CCl_4.
1 kg of CCl_4 × (1,000 g/1 kg) × (mL/1.59 g) = 629 mL CCl_4

Mole fraction

Mole fraction is a unit of concentration, defined to be equal to the number of moles of a component divided by the total number of moles of a solution. Because it is a ratio, mole fraction is a unitless expression. The mole fraction of all components of a solution, when added together, will equal 1.

Mole Fraction Example

In a solution of 1 mol benzene, 2 mol carbon tetrachloride, and 7 mol acetone, the mole fraction of the acetone is 0.7. This is determined by adding up the number of moles of acetone in the solution and dividing the value by the total number of moles of components of the solution:

Number of Moles of Acetone: 7 moles
Total Number of Moles in Solution = 1 moles (benzene) + 2 moles (carbon tetrachloride) + 7 moles (acetone)

Total Number of Moles in Solution = 10 moles
Mole Fraction of Acetone = moles acetone / total moles solution
Mole Fraction of Acetone = 7/10
Mole Fraction of Acetone = 0.7

Similarly, the mole fraction of benzene would be 1/10 or 0.1 and the mole fraction of carbon tetrachloride would be 2/10 or 0.2.

parts per million

A weight to weight ratio used to describe concentrations. Parts per million (ppm) is the number of units of mass of a contaminant per million units of total mass.

ppm (or ppm_m) is used to measure the concentration of a contaminant in soils and sediments. In that case 1 ppm equals 1 mg of substance per kg of solid (mg/kg).

ppm (or ppmm) is also sometimes used to describe small concentrations in water, in which case 1 ppm is equivalent to 1 mg/l because a liter of water weighs approximately a 1000 g. This use of ppm tends to be phased out in favour of mg/l.

ppm (or ppm_V) is often used to describe concentrations of contaminants in air (as a volume fraction). In this case the conversion of ppm to mg/m^3 depends on the molecular weight of the contaminant.

For example, 1 ppm chlorine represents one part of chlorine in one million parts of air by weight, which is 1.45 mg/m^3.

The ppm unit is mainly used in North America.

Solutions of Gaseous Solutes in Liquid Solvents

Gases dissolve in liquids, but usually only to a small extent. When a gas dissolves in a liquid, the ability of the gas molecules to move freely throughout the volume of the solvent is greatly restricted. If this latter volume is small, as is often the case, the gas is effectively being compressed. Both of these effects amount to a decrease in the entropy of the gas that is not usually compensated by the entropy increase due to mixing of the two kinds of molecules. Such processes greatly restrict the solubility of gases in liquids.

liquid solvent, solute →	gas
energy to disperse solute	nil
energy to introduce into solvent	medium to large
increase in entropy	negative
miscibility	**usually very limited**

Solubility of gases in water

One important consequence of the entropy decrease when a gas dissolves in a liquid is that the solubility of a gas decreases at higher temperatures; this is in contrast to most other situations, where a rise in temperature usually leads to increased solubility. Bringing a liquid to its boiling point will completely remove a gaseous solute. Some typical gas solubilities, expressed in the number of moles of gas at 1 atm pressure that will dissolve in a liter of water at 25° C, are given below:

solute	formula	solubility, mol L^{-1} atm^{-1}
ammonia	NH_3	57
carbon dioxide	CO_2	0.0308
methane	CH_4	0.00129
nitrogen	N_2	0.000661
oxygen	O_2	0.00126
sulfur dioxide	SO_2	1.25

Inspection of the above table reveals that ammonia is a champion in this regard. At 0° C, one liter of water will dissolve about 90 g (5.3 mol) of ammonia. The reaction of ammonia with water according to

$NH3+H2O \rightarrow NH+4+OH–$makes no significant contribution to its solubility; the equilibrium lies heavily on the left side (as evidenced by the strong odor of ammonia solutions). Only about four out of every 1000 NH_3molecules are in the form of ammonium ions at equilibrium. This is truly impressive when one calculates that this quantity of NH_3 would occupy (5.3 mol) × (22.4 L mol^{-1}) = 119 L at STP. Thus one volume of water will dissolve over 100 volumes of this gas. It is even more impressive when you realize that in order to compress 119 L of an ideal gas into a volume of 1 L, a pressure of 119 atm would need to be applied! This, together with the observation that dissolution of ammonia is accompanied by the liberation of a considerable amount of heat, tells us that the high solubility of ammonia is due to the formation of more hydrogen bonds (to H_2O) than are broken within the water structure in order to accommodate the NH_3 molecule.

If we actually compress 90 g of pure NH_3 gas to 1 L, it will liquefy, and the vapor pressure of the liquid would be about 9 atm. In other words, the escaping tendency of NH_3 molecules from H_2O is only about 1/9th of what it is from liquid NH_3. One way of interpreting this is that the strong intermolecular (dipole-dipole) attractions between NH_3 and the solvent H_2O give rise to a force that has the effect of a negative pressure of 9 atm.

Solubility of gases decreases with Temperature

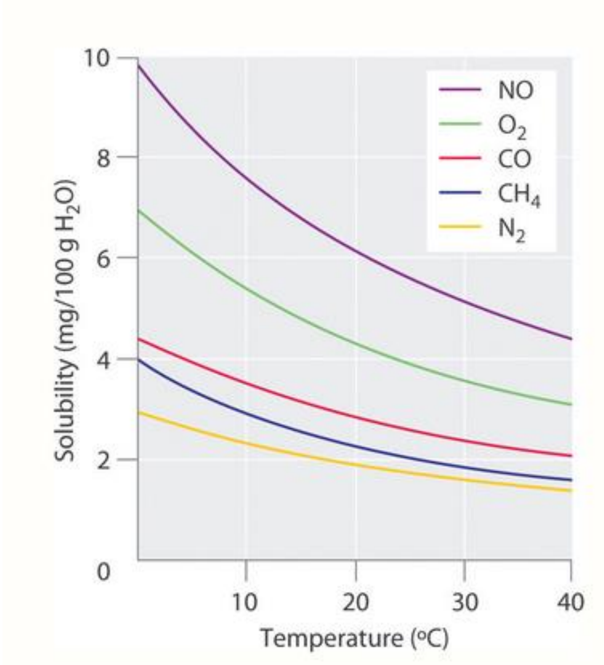
Recall that entropy is a measure of the ability of thermal energy to spread and be shared and exchanged by molecules in the system. Higher temperature exerts a kind of multiplying effect on a positive entropy change by increasing the amount of thermal energy available for sharing. Have you ever noticed the tiny bubbles that form near the bottom of a container of water when it is placed on a hot stove? These bubbles contain air that was previously dissolved in the water, but reaches its solubility limit as the water is warmed. You can completely rid a liquid of any dissolved gases (including unwanted ones such as Cl_2 or H_2S) by boiling it in an open container.

This is quite different from the behavior of most (but not all) solutions of solid or liquid solutes in liquid solvents. The reason for this behavior is the very large entropy increase that gases undergo when they are released from the confines of a condensed phase .

Solubility of Oxygen in water

Fresh water at sea level dissolves 14.6 mg of oxygen per liter at 0°C and 8.2 mg/L at 25°C. These saturation levels ensure that fish and other gilled aquatic animals are able to extract sufficient oxygen to meet their respiratory needs. But in actual aquatic environments, the presence of decaying organic matter or nitrogenous runoff can reduce these levels far below saturation. The health and survival of these organisms is severely curtailed when oxygen concentrations fall to around 5 mg/L.

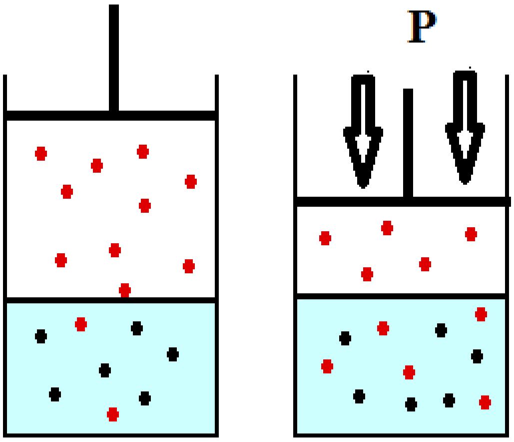
The temperature dependence of the solubility of oxygen in water is an important consideration for the well-being of aquatic life; thermal pollution of natural waters (due to the influx of cooling water from power plants) has been known to reduce the dissolved oxygen concentration to levels low enough to kill fish. The advent of summer temperatures in a river can have the same effect if the oxygen concentration has already been partially depleted by reaction with organic pollutants.



Effect of pressure:

The solubility of gases in liquids is greatly affected by pressure and temperature. The solubility of gases increases with the increase in pressure.

For a solution of gases in a solvent, consider a system as shown in the following fig (a). The lower part is the solution and the upper part is the gaseous system at pressure P and temperature T. Assume this system to be in a state of dynamic equilibrium, i.e., under these conditions rate of gaseous particles entering and leaving the solution phase is the same.



Now increase the pressure over the solution phase by compressing the gas to a smaller volume. This will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of the solution to enter it. The solubility of the gas will increase until a new equilibrium is reached resulting in an increase in the pressure of a gas above the solution and thus its solubility increases.

It is to be noted that the pressure does not have any significant effect on so the ability of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure. The effect of pressure on the solubility of a gas in a liquid is given by Henry’s law.

Henry's Law of Solubility:

Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent which is known as Henry's law. The law states that at a constant temperature, the solubility (S) of a gas in a liquid is directly proportional to the pressure (P) of the gas.

$$P = k_H C$$

- P is the partial pressure of the gas above the liquid,
- C is the concentration of gas dissolved in the liquid, and
- k_H is the *Henry's law constant*, which can be expressed in various units, and in some instances is defined in different ways, so be very careful to note these units when using published values.

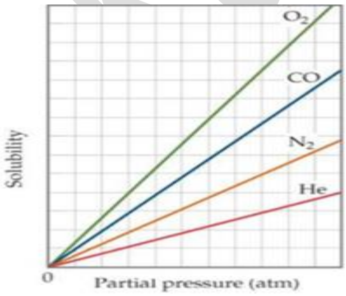
$$k_H = \frac{\text{partial pressure of gas in atm}}{\text{concentration in liquid } mol\ L^{-1}}$$

X, k_H is given as

***X:** Henry's law constants in water at 25° C, L atm mol^{-1}*

gas	He	N_2	O_2	CO_2	CH_4	NH_3
K_H	2703	1639	769	29.4	0.00129	57

If we draw a graph of the partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown. Different gases have different K_H values at the same temperature. This suggests that K_H is a function of the nature of the gas. From the above equation, we can conclude that the higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.



Applications of Henry's Law of Solubility:

Henry's law finds several applications in industry and explains some biological phenomena.

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

- Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in the blood. When the divers come towards the surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- At high altitudes, the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

Limitations of Henry's Law:

Henry's law is applicable only under the following conditions.

- The pressure of the gas is not too high.
- The temperature is not too low.
- The gas should not undergo any chemical reaction with the solvent.
- The gas should not undergo dissociation in the solvent.

Henry's Law is not strictly followed.

Higher Solubility than expected:

Ammonia not only dissolves in water but also reacts with it. The reaction is as follows.

$NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$

CO_2 not only dissolves in water but also reacts with it. The reaction is as follows.

$CO_2 + H_2O \rightarrow H_2CO_3$

In both cases, higher solubilities result than expected. Water is sparingly soluble in water but is highly soluble in the blood to the presence of hemoglobin of the blood.

Salting out effect:

Salting out is an effect based on the electrolyte-non electrolyte interaction, in which the non-electrolyte could be less soluble at high salt concentrations. Gases are less soluble in aqueous solutions of electrolytes. Similarly, sugar the non-electrolyte decreases the solubility of a gas in water.

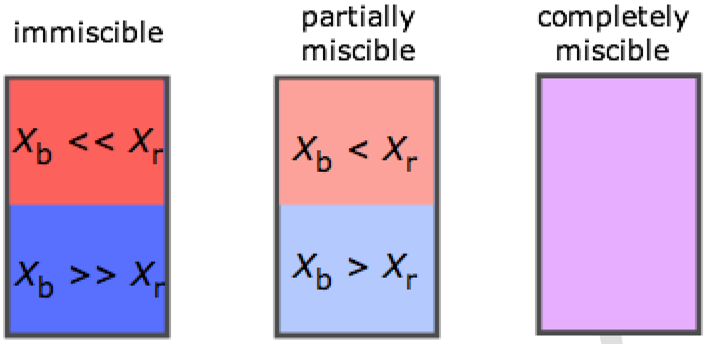
Solutions of liquid in liquid

Whereas all gases will mix to form solutions regardless of the proportions, liquids are much more fussy. Some liquids, such as ethyl alcohol and water, are miscible in all proportions. Others, like the proverbial oil and water, are not; each liquid has only a limited solubility in the other, and once either of these limits is exceeded, the mixture separates into two phases.

solute →	**liquid**
energy to disperse solute	varies
energy to introduce into solvent	varies

solute →	**liquid**
increase in entropy	moderate
miscibility	**"like dissolves like"**

The reason for this variability is apparent from the table. Mixing of two liquids can be exothermic, endothermic, or without thermal effect, depending on the particular substances. Whatever the case, the energy factors are not usually very large, but neither is the increase in randomness; the two factors are frequently sufficiently balanced to produce limited miscibility.



The range of possibilities is shown here in terms of the mole fractions *X* of two liquids A and B. If A and B are only slightly miscible, they separate into two layers according to their relative densities. Note that when one takes into account trace levels, no two liquids are totally immiscible.

Substances such as the alcohols, $CH_3(CH_2)_nOH$, which are hydrogen-bonding (and thus hydrophilic) at one end and hydrophobic at the other, tend to be at least partially miscible with both kinds of solvents. If *n* is large, the hydrocarbon properties dominate and the alcohol has only a limited solubility in water. Very small values of *n* allow the –OH group to dominate, so miscibility in water increases and becomes unlimited in ethanol ($n = 1$) and methanol ($n = 0$), but miscibility with hydrocarbons decreases owing to the energy required to break alcohol-alcohol hydrogen bonds when the non polar liquid is added.

These considerations have become quite important in the development of alternative automotive fuels based on mixing these alcohols with gasoline. At ordinary temperatures the increased entropy of the mixture is great enough that the unfavorable energy factor is entirely overcome, and the mixture is completely miscible. At low temperatures, the entropy factor becomes less predominant, and the fuel mixture may separate into two phases, presenting severe problems to the fuel filter and carburetor.

Like Dissolves Like

A useful general rule is that liquids are completely miscible when their intermolecular forces are very similar in nature; “like dissolves like”. Thus water is miscible with other liquids that can engage in hydrogen bonding, whereas a hydrocarbon liquid in which London or dispersion forces are the only significant intermolecular effect will only be completely miscible with similar kinds of liquids.

Binary liquid mixture

A binary system has two components; CC equals 22, and the number of degrees of freedom is F=4−PF=4−P. There must be at least one phase, so the maximum possible value of FF is 3. Since FF cannot be negative, the equilibrium system can have no more than four phases.

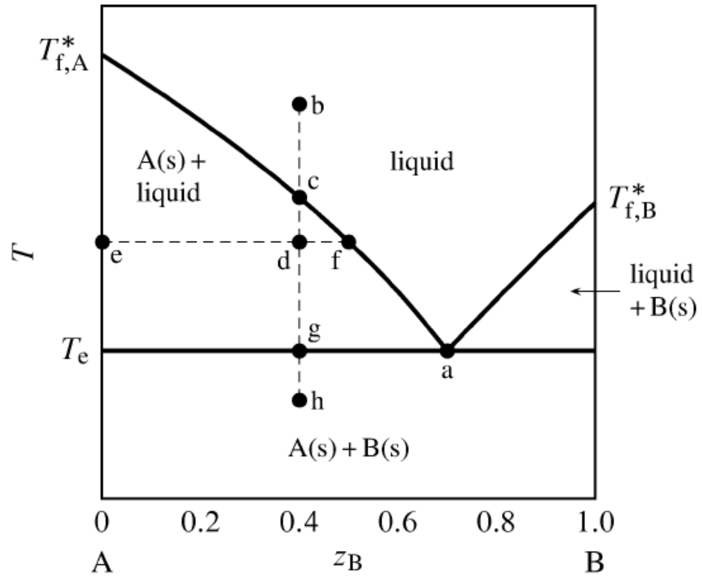
We can independently vary the temperature, pressure, and composition of the system as a whole. Instead of using these variables as the coordinates of a three-dimensional phase diagram, we usually draw a two-dimensional phase diagram that is either a temperature–composition diagram at a fixed pressure or a pressure–composition diagram at a fixed temperature. The position of the system point on one of these diagrams then corresponds to a definite temperature, pressure, and overall composition. The composition variable usually varies along the horizontal axis and can be the mole fraction, mass fraction, or mass percent of one of the components, as will presently be illustrated by various examples.

The way in which we interpret a two-dimensional phase diagram to obtain the compositions of individual phases depends on the number of phases present in the system.

- If the system point falls within a *one-phase* area of the phase diagram, the composition variable is the composition of that single phase. There are three degrees of freedom. On the phase diagram, the value of either TT or pp has been fixed, so there are two other independent intensive variables. For example, on a temperature–composition phase diagram, the pressure is fixed and the temperature and composition can be changed independently within the boundaries of the one-phase area of the diagram.
- If the system point is in a *two-phase* area of the phase diagram, we draw a horizontal *tie line* of constant temperature (on a temperature–composition phase diagram) or constant pressure (on a pressure–composition phase diagram). The lever rule applies. The position of the point at each end of the tie line, at the boundary of the two-phase area, gives the value of the composition variable of one of the phases and also the physical state of this phase: either the state of an adjacent one-phase area, or the state of a phase of fixed composition when the boundary is a vertical line. Thus, a boundary that separates a two-phase area for phases αα and ββ from a one-phase area for phase αα is a curve that describes the composition of phase αα as a function of TT or pp when it is in equilibrium with phase ββ. The curve is called a *solidus*, *liquidus*, or *vaporus* depending on whether phase αα is a solid, liquid, or gas.
- A binary system with *three* phases has only one degree of freedom and cannot be represented by an area on a two-dimensional phase diagram. Instead, there is a horizontal boundary line between areas, with a special point along the line at the junction of several areas. The compositions of the three phases are given by the positions of this point and the points at the two ends of the line. The position of the system point on this line does not uniquely specify the relative amounts in the three phases.

The examples that follow show some of the simpler kinds of phase diagrams known for binary systems.

Solid–liquid systems



A temperature–composition phase diagram at a fixed pressure. The composition variable zBzB is the mole fraction of component B in the system as a whole. The phases shown are a binary liquid mixture of A and B, pure solid A, and pure solid B.

The one-phase liquid area is bounded by two curves, which we can think of either as freezing-point curves for the liquid or as solubility curves for the solids. These curves comprise the liquidus. As the mole fraction of either component in the liquid phase decreases from unity, the freezing point decreases. The curves meet at point a, which is a **eutectic point**. At this point, both solid A and solid B can coexist in equilibrium with a binary liquid mixture. The composition at this point is the *eutectic composition*, and the temperature here (denoted TeTe) is the *eutectic temperature*. (“Eutectic” comes from the Greek for *easy melting*.) TeTe is the lowest temperature for the given pressure at which the liquid phase is stable.

Suppose we combine 0.60mol0.60mol A and 0.40mol0.40mol B (zB=0.40zB=0.40) and adjust the temperature so as to put the system point at b. This point is in the one-phase liquid area, so the equilibrium system at this temperature has a single liquid phase. If we now place the system in thermal contact with a cold reservoir, heat is transferred out of the system and the system point moves down along the *isopleth* (path of constant overall composition) b–h. The cooling rate depends on the temperature gradient at the system boundary and the system’s heat capacity.

At point c on the isopleth, the system point reaches the boundary of the one-phase area and is about to enter the two-phase area labeled A(s) + liquid. At this point in the cooling process, the liquid is saturated with respect to solid A, and solid A is about to freeze out from the liquid. There is an abrupt decrease (break) in the cooling rate at this point, because the freezing process involves an extra enthalpy decrease.

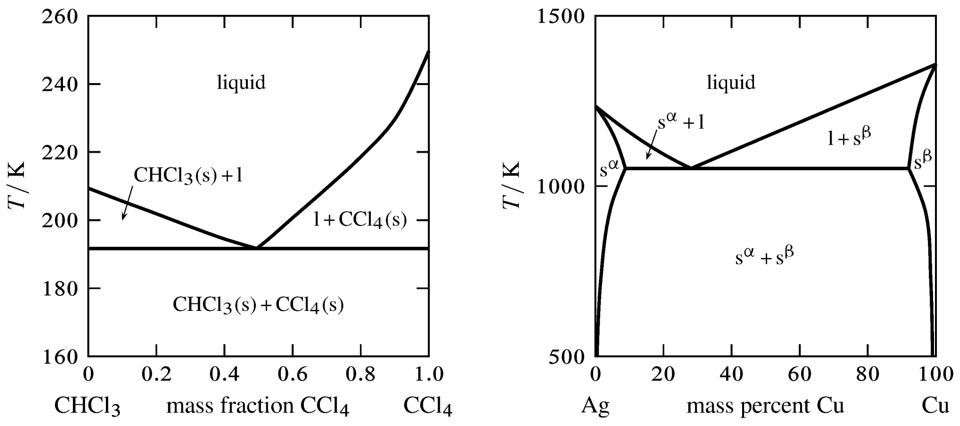
At the still lower temperature at point d, the system point is within the two-phase solid–liquid area. The tie line through this point is line e–f. The compositions of the two phases are given by the values of zBzB at the ends of the tie line: xsB=0xBs=0 for the solid and xlB=0.50xBl=0.50 for the liquid. From the general lever rule (Eq. 8.2.8), the ratio of the amounts in these phases is

$$\frac{n^{\mathrm{l}}}{n^{\mathrm{s}}} = \frac{z_{\mathrm{B}} - x_{\mathrm{B}}^{\mathrm{s}}}{x_{\mathrm{B}}^{\mathrm{l}} - z_{\mathrm{B}}} = \frac{0.40 - 0}{0.50 - 0.40} = 4.0$$

Since the total amount is ns+nl=1.00molns+nl=1.00mol, the amounts of the two phases must be ns=0.20molns=0.20mol and nl=0.80molnl=0.80mol.

When the system point reaches the eutectic temperature at point g, cooling halts until all of the liquid freezes. Solid B freezes out as well as solid A. During this *eutectic halt*, there are at first three phases: liquid with the eutectic composition, solid A, and solid B. As heat continues to be withdrawn from the system, the amount of liquid decreases and the amounts of the solids increase until finally only 0.60mol0.60mol of solid A and 0.40mol0.40mol of solid B are present. The temperature then begins to decrease again and the system point enters the two-phase area for solid A and solid B; tie lines in this area extend from zB=0zB=0 to zB=1zB=1.

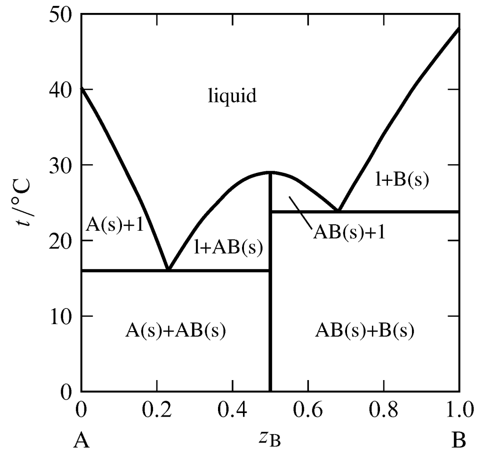
Temperature–composition phase diagrams such as this are often mapped out experimentally by observing the cooling curve (temperature as a function of time) along isopleths of various compositions. This procedure is *thermal analysis*. A break in the slope of a cooling curve at a particular temperature indicates the system point has moved from a one-phase liquid area to a two-phase area of liquid and solid. A temperature halt indicates the temperature is either the freezing point of the liquid to form a solid of the same composition, or else a eutectic temperature.



(a) (b)

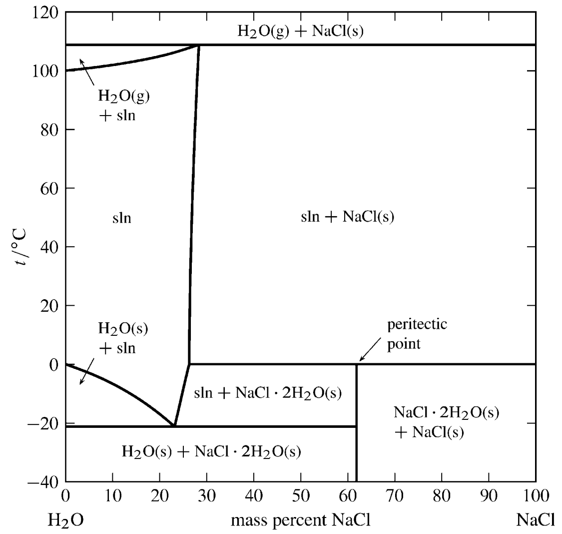
(b) Two solid solutions and a liquid mixture.

two temperature–composition phase diagrams with single eutectic points. The left-hand diagram is for the binary system of chloroform and carbon tetrachloride, two liquids that form nearly ideal mixtures. The solid phases are pure crystals, as in Fig. 13.1. The right-hand diagram is for the silver–copper system and involves solid phases that are solid solutions (substitutional alloys of variable composition). The area labeled sαα is a solid solution that is mostly silver, and sββ is a solid solution that is mostly copper. Tie lines in the two-phase areas do not end at a vertical line for a pure solid component as they do in the system shown in the left-hand diagram. The three phases that can coexist at the eutectic temperature of 1,052K1,052K are the melt of the eutectic composition and the two solid solutions.



The solid compound contains equal amounts of the two components αα-naphthylamine and phenol. The possible solid phases are pure A, pure B, and the solid compound AB. Only one or two of these solids can be present simultaneously in an equilibrium state. The vertical line in the figure at zB=0.5zB=0.5 represents the solid compound. The temperature at the upper end of this line is the melting point of the solid compound, 29^{o}C. The solid melts *congruently* to give a liquid of the same composition. A melting process with this behavior is called a *dystectic reaction*. The cooling curve for liquid of this composition would display a halt at the melting point.

There is one important difference: the slope of the freezing-point curve (liquidus curve) is nonzero at the composition of a pure component, but is zero at the composition of a solid compound that is completely dissociated. Thus, the curve in Fig. 13.3 has a relative maximum at the composition of the solid compound (zB=0.5zB=0.5) and is rounded there, instead of having a cusp—like a Romanesque arch rather than a Gothic arch.

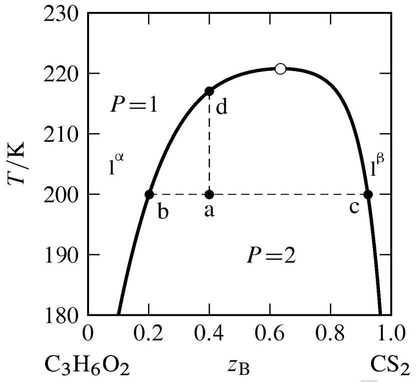


An example of a solid compound that does not melt congruently is shown in Figure. The solid hydrate NaCl·2H2ONaCl·2H2O is 61.9%61.9% NaCl by mass. It decomposes at 0°C0°C to form an aqueous solution of composition 26.3%26.3% NaCl by mass and a solid phase of anhydrous NaCl. These three phases can coexist at equilibrium at 0^{o}C. A phase transition like this, in which a solid compound changes into a liquid and a different solid, is called *incongruent* or *peritectic*melting, and the point on the phase diagram at this temperature at the composition of the liquid is a *peritectic point*.

there are two other temperatures at which three phases can be present simultaneously: −21◦C, where the phases are ice, the solution at its eutectic point, and the solid hydrate; and 109◦C, where the phases are gaseous H_2O, a solution of composition 28.3% NaCl by mass, and solid NaCl. Note that both segments of the right-hand boundary of the one-phase solution area have positive slopes, meaning that the solubilities of the solid hydrate and the anhydrous salt both increase with increasing temperature.

Partially-miscible liquids

When two liquids that are partially miscible are combined in certain proportions, phase separation occurs. Two liquid phases in equilibrium with one another are called *conjugate phases*. Obviously the two phases must have different compositions or they would be identical; the difference is called a *miscibility gap*. A binary system with two phases has two degrees of freedom, so that at a given temperature and pressure each conjugate phase has a fixed composition.



The typical dependence of a miscibility gap on temperature. The miscibility gap (the difference in compositions at the left and right boundaries of the two-phase area) decreases as the temperature increases until at the *upper consolute temperature*, also called the *upper critical solution temperature*, the gap vanishes. The point at the maximum of the boundary curve of the two-phase area, where the temperature is the upper consolute temperature, is the *consolute point* or *critical point*. At this point, the two liquid phases become identical, just as the liquid and gas phases become identical at the critical point of a pure substance. Critical opalescence is observed in the vicinity of this point, caused by large local composition fluctuations. At temperatures at and above the critical point, the system is a single binary liquid mixture.

Suppose we combine 6.0mol6.0mol of component A (methyl acetate) and 4.0mol of component B (carbon disulfide) in a cylindrical vessel and adjust the temperature to 200K. The overall mole fraction of B is zB=0.40. The system point is at point a in the two-phase region. From the positions of points b and c at the ends of the tie line through point a, we find the two liquid layers have compositions xαB=0.20xBα=0.20 and xβB=0.92xBβ=0.92. Since carbon disulfide is the more dense of the two pure liquids, the bottom layer is phase ββ, the layer that is richer in carbon disulfide. According to the lever rule, the ratio of the amounts in the two phases is given by

nβnα=zB−xαBxβB−zB=0.40−0.200.92−0.40=0.38(13.2.2)

$$\frac{n^\beta}{n^\alpha} = \frac{z_\mathrm{B} - x_\mathrm{B}^\alpha}{x_\mathrm{B}^\beta - z_\mathrm{B}} = \frac{0.40 - 0.20}{0.92 - 0.40} = 0.38$$

Combining this value with nα+nβ=10.0mol$n^\alpha + n^\beta = 10.0\,\mathrm{mol}$ gives us nα=7.2mol$n^\alpha = 7.2\,\mathrm{mol}$ and nβ=2.8mol$n^\beta = 2.8\,\mathrm{mol}$.

Ideal and non ideal solutions

We have found the chemical potential of any component in an ideal solution. Now let us find some other thermodynamic properties of an ideal solution. The value of an extensive thermodynamic property of the solution will be the sum of the values of that property for the separate pure components plus the change that occurs when these components are mixed. (The initial state of the system comprises the pure, separate components at a particular temperature and pressure. The mixed state is a homogeneous liquid solution at the same temperature and pressure.) If the solution contains nA moles of component A and nB moles of component BB, the Gibbs free energy is

$G_{solution}$(nA,nB)=nAuA+nBuB

> 0. The potential energy of the mixed state would be greater than that of the separate components; the mixing process would consume heat at constant temperature; we would find ΔmixE‾‾‾‾‾>0$\Delta_{\text{mix}} \overline{E} > 0$.

In an ideal gas, molecules do not interact at all. In an ideal solution, the molecules must interact, because only their mutual attraction can keep them in the liquid state. The ideal solution behaves ideally not because the intermolecular interactions are zero but rather because the intermolecular interactions are the same for all of the kinds of molecules present in the mixture. This interpretation implies that the vapor pressures of the pure components of an ideal solution should be equal. Even for solutions that follow Raoult's law quite closely, this expected equality is often imperfectly realized. Not surprisingly, ideal-solution behavior is best exhibited when the components are isotopically-substituted versions of the same compound.

In an ideal solution, the activities of the components are equal to their mole fractions. The activity of the solvent depends only on the solvent mole fraction. The properties of the solvent in an ideal solution are independent of the specific substance that comprises the solute; they depend only on the concentration of solute particles present. Systems in which this is a useful approximation are sufficiently common that their properties are given a special name: A ***colligative property*** of a solution is a property that depends only on the concentration of solute particles and not on the specific chemical properties of the solute. We expect this approximation to become better as the solute concentration approaches zero. When a solute obeys Raoult's law or Henry's law, its effects on the thermodynamic properties of the solvent depend only on the concentration of the solute. Consequently, Raoult's law and Henry's law prove to be useful when we seek to model colligative properties.

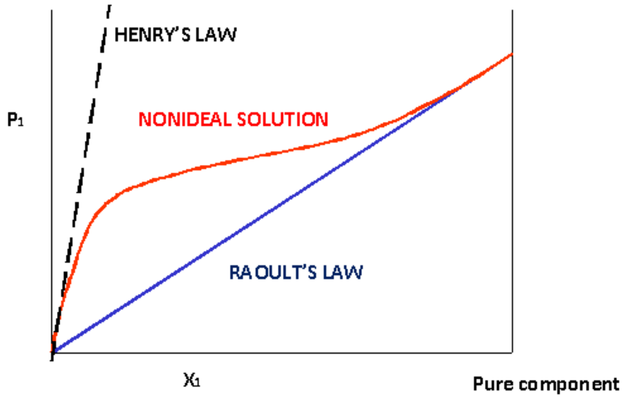
Raoult's law

Raoult's law states that the vapor pressure of a solvent above a solution is *equal* to the vapor pressure of the pure solvent at the same temperature *scaled* by the mole fraction of the solvent present:

$$P_{solution} = \chi_{solvent} P^{o}_{solvent}$$

Ideal vs. Nonideal Solutions

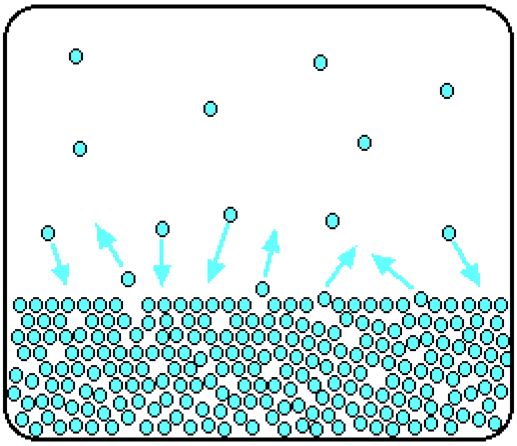
Raoult's Law only works for ideal solutions. "An ideal solution shows thermodynamic mixing characteristics identical to those of ideal gas mixtures [except] ideal solutions have intermolecular interactions equal to those of the pure components."[2] Like many other concepts explored in Chemistry, Raoult's Law only applies under ideal conditions in an ideal solution. However, it still works fairly well for the solvent in dilute solutions. In reality though, the decrease in vapor pressure will be greater than that calculated by Raoult's Law for extremely dilute solutions.



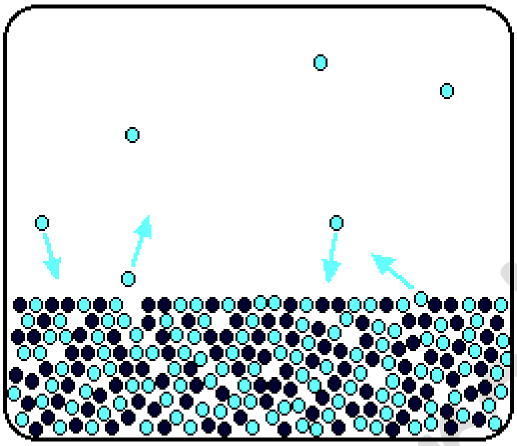
Why Raoult's Law works

In the concepts of colligative properties, you will find that adding a solute lowers vapor pressure because the additional solute particles will fill the gaps between the solvent particles and take up space. This means less of the solvent will be on the surface and less will be able to break free to enter the gas phase, resulting in a lower vapor pressure. There are two ways of explaining why Raoult's Law works - a simple visual way, and a more sophisticated way based on entropy. Below is the simple approach.

Remember that saturated vapor pressure is what you get when a liquid is in a sealed container. An equilibrium is set up where the number of particles breaking away from the surface is exactly the same as the number sticking on to the surface again.



Now suppose solute molecules were added so that the solvent molecules occupied only 50% of the surface of the solution.

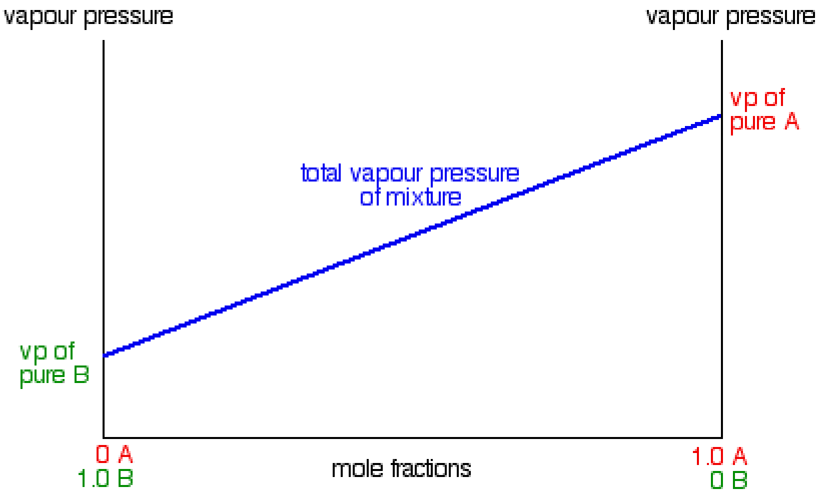


A certain fraction of the solvent molecules will have sufficient energy to escape from the surface (e.g., 1 in 1000 or 1 in a million). If you reduce the number of solvent molecules on the surface, you are going to reduce the number which can escape in any given time. But it will not make any difference to the ability of molecules in the vapor to stick to the surface again. If a solvent molecule in the vapor hits a bit of surface occupied by the solute particles, it may well stick. There are obviously attractions between solvent and solute otherwise you would not have a solution in the first place.

The net effect of this is that when equilibrium is established, there will be *fewer* solvent molecules in the vapor phase - it is less likely that they are going to break away, but there is not any problem about them returning. However, if there are fewer particles in the vapor at equilibrium, the saturated vapor pressure is lower.

Ideal Solutions follow Raoult's Law and Real Solutions Do Not

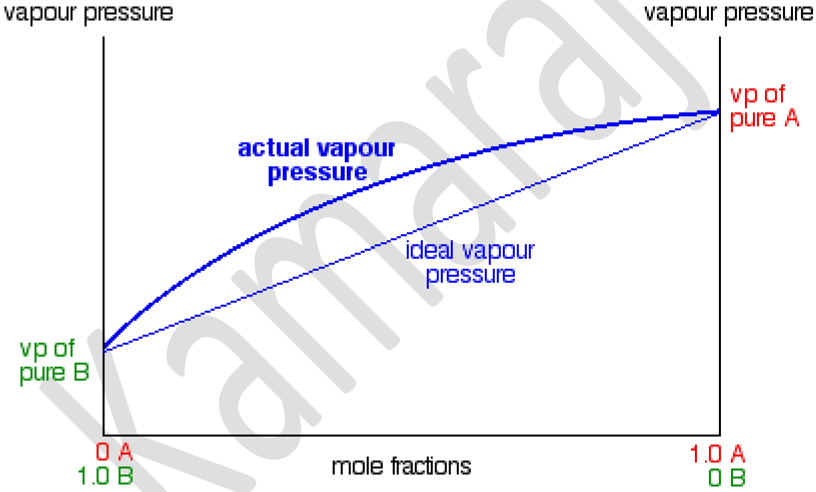
Due to Raoult's Law, a plot the vapor pressure of an ideal mixture of two liquids against their composition will result in a straight line:



Ideal solution that follows Raoult's Law

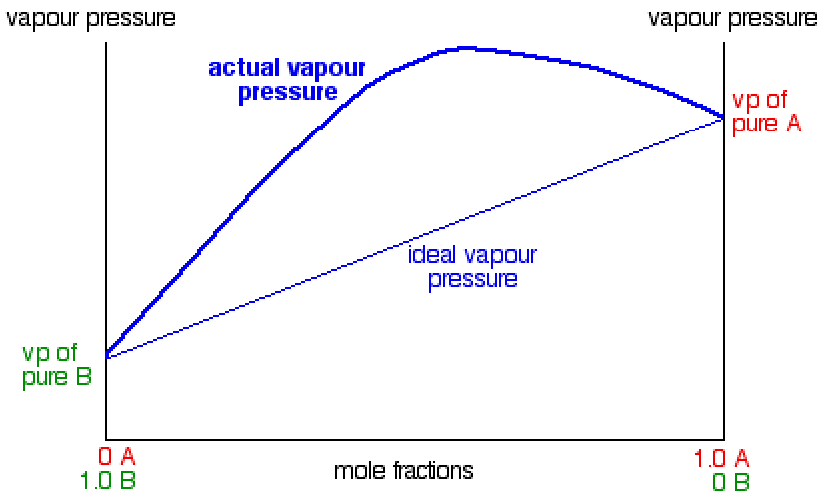
In this case, pure A has the higher vapor pressure and so is the more volatile component. Raoult's Law only works for ideal mixtures. In these, the forces between the particles in the mixture are exactly the same as those in the pure liquids. The tendency for the particles to escape is the same in the mixture and in the pure liquids. That's not true in non-ideal mixtures.

In mixtures showing a positive deviation from Raoult's Law, the vapor pressure of the mixture is always higher than you would expect from an ideal mixture. The deviation can be small - in which case, the straight line in the last graph turns into a slight curve.



Positive deviations from Raoult's Law.

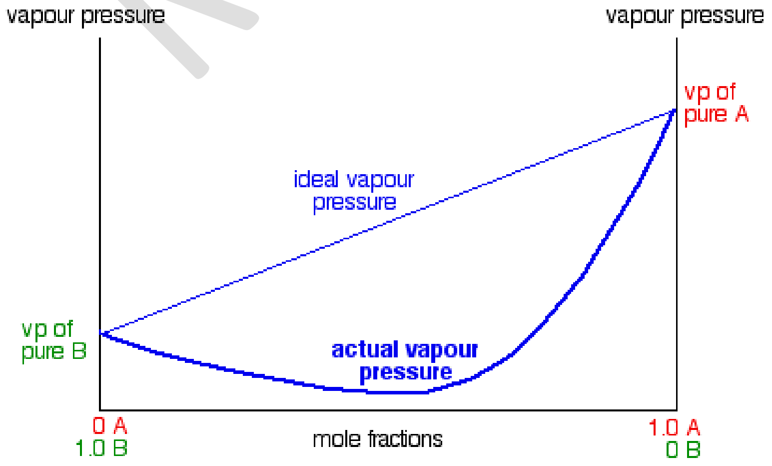
Notice that the highest vapor pressure anywhere is still the vapor pressure of pure A. Cases like this, where the deviation is small, behave just like ideal mixtures as far as distillation is concerned, and we do not need to say anything more about them. But some liquid mixtures have very large positive deviations from Raoult's Law, and in these cases, the curve becomes very distorted.



Extreme positive deviation from Raoult's Law. The fact that the vapor pressure is higher than ideal in these mixtures means that molecules are breaking away more easily than they do in the pure liquids. That is because the intermolecular forces between molecules of A and B are less than they are in the pure liquids.

Notice that mixtures over a range of compositions have higher vapor pressures than either pure liquid. The maximum vapor pressure is no longer that of one of the pure liquids. This has important consequences when we look at boiling points and distillation further down the page. The fact that the vapor pressure is higher than ideal in these mixtures means that molecules are breaking away more easily than they do in the pure liquids. That is because the intermolecular forces between molecules of A and B are less than they are in the pure liquids.

You can see this when you mix the liquids. Less heat is evolved when the new attractions are set up than was absorbed to break the original ones. Heat will therefore be absorbed when the liquids mix. The enthalpy change of mixing is endothermic. The classic example of a mixture of this kind is ethanol and water. This produces a highly distorted curve with a maximum vapor pressure for a mixture containing 95.6% of ethanol by mass.
In exactly the same way, you can have mixtures with vapor pressures which are less than would be expected by Raoult's Law. In some cases, the deviations are small, but in others they are much greater giving a minimum value for vapor pressure lower than that of either pure component.



Negative deviations from Raoult's Law. New stronger forces must exist in the mixture than in the original liquids.

These are cases where the molecules break away from the mixture less easily than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids. You can recognize this happening because heat is evolved when you mix the liquids - more heat is given out when the new stronger bonds are made than was used in breaking the original weaker ones. Many (although not all) examples of this involve actual reaction between the two liquids. The example of a major negative deviation is a mixture of nitric acid and water. These two covalent molecules react to give hydroxonium ions and nitrate ions.

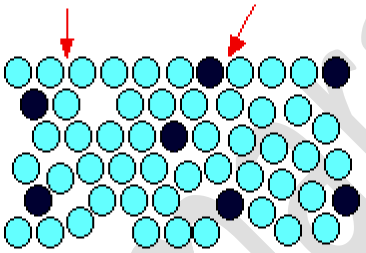
Limitations on Raoult's Law

In practice, there's no such thing as an ideal solution! However, features of one include:

- Ideal solutions satisfy Raoult's Law. The solution in the last diagram of Figure 3
- above would not actually obey Raoult's Law - it is far too concentrated, but was drawn so concentrated to emphasized the point.
- In an ideal solution, it takes exactly the same amount of energy for a solvent molecule to break away from the surface of the solution as it did in the pure solvent. The forces of attraction between solvent and solute are exactly the same as between the original solvent molecules - not a very likely event!
-

In an ideal solution, the forces between the solvent molecules . . .

. . . are exactly the same as those between solvent and solute.



That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

Suppose that in the pure solvent, 1 in 1000 molecules had enough energy to overcome the intermolecular forces and break away from the surface in any given time. In an ideal solution, that would still be exactly the same proportion. Fewer would, of course, break away because there are now fewer solvent molecules on the surface - but of those that are on the surface, the same proportion still break away. If there were strong solvent-solute attractions, this proportion may be reduced to 1 in 2000, or 1 in 5000 or whatever.

In any real solution of, say, a salt in water, there are strong attractions between the water molecules and the ions. That would tend to slow down the loss of water molecules from the surface. However, if the solution is sufficiently dilute, there will be good-sized regions on the surface where you still have water molecules on their own. The solution will then approach ideal behavior.

Deviations from Idal Gas Law Behavior

The behavior of real gases usually agrees with the predictions of the ideal gas equation to within ±5% at normal temperatures and pressures. At low temperatures or high pressures, real gases deviate significantly from ideal gas behavior. In 1873, while searching for a way to link the behavior of liquids and gases, the Dutch physicist Johannes van der Waals developed an explanation for these deviations and an equation that was able to fit the behavior of real gases over a much wider range of pressures.

Van der Waals realized that two of the assumptions of the kinetic molecular theory were questionable. The kinetic theory assumes that gas particles occupy a negligible fraction of the total volume of the gas. It also assumes that the force of attraction between gas molecules is zero.

The first assumption works at pressures close to 1 atm. But something happens to the validity of this assumption as the gas is compressed. Imagine for the moment that the atoms or molecules in a gas were all clustered in one corner of a cylinder, as shown in the figure below. At normal pressures, the volume occupied by these particles is a negligibly small fraction of the total volume of the gas. But at high pressures, this is no longer true. As a result, real gases are not as compressible at high pressures as an ideal gas. The volume of a real gas is therefore larger than expected from the ideal gas equation at high pressures.

Van der Waals proposed that we correct for the fact that the volume of a real gas is too large at high pressures by *subtracting* a term from the volume of the real gas before we substitute it into the ideal gas equation. He therefore introduced a constant (*b*) into the ideal gas equation that was equal to the volume actually occupied by a mole of gas particles. Because the volume of the gas particles depends on the number of moles of gas in the container, the term that is subtracted from the real volume of the gas is equal to the number of moles of gas times*b*.

$$P(V - nb) = nRT$$

When the pressure is relatively small, and the volume is reasonably large, the *nb* term is too small to make any difference in the calculation. But at high pressures, when the volume of the gas is small, the *nb* term corrects for the fact that the volume of a real gas is larger than expected from the ideal gas equation.

The assumption that there is no force of attraction between gas particles cannot be true. If it was, gases would never condense to form liquids. In reality, there is a small force of attraction between gas molecules that tends to hold the molecules together. This force of attraction has two consequences: (1) gases condense to form liquids at low temperatures and (2) the pressure of a real gas is sometimes smaller than expected for an ideal gas.

To correct for the fact that the pressure of a real gas is smaller than expected from the ideal gas equation, van der Waals *added* a term to the pressure in this equation. This term contained a second constant (*a*) and has the form: an^2/V^2. The complete **van der Waals equation** is therefore written as follows.

$$[P + \frac{an^2}{V^2}](V - nb) = nRT$$

This equation is something of a mixed blessing. It provides a much better fit with the behavior of a real gas than the ideal gas equation. But it does this at the cost of a loss in generality. The ideal gas equation is equally valid for any gas, whereas the van der Waals equation contains a pair of constants (*a* and*b*) that change from gas to gas.

The ideal gas equation predicts that a plot of *PV* versus *P* for a gas would be a horizontal line because *PV* should be a constant. Experimental data for *PV* versus *P* for H_2 and N_2 gas at 0°C and CO_2 at 40°C are given in the figure below. Values of the van der Waals constants for these and other gases are given in the table below.

van der Waals Constants for Various Gases

Compound	*a* (L^2*-atm/mol*^{2})	*b* (*L/mol*)
He	0.03412	0.02370
Ne	0.2107	0.01709
H_2	0.2444	0.02661
Ar	1.345	0.03219
O_2	1.360	0.03803
N_2	1.390	0.03913
CO	1.485	0.03985
CH_4	2.253	0.04278
CO_2	3.592	0.04267
NH_3	4.170	0.03707

The magnitude of the deviations from ideal gas behavior can be illustrated by comparing the results of calculations using the ideal gas equation and the van der Waals equation for 1.00 mole of CO_2 at 0°C in containers of different volumes. Let's start with a 22.4 L container.
According to the ideal gas equation, the pressure of this gas should be 1.00 atm.

$$P = \frac{nRT}{V} = \frac{(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(273\ K)}{(22.4\ L)} = 1.00\ atm$$

Substituting what we know about CO_2 into the van der Waals equation gives a much more complex equation.

$$[P + \frac{an^2}{V^2}](V - nb) = nRT$$

$$[P + \frac{(3.592\ \frac{L^2\ atm}{mol^2})(1.00\ mol)^2}{(22.4\ L)^2}][22.4\ L - (1.00\ mol)(0.0426$$

$$(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(27$$

This equation can be solved, however, for the pressure of the gas.
P = 0.995 atm

At normal temperatures and pressures, the ideal gas and van der Waals equations give essentially the same results.

Let's now repeat this calculation, assuming that the gas is compressed so that it fills a container that has a volume of only 0.200 liters. According to the ideal gas equation, the pressure would have to be increased to 112 atm to compress 1.00 mol of CO_2 at 0C to a volume of 0.200 L.

$$P = \frac{nRT}{V} = \frac{(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(273\ K)}{(0.200\ L)} = 112\ atm$$

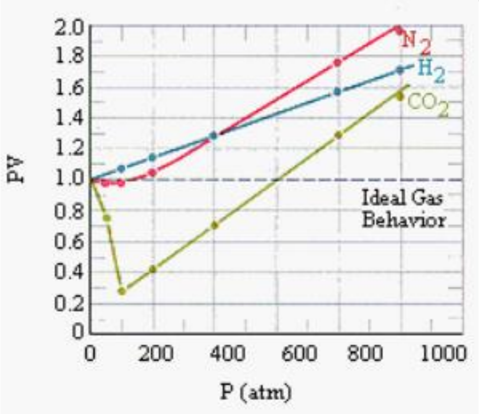
The van der Waals equation, however, predicts that the pressure will only have to increase to 52.6 atm to achieve the same results.

$$[P + \frac{(3.592\ \frac{L^2\ atm}{mol^2})(1.00\ mol)^2}{(0.200\ L)^2}][0.200\ L - (1.00\ mol)(0.0426$$

$$(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(27$$

P = 52.6 atm

As the pressure of CO_2 increases the van der Waals equation initially gives pressures that are *smaller* than the ideal gas equation, as shown in the figure below, because of the strong force of attraction between CO_2 molecules.



Let's now compress the gas even further, raising the pressure until the volume of the gas is only 0.0500 liters. The ideal gas equation predicts that the pressure would have to increase to 448 atm to condense 1.00 mole of CO_2 at 0°C to a volume of 0.0500 L.

$$P = \frac{nRT}{V} = \frac{(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(273\ K)}{(0.050\ L)} = 448\ atm$$

The van der Waals equation predicts that the pressure will have to reach 1620 atm to achieve the same results.

$$[P + \frac{(3.592\ \frac{L^2\ atm}{mol^2})(1.00\ mol)^2}{(0.050\ L)^2}][0.050\ L - (1.00\ mol)(0.0426$$

$$(1.00\ mol)(0.08206\ \frac{L\ atm}{mol\ K})(27$$

P = 1620 atm

The van der Waals equation gives results that are *larger* than the ideal gas equation at very high pressures, as shown in the figure above, because of the volume occupied by the CO_2 molecules.

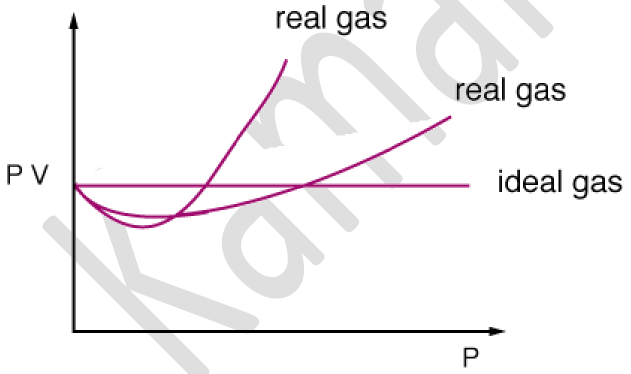
Causes of Deviation from Ideal Behaviour

The causes of deviations from ideal behaviour may be due to the following two assumptions of kinetic theory of gases.

The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas.

The forces of attraction between gas molecules are negligible.

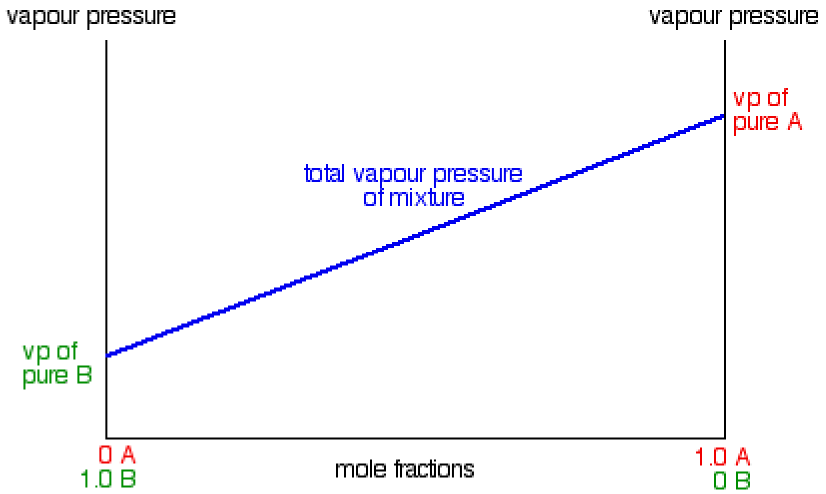
The first assumption is valid only at low pressures and high temperature, when the volume occupied by the gas molecules is negligible as compared to the total volume of the gas. But at low temperature or at high pressure, the molecules being in compressible the volumes of molecules are no more negligible as compared to the total volume of the gas.



The second assumption is not valid when the pressure is high and temperature is low. But at high pressure or low temperature when the total volume of gas is small, the forces of attraction become appreciable and cannot be ignored.

Vapour pressure / composition diagrams for non-ideal mixtures

You will remember that, because of Raoult's Law, if you plot the vapour pressure of an ideal mixture of two liquids against their composition, you get a straight line graph like this:



In this case, pure A has the higher vapour pressure and so is the more volatile component.

Raoult's Law only works for ideal mixtures. In these, the forces between the particles in the mixture are exactly the same as those in the pure liquids. The tendency for the particles to escape is the same in the mixture and in the pure liquids.
That's not true in non-ideal mixtures.

Boiling point / composition diagrams for non-ideal mixtures
A large positive deviation from Raoult's Law: ethanol and water mixtures

If you look back up the page, you will remember that a large positive deviation from Raoult's Law produces a vapour pressure curve with a maximum value at some composition other than pure A or B.

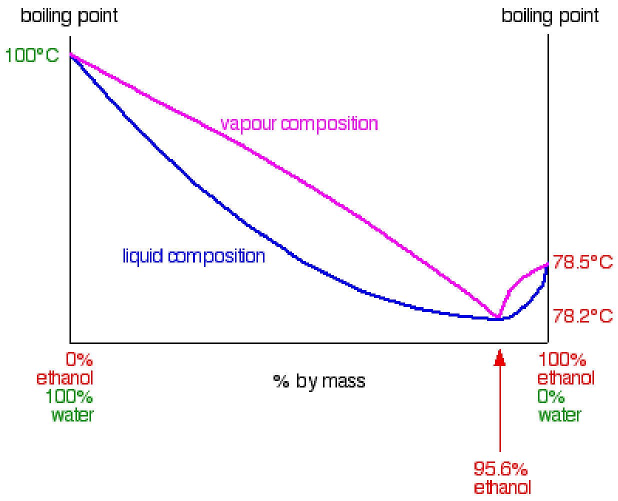
If a mixture has a high vapour pressure it means that it will have a low boiling point. The molecules are escaping easily and you won't have to heat the mixture much to overcome the intermolecular attractions completely.

The implication of this is that the boiling point / composition curve will have a minimum value lower than the boiling points of either A or B.

In the case of mixtures of ethanol and water, this minimum occurs with 95.6% by mass of ethanol in the mixture. The boiling point of this mixture is 78.2°C, compared with the boiling point of pure ethanol at 78.5°C, and water at 100°C.

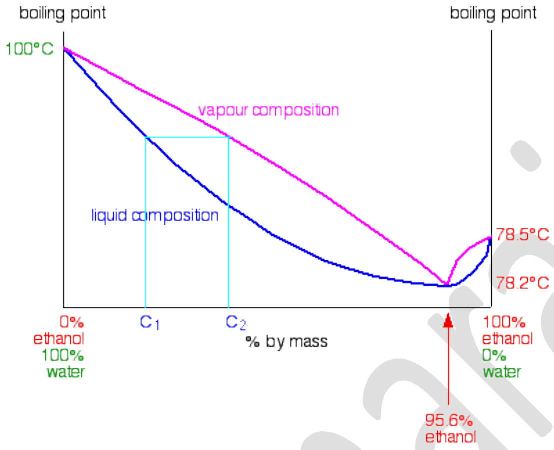
You might think that this 0.3°C doesn't matter much, but it has huge implications for the separation of ethanol / water mixtures.

The next diagram shows the boiling point / composition curve for ethanol / water mixtures. I've also included on the same diagram a vapour composition curve in exactly the same way as we looked at on the previous pages about phase diagrams for ideal mixtures.

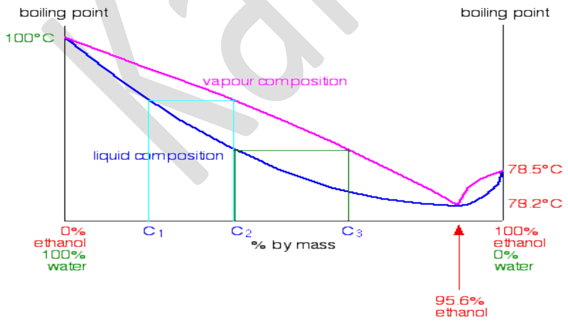


Using the diagram

Suppose you are going to distil a mixture of ethanol and water with composition C_1 as shown on the next diagram. It will boil at a temperature given by the liquid curve and produce a vapour with composition C_2.



When that vapour condenses it will, of course, still have the composition C_2. If you reboil that, it will produce a new vapour with composition C_3.



if you carried on with this boiling-condensing-reboiling sequence, you would eventually end up with a vapour with a composition of 95.6% ethanol. If you condense that you obviously get a liquid with 95.6% ethanol.

What happens if you reboil that liquid?

The liquid curve and the vapour curve meet at that point. The vapour produced will have that same composition of 95.6% ethanol. If you condense it again, it will still have that same composition.

You have hit a barrier. It is impossible to get pure ethanol by distilling any mixture of ethanol and water containing less than 95.6% of ethanol.

This particular mixture of ethanol and water boils as if it were a pure liquid. It has a constant boiling point, and the vapour composition is exactly the same as the liquid.

It is known as a ***constant boiling mixture*** or an ***azeotropic mixture*** or an ***azeotrope***.

The implications of this for fractional distillation of dilute solutions of ethanol are obvious. The liquid collected by condensing the vapour from the top of the fractionating column can't be pure ethanol. The best you can produce by simple fractional distillation is 95.6% ethanol.

What you *can* get (although it isn't very useful!) from the mixture is pure water. As ethanol rich vapour is given off from the liquid boiling in the distillation flask, it will eventually lose all the ethanol to leave just water.

A large negative deviation from Raoult's Law: nitric acid and water mixtures

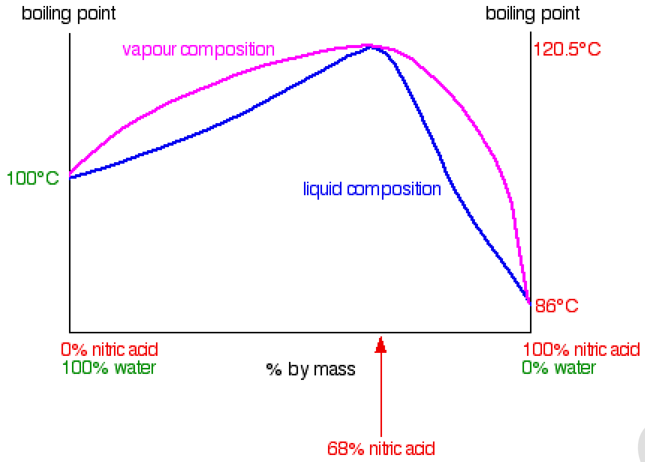
Nitric acid and water form mixtures in which particles break away to form the vapour with much more difficulty than in either of the pure liquids. You can see this from the vapour pressure / composition curve discussed further up the page.

That means that mixtures of nitric acid and water can have boiling points higher than either of the pure liquids because it needs extra heat to break the stronger attractions in the mixture.

In the case of mixtures of nitric acid and water, there is a maximum boiling point of 120.5°C when the mixture contains 68% by mass of nitric acid. That compares with the boiling point of pure nitric acid at 86°C, and water at 100°C.

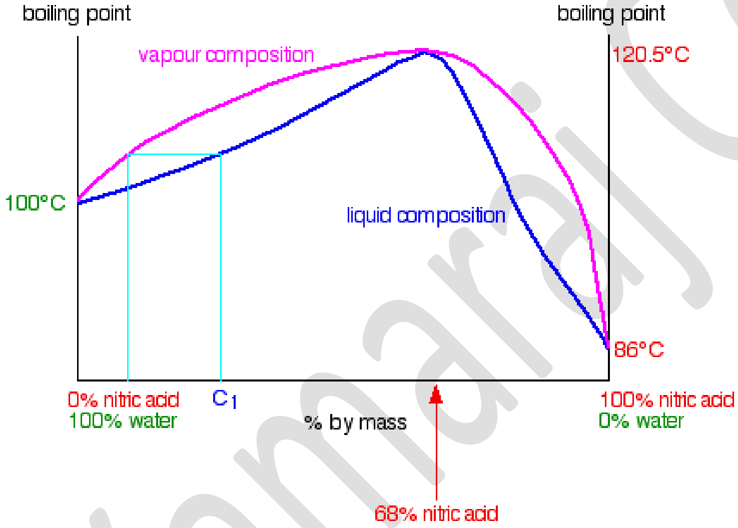
Notice the much bigger difference this time due to the presence of the new ionic interactions.

The phase diagram looks like this:



Using the diagram *Distilling dilute nitric acid*

Start with a dilute solution of nitric acid with a composition of C_1 and trace through what happens.



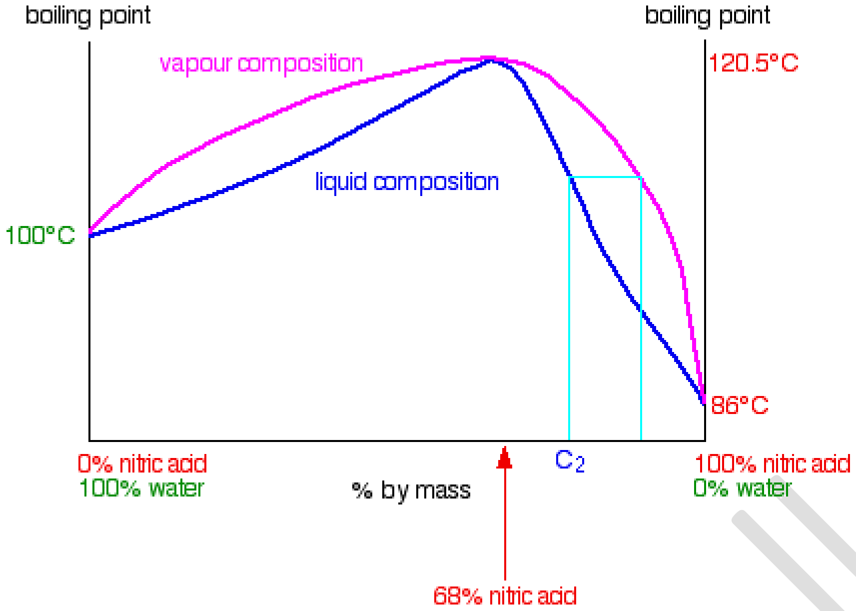
The vapour produced is richer in water than the original acid. If you condense the vapour and reboil it, the new vapour is even richer in water. Fractional distillation of dilute nitric acid will enable you to collect pure water from the top of the fractionating column.

As the acid loses water, it becomes more concentrated. Its concentration gradually increases until it gets to 68% by mass of nitric acid. At that point, the vapour produced has exactly the same concentration as the liquid, because the two curves meet.

You produce a constant boiling mixture (or azeotropic mixture or azeotrope). If you distil dilute nitric acid, that's what you will eventually be left with in the distillation flask. You can't produce pure nitric acid from the dilute acid by distilling it.

Distilling nitric acid more concentrated than 68% by mass

This time you are starting with a concentration C_2 to the right of the azeotropic mixture.



The vapour formed is richer in nitric acid. If you condense and reboil this, you will get a still richer vapour. If you continue to do this all the way up the fractionating column, you can get pure nitric acid out of the top.

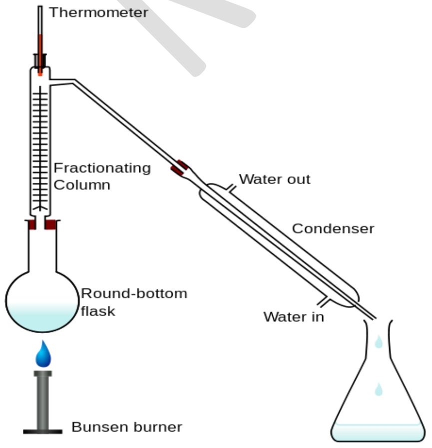
As far as the liquid in the distillation flask is concerned, it is gradually losing nitric acid. Its concentration drifts down towards the azeotropic composition. Once it reaches that, there can't be any further change, because it then boils to give a vapour with the same composition as the liquid.

Distilling a nitric acid / water mixture containing more than 68% by mass of nitric acid gives you pure nitric acid from the top of the fractionating column and the azeotropic mixture left in the distillation flask.

Fractional Distillation of Ideal Mixtures

Fractional Distillation in the lab

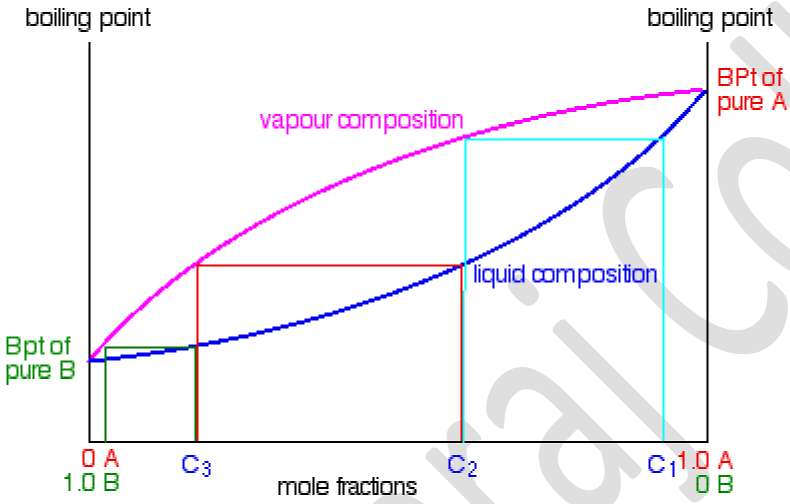
A typical lab fractional distillation would look like this:



The fractionating column is packed with glass beads (or something similar) to give the maximum possible surface area for vapor to condense on. Some fractionating columns have spikes of glass sticking out from the sides which serve the same purpose. If you sketch this, make sure that you do not completely seal the apparatus. There has to be a vent in the system otherwise the pressure build-up when you heat it will blow the apparatus apart. In some cases, where you are collecting a liquid with a very low boiling point, you may need to surround the collecting flask with a beaker of cold water or ice. The mixture is heated at such a rate that the thermometer is at the temperature of the boiling point of the more volatile component. Notice that the thermometer bulb is placed exactly at the outlet from the fractionating column.

Using the phase diagram

On the last page, we looked at how the phase diagram for an ideal mixture of two liquids was built up. I want to start by looking again at material from the last part of that page. The next diagram is new - a modified version of diagrams from the previous page.

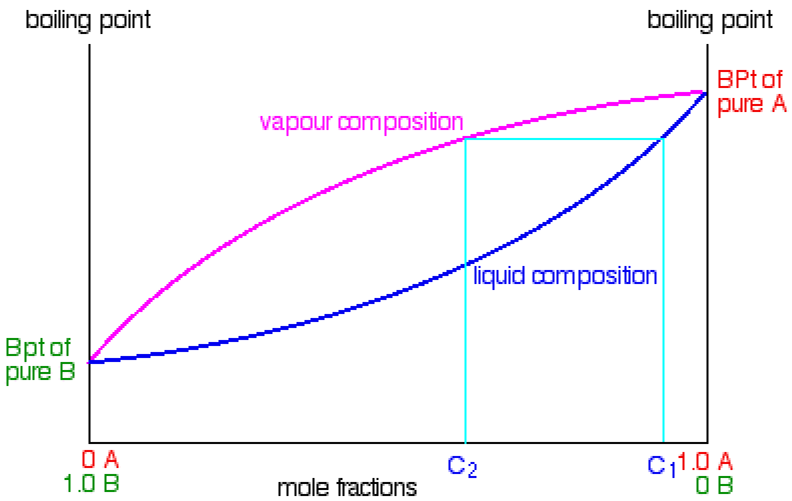


- liquid mixture C_1, a vapor with composition C_2, which you can condense to give a liquid of that same composition (the pale blue lines).
- liquid C_2, it will give a vapor with composition C_3. Again condense that to give a liquid of the same new composition (the red lines).
- Reboiling the liquid C_3 will give a vapor still richer in the more volatile component B (the green lines). once or twice more, able to collect a liquid which was virtually pure B.

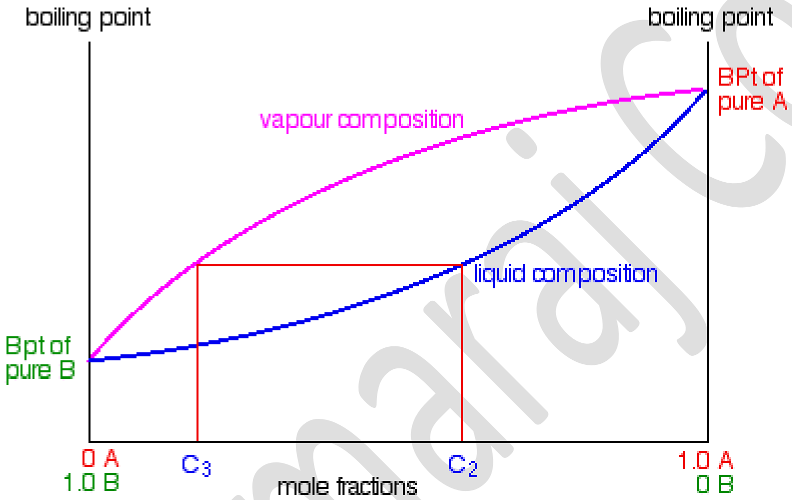
The secret of getting the more volatile component from a mixture of liquids is obviously to do a succession of boiling-condensing-reboiling operations. It is not quite so obvious how you get a sample of pure A out of this.

Relating what happens in the fractionating column to the phase diagram

The vapor over the top of the boiling liquid will be richer in the more volatile component, and will have the composition C_2.



That vapor now starts to travel up the fractionating column. Eventually it will reach a height in the column where the temperature is low enough that it will condense to give a liquid. The composition of that liquid will, of course, still be C_2. So what happens to that liquid now? It will start to trickle down the column where it will meet new hot vapor rising. That will cause the already condensed vapor to reboil.



Some of the liquid of composition C_2 will boil to give a vapor of composition C_3. Let's concentrate first on that new vapor and think about the un-vaporized part of the liquid afterwards.

The vapor

This new vapor will again move further up the fractionating column until it gets to a temperature where it can condense. Then the whole process repeats itself. Each time the vapor condenses to a liquid, this liquid will start to trickle back down the column where it will be reboiled by up-coming hot vapor. Each time this happens the new vapor will be richer in the more volatile component. The aim is to balance the temperature of the column so that by the time vapor reaches the top after huge numbers of condensing and reboiling operations, it consists only of the more volatile component - in this case, B.

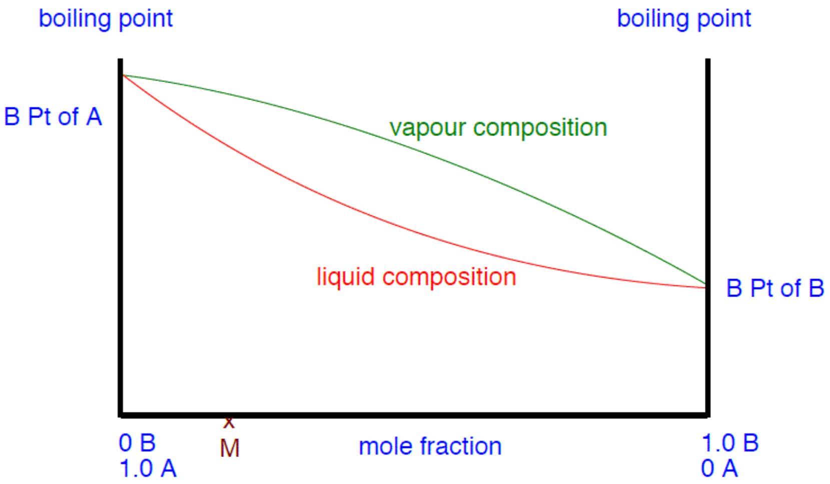
Whether or not this is possible depends on the difference between the boiling points of the two liquids. The closer they are together, the longer the column has to be.

The liquid

So what about the liquid left behind at each reboiling? Obviously, if the vapor is richer in the more volatile component, the liquid left behind must be getting richer in the other one. As the condensed liquid trickles down the column constantly being reboiled by up-coming vapor, each reboiling makes it richer and richer in the less volatile component - in this case, A. By the time the liquid drips back into the flask, it will be very rich in A indeed. So, over time, as B passes out of the top of the column into the condenser, the liquid in the flask will become richer in A. If you are very, very careful over temperature control, eventually you will have separated the mixture into B in the collecting flask and A in the original flask. Finally, what is the point of the packing in the column?

To make the boiling-condensing-reboiling process as effective as possible, it has to happen over and over again. By having a lot of surface area inside the column, you aim to have the maximum possible contact between the liquid trickling down and the hot vapor rising. If you didn't have the packing, the liquid would all be on the sides of the condenser, while most of the vapor would be going up the middle and never come into contact with it.

a. Use the phase diagram below to explain how you can obtain a pure sample of B from a mixture M by successively boiling and condensing the liquid mixture.



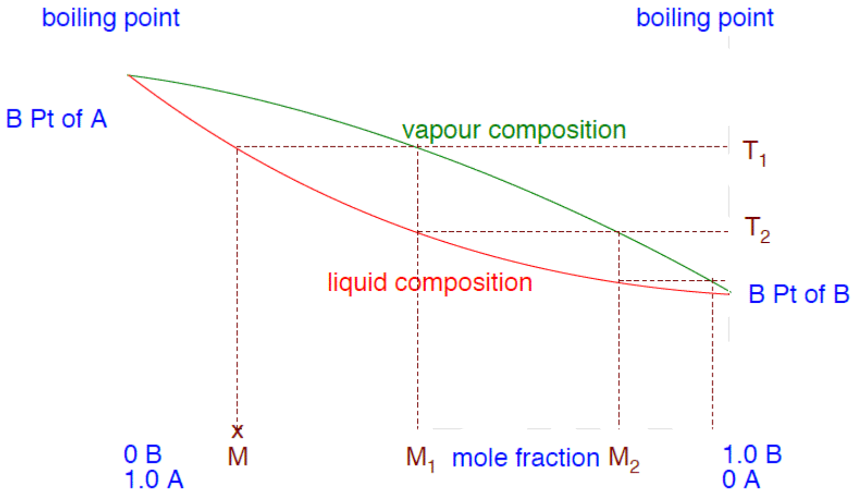
b. Why is it important to carefully control how strongly the original mixture is heated during the separation?
c. Explain briefly how the separation occurs, making use of the phase diagram above if you think it helps.

Solution

a. If you boil the mixture M, it will boil at a temperature T1. The vapor above the liquid at this temperature will be richer in the more volatile substance B. If you condense that vapor, it will give a liquid of the composition M1. If you re-boil that, it will boil at a temperature T2. The vapor over that liquid will have a composition M2, still richer in B. If you go on doing that, reboiling and re-condensing, then the vapor becomes richer and richer in B until it eventually becomes pure B. When you finally get to that point and condense the vapor, then you will have pure B liquid.
b. You have to be sure that only the vapor of the more volatile of the two liquids passes into the condenser. That means that the thermometer has to read exactly the boiling

point of the more volatile liquid. If it is below that, then nothing is going to pass out into the condenser. If it is above that, then your distillate will still contain some of the less volatile component.

c. B is the more volatile liquid; A is the less volatile one. The vapor over the boiling liquid in the flask will be richer in B than the original liquid is. That vapor will pass up the column until the temperature falls enough for it to condense to give a liquid richer in B than the one in the flask (equivalent to M1 in the diagram). This will start to trickle down the column. Hot vapor coming up from the flask will reboil the condensed liquid, giving a vapor which will be even richer in B (M2 on the diagram). This will condense to a liquid, trickle down the column and then be reboiled. This continuous process will go on until the vapor is entirely B. The column is heated so that this is finally complete right at the top of the column. Meanwhile, the liquids trickling down the column get richer and richer in A as the B is removed and carried up the column. Eventually, the liquid in the flask will end up as pure A.

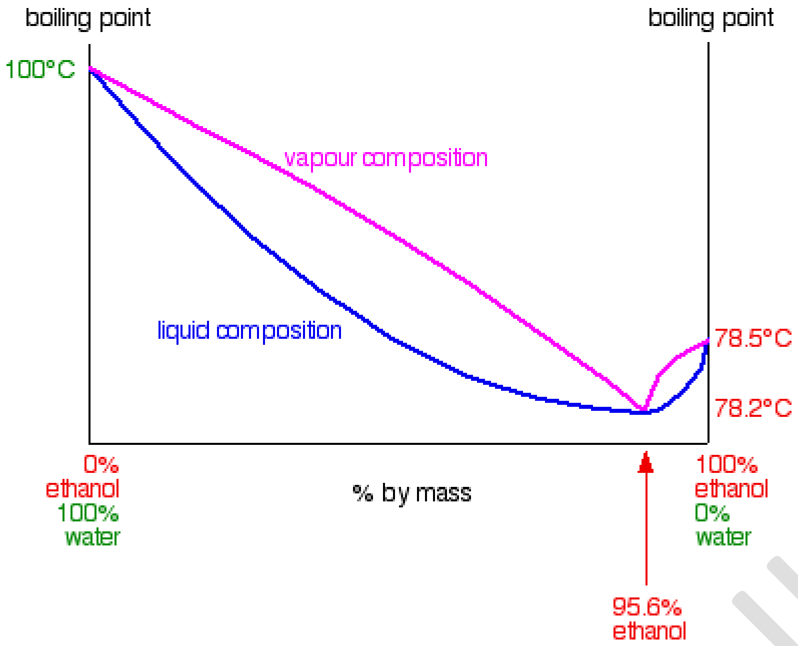


Fractional Distillation of Non-ideal Mixtures (Azeotropes)

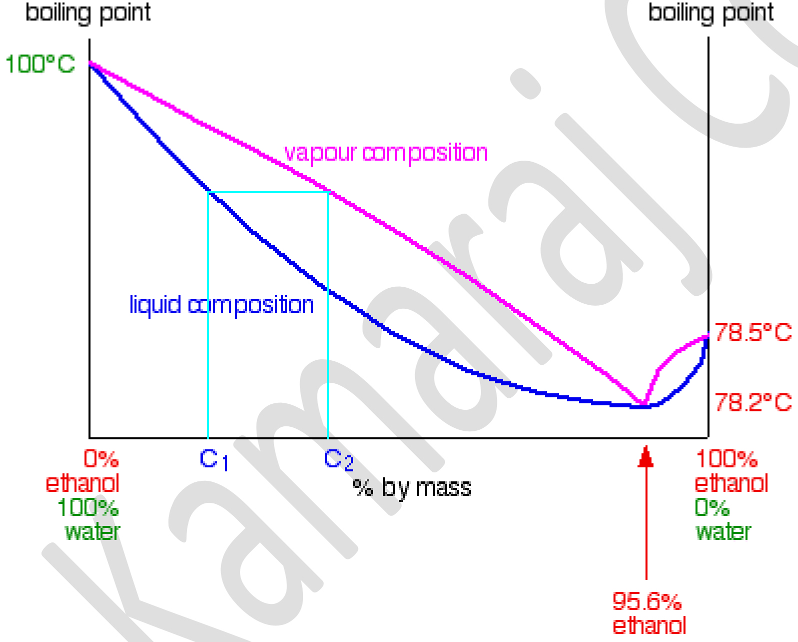
Positive Deviation from Raoult's Law

Remember that a large positive deviation from Raoult's Law produces a vapor pressure curve with a maximum value at some composition other than pure A or B. If a mixture has a high vapor pressure it means that it will have a low boiling point. The molecules are escaping easily and you won't have to heat the mixture much to overcome the intermolecular attractions completely. The implication of this is that the boiling point / composition curve will have a minimum value lower than the boiling points of either A or B.

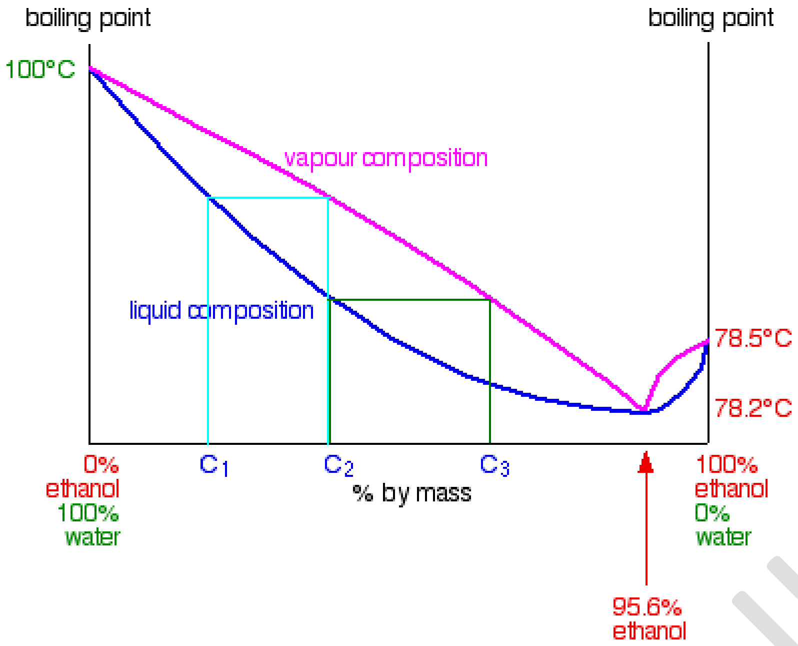
In the case of mixtures of ethanol and water, this minimum occurs with 95.6% by mass of ethanol in the mixture. The boiling point of this mixture is 78.2°C, compared with the boiling point of pure ethanol at 78.5°C, and water at 100°C. You might think that this 0.3°C doesn't matter much, but it has huge implications for the separation of ethanol / water mixtures. The next diagram shows the boiling point / composition curve for ethanol / water mixtures. I've also included on the same diagram a vapor composition curve in exactly the same way as we looked at on the previous pages about phase diagrams for ideal mixtures.



Suppose you are going to distil a mixture of ethanol and water with composition C_1 as shown on the next diagram. It will boil at a temperature given by the liquid curve and produce a vapor with composition C_2.



When that vapor condenses it will, of course, still have the composition C_2. If you reboil that, it will produce a new vapor with composition C_3.



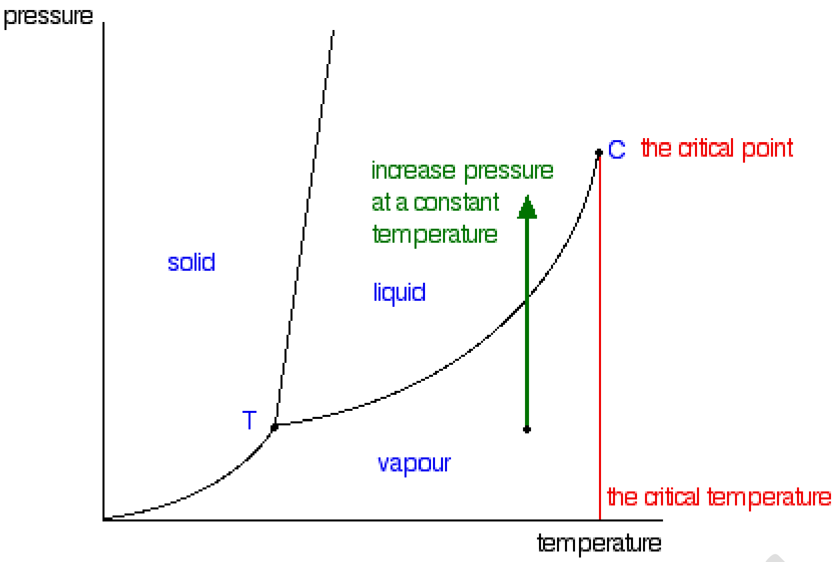
You can see that if you carried on with this boiling-condensing-reboiling sequence, you would eventually end up with a vapor with a composition of 95.6% ethanol. If you condense that you obviously get a liquid with 95.6% ethanol.

What happens if you reboil that liquid? The liquid curve and the vapor curve meet at that point. The vapor produced will have that same composition of 95.6% ethanol. If you condense it again, it will still have that same composition. You have hit a barrier. It is impossible to get pure ethanol by distilling any mixture of ethanol and water containing less than 95.6% of ethanol. This particular mixture of ethanol and water boils as if it were a pure liquid. It has a constant boiling point, and the vapor composition is exactly the same as the liquid. It is known as a constant boiling mixture or an azeotropic mixture or an azeotrope.

The implications of this for fractional distillation of dilute solutions of ethanol are obvious. The liquid collected by condensing the vapor from the top of the fractionating column cannot be pure ethanol. The best you can produce by simple fractional distillation is 95.6% ethanol. What you can get (although it isn't very useful!) from the mixture is pure water. As ethanol rich vapor is given off from the liquid boiling in the distillation flask, it will eventually lose all the ethanol to leave just water.

Critical Point

At the critical point, the particles in a closed container are thought to be vaporizing at such a rapid rate that the density of liquid and vapor are equal, and thus form a supercritical fluid. As a result of the high rates of change, the surface tension of the liquid eventually disappears. You will have noticed that this liquid-vapor equilibrium curve has a top limit (labeled as C in the phase diagram in Figure 1), which is known as the critical point. The temperature and pressure corresponding to this are known as the critical temperature and critical pressure. If you increase the pressure on a gas (vapor) at a temperature lower than the critical temperature, you will eventually cross the liquid-vapor equilibrium line and the vapor will condense to give a liquid.



This works fine as long as the gas is below the critical temperature. What, though, if your temperature was above the critical temperature? There wouldn't be any line to cross! That is because, above the critical temperature, it is impossible to condense a gas into a liquid just by increasing the pressure. All you get is a highly compressed gas. The particles have too much energy for the intermolecular attractions to hold them together as a liquid. The critical temperature obviously varies from substance to substance and depends on the strength of the attractions between the particles. The stronger the intermolecular attractions, the higher the critical temperature.

Why the Critical Point is Important

The condensation of a gas will never occur above the critical point. A massive amount of pressure can be applied to a gas in a closed container, and it may become highly dense, but will not exhibit a meniscus. Molecules at critical temperatures possess high kinetic energy, and as a result the intermolecular forces in the molecules are weakened.

The Declined Critical Points of Polymer Solutions

A novel discovery made by the University of Manchester, identified that lower critical temperatures are existent in polymer solutions. It has been manifested that hydrocarbon polymers integrated with a hydrocarbon solution portrays what the university terms a "L.C.S.T." or a lower critical solution temperature. This lower critical solution temperature of polymers has been proclaimed to be in a range near the gas- liquid critical point of the polymer's solvent, and can reach up to 170 degrees Celsius. Such a lower critical solution temperature can be contributed to the assimilation of the heat and volume of the substance n-pentane with most hydrocarbon polymers at room temperature (Freeman, P.I., Rowlinson, J.S.).

The Effects of Wetting on the Critical Point

When a fluid is present in two phases, in a container, and a critical point is near establishment, contact with the imminently forming third phase does not occur. This phenomena can be accounted for by examining the other two existing phases; the third phase does not immediately form because one of the other two phases wets the third phase, causing it to be eliminated. This wetting phase will continually occur when a phase is not entirely stable as a whole.

Supercritical Fluids

To understand what happens at the critical point, consider the effects of temperature and pressure on the densities of liquids and gases, respectively. As the temperature of a liquid increases, its density decreases. As the pressure of a gas increases, its density increases. At the critical point, the liquid and gas phases have exactly the same density, and only a single phase exists. This single phase is called a supercritical fluidThe single, dense fluid phase that exists above the critical temperature of a substance., which exhibits many of the properties of a gas but has a density more typical of a liquid. For example, the density of water at its critical point (T = 374°C, P = 217.7 atm) is 0.32 g/mL, about one-third that of liquid water at room temperature but much greater than that of water vapor under most conditions. The transition between a liquid/gas mixture and a supercritical phase is demonstrated for a sample of chlorine At the critical temperature, the meniscus separating the liquid and gas phases disappears.

In the last few years, supercritical fluids have evolved from laboratory curiosities to substances with important commercial applications. For example, carbon dioxide has a low critical temperature (31°C), a comparatively low critical pressure (73 atm), and low toxicity, making it easy to contain and relatively safe to manipulate. Because many substances are quite soluble in supercritical CO_2, commercial processes that use it as a solvent are now well established in the oil industry, the food industry, and others. Supercritical CO_2 is pumped into oil wells that are no longer producing much oil to dissolve the residual oil in the underground reservoirs. The less-viscous solution is then pumped to the surface, where the oil can be recovered by evaporation (and recycling) of the CO_2. In the food, flavor, and fragrance industry, supercritical CO_2 is used to extract components from natural substances for use in perfumes, remove objectionable organic acids from hops prior to making beer, and selectively extract caffeine from whole coffee beans without removing important flavor components. The latter process was patented in 1974, and now virtually all decaffeinated coffee is produced this way. The earlier method used volatile organic solvents such as methylene chloride (dichloromethane [CH_2Cl_2], boiling point = 40°C), which is difficult to remove completely from the beans and is known to cause cancer in laboratory animals at high doses.

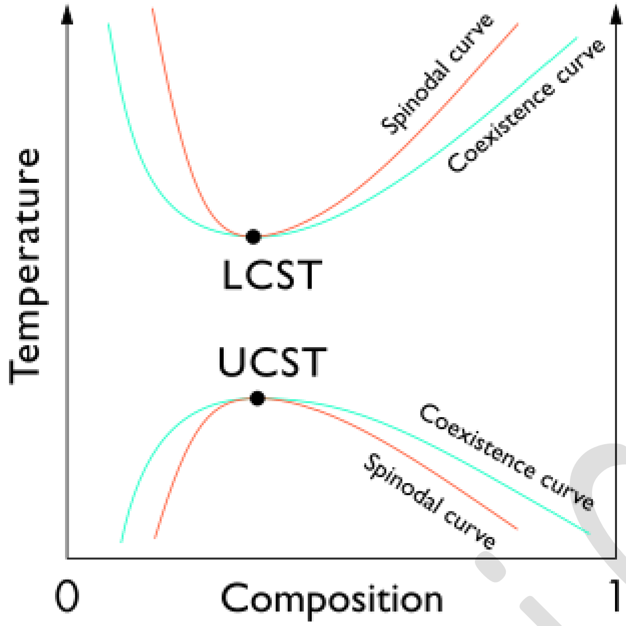
Upper critical solution temperature

The upper critical solution temperature (UCST) or upper consulate temperature is the critical temperature above which the components of a mixture are miscible in all proportions.[1] The word *upper* indicates that the UCST is an upper bound to a temperature range of partial miscibility, or miscibility for certain compositions only. For example, hexane-nitrobenzene mixtures have a UCST of 19 °C, so that these two substances are miscible in all proportions above 19 °C but not at lower temperatures.[2] Examples at higher temperatures are the aniline-water system at 168 °C (at pressures high enough for liquid water to exist at that temperature),[3] and the lead-zinc system at 798 °C (a temperature where both metals are liquid).[4]

A solid state example is the palladium-hydrogen system which has a solid solution phase (H_2 in Pd) in equilibrium with a hydride phase (PdH_n) below the UCST at 300 °C. Above this temperature there is a single solid solution phase.[5]

In the phase diagram of the mixture components, the UCST is the shared maximum of the concave down spinodal and binodal (or coexistence) curves. The UCST is in general dependent on pressure.

The phase separation at the UCST is in general driven by unfavorable energetics; in particular, interactions between components favor a partially demixed state.



Lower critical solution temperature

The lower critical solution temperature (LCST) or lower consulate temperature is the critical temperature below which the components of a mixture are miscible for all compositions.[1][2] The word *lower* indicates that the LCST is a lower bound to a temperature interval of partial miscibility, or miscibility for certain compositions only.

The phase behavior of polymer solutions is an important property involved in the development and design of most polymer-related processes. Partially miscible polymer solutions often exhibit two solubility boundaries, the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST), which both depend on the molar mass and the pressure. At temperatures below LCST, the system is completely miscible in all proportions, whereas above LCST partial liquid miscibility occurs.

In the phase diagram of the mixture components, the LCST is the shared minimum of the concave up spinodal and binodal (or coexistence) curves. It is in general pressure dependent, increasing as a function of increased pressure.

For small molecules, the existence of an LCST is much less common than the existence of an upper critical solution temperature (UCST), but some cases do exist. For example, the system triethylamine-water has an LCST of 19 °C, so that these two substances are miscible in all proportions below 19 °C but not at higher temperatures. The nicotine-water system has an LCST of 61 °C, and also a UCST of 210 °C at pressures high enough for liquid water to exist at that temperature. The components are therefore miscible in all proportions below 61 °C and above 210 °C (at high pressure), and partially miscible in the interval from 61 to 210 °C.

Some polymer solutions have an LCST at temperatures higher than the UCST. As shown in the diagram, this means that there is a temperature interval of complete miscibility, with partial miscibility at both higher and lower temperatures.

In the case of polymer solutions, the LCST also depends on polymer degree of polymerization, polydispersity and branching as well as on the polymer's composition and architecture.[7] A prominent polymer possessing an LCST is Poly(N-isopropylacrylamide) in water, which undergoes a reversible collapse transition related to the LCST at 33 °C. Another monomer whose homo- and co-polymers exhibit LCST behavior in solution is 2-(dimethylamino)ethyl methacrylate.

The LCST depends on the polymer preparation and in the case of copolymers, the monomer ratios, as well as the hydrophobic or hydrophilic nature of the polymer.

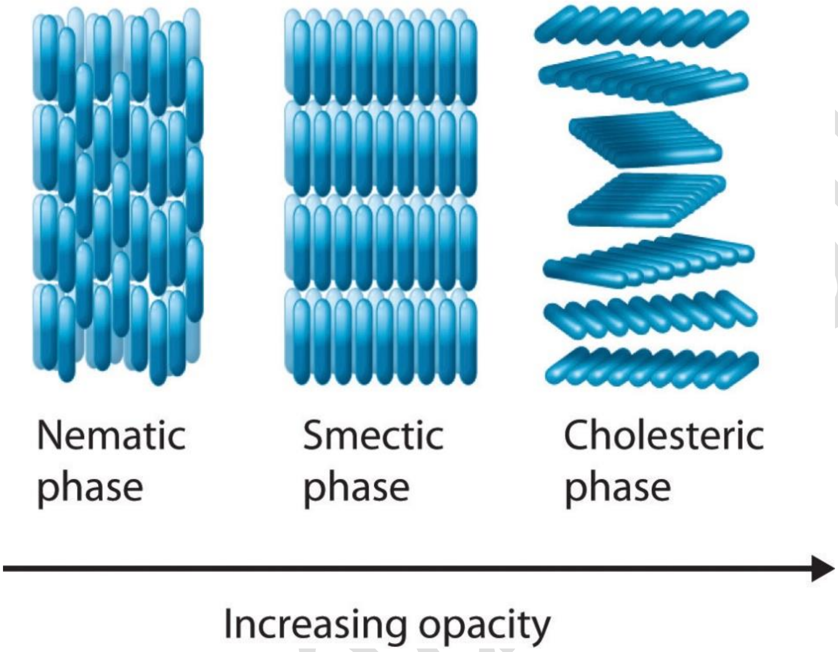
To date, over 70 examples of non-ionic polymers with an LCST in aqueous solution have been found.

When cooled, most liquids undergo a simple phase transition to an ordered crystalline solid, a relatively rigid substance that has a fixed shape and volume. In the phase diagrams for these liquids, there are no regions between the liquid and solid phases. Thousands of substances are known, however, that exhibit one or more phases intermediate between the liquid state, in which the molecules are free to tumble and move past one another, and the solid state, in which the molecules or ions are rigidly locked into place. In these intermediate phases, the molecules have an ordered arrangement and yet can still flow like a liquid. Hence they are called liquid crystals, and their unusual properties have found a wide range of commercial applications. They are used, for example, in the liquid crystal displays (LCDs) in digital watches, calculators, and computer and video displays.

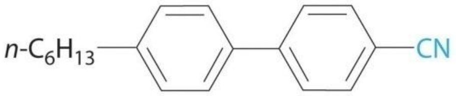
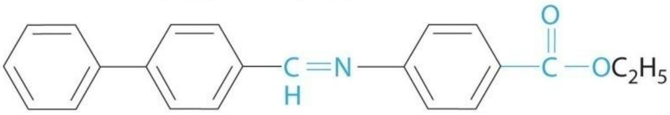
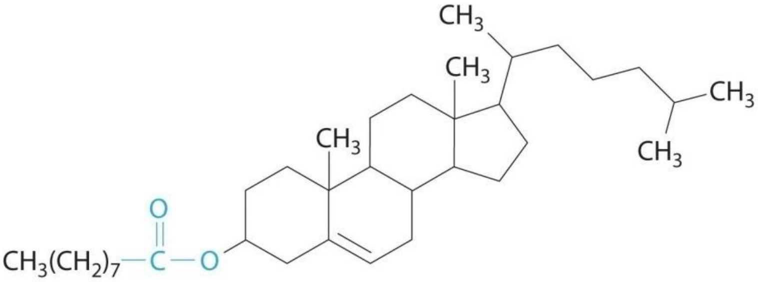
The first documented example of a liquid crystal was reported by the Austrian Frederick Reinitzer in 1888. Reinitzer was studying the properties of a cholesterol derivative, cholesteryl benzoate, and noticed that it behaved strangely as it melted. The white solid first formed a cloudy white liquid phase at 145°C, which reproducibly transformed into a clear liquid at 179°C (Figure 11.8.1). The transitions were completely reversible: cooling molten cholesteryl benzoate below 179°C caused the clear liquid to revert to a milky one, which then crystallized at the melting point of 145°C.

In a normal liquid, the molecules possess enough thermal energy to overcome the intermolecular attractive forces and tumble freely. This arrangement of the molecules is described as **isotropic**, which means that it is equally disordered in all directions. Liquid crystals, in contrast, are **anisotropic**: their properties depend on the direction in which they are viewed. Hence liquid crystals are not as disordered as a liquid because the molecules have some degree of alignment.

Most substances that exhibit the properties of liquid crystals consist of long, rigid rod- or disk-shaped molecules that are easily polarizable and can orient themselves in one of three different ways, In the nematic phase, the molecules are not layered but are pointed in the same direction. As a result, the molecules are free to rotate or slide past one another. In the **smectic phase**, the molecules maintain the general order of the **nematic phase** but are also aligned in layers. Several variants of the smectic phase are known, depending on the angle formed between the molecular axes and the planes of molecules. The simplest such structure is the so-called smecticA phase, in which the molecules can rotate about their long axes within a given plane, but they cannot readily slide past one another. In the cholesteric phase, the molecules are directionally oriented and stacked in a helical pattern, with each layer rotated at a slight angle to the ones above and below it. As the degree of molecular ordering increases from the nematic phase to the**cholesteric phase**, the liquid becomes more opaque, although direct comparisons are somewhat difficult because most compounds form only one of these liquid crystal phases when the solid is melted or the liquid is cooled.



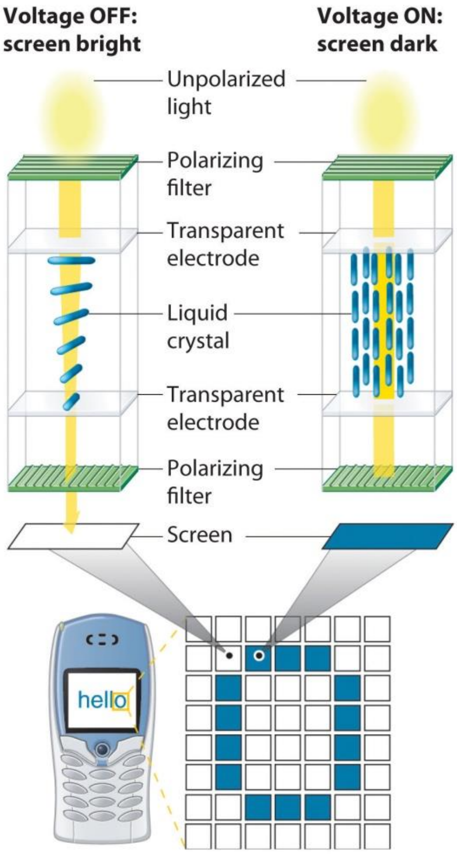
Molecules that form liquid crystals tend to be rigid molecules with polar groups that exhibit relatively strong dipole–dipole or dipole–induced dipole interactions, hydrogen bonds, or some combination of both. Some examples of substances that form liquid crystals are listed in Figure 11.8.3 along with their characteristic phase transition temperature ranges. In most cases, the intermolecular interactions are due to the presence of polar or polarizable groups. Aromatic rings and multiple bonds between carbon and nitrogen or oxygen are especially common. Moreover, many liquid crystals are composed of molecules with two similar halves connected by a unit having a multiple bond.

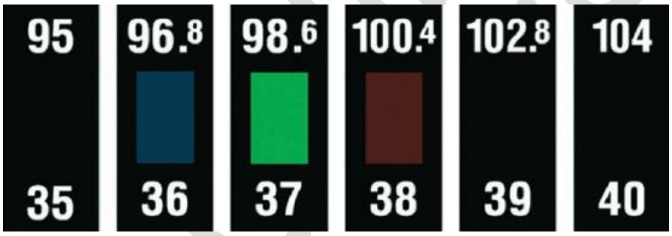
Structure	Liquid Crystal Phase	Liquid Crystalline Temperature Range (°C)
	Nematic	14–28
	Smectic	121–131
	Cholesteric	78–90

Because of their anisotropic structures, liquid crystals exhibit unusual optical and electrical properties. The intermolecular forces are rather weak and can be perturbed by an applied electric field. Because the molecules are polar, they interact with an electric field, which causes them to change their orientation slightly. Nematic liquid crystals, for example, tend to be relatively translucent, but many of them become opaque when an electric field is applied and the molecular orientation changes. This behavior is ideal for producing dark images on a light or an opalescent background, and it is used in the LCDs in digital watches; handheld calculators; flat-screen monitors; and car, ship, and aircraft instrumentation. Although each application differs in the details of its construction and operation, the basic principles are similar, as illustrated in Figure

Applying a voltage to selected segments of the device will produce any of the numbers. The device is a sandwich that contains several very thin layers, consisting of (from top to bottom) a sheet of polarizer to produce polarized light, a transparent electrode, a thin layer of a liquid crystalline substance, a second transparent electrode, a second polarizer, and a screen. Applying an electrical voltage to the liquid crystal changes its orientation slightly, which rotates the plane of the polarized light and makes the area appear dark.

Changes in molecular orientation that are dependent on temperature result in an alteration of the wavelength of reflected light. Changes in reflected light produce a change in color, which can be customized by using either a single type of liquid crystalline material or mixtures. It is therefore possible to build a liquid crystal thermometer that indicates temperature by color and to use liquid crystals in heat-sensitive films to detect flaws in electronic board connections where overheating can occur.

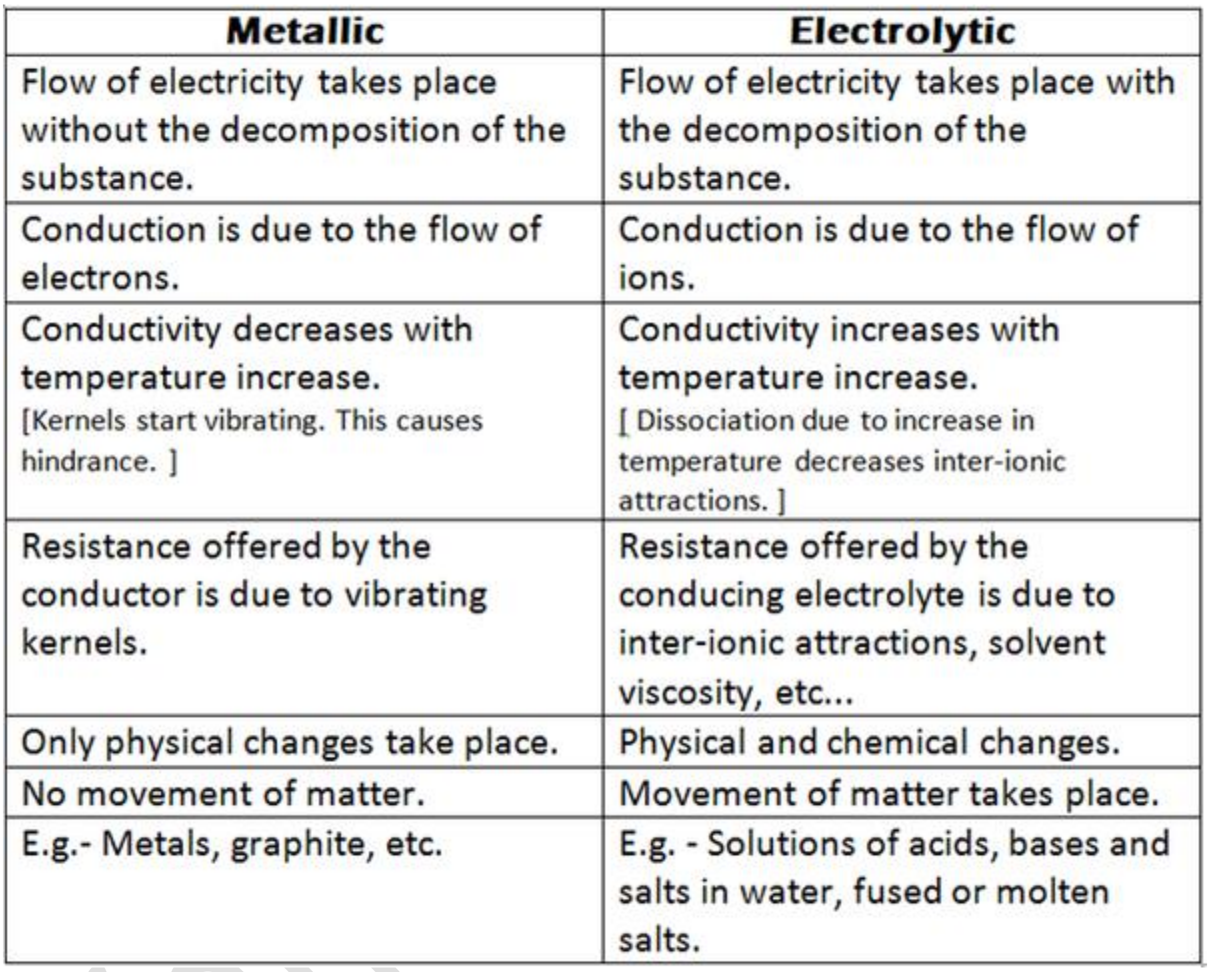

Voltage OFF: screen bright
Voltage ON: screen dark
Unpolarized light
Polarizing filter
Transparent electrode
Liquid crystal
Transparent electrode
Polarizing filter
Screen
hello


95
96.8
98.6
100.4
102.8
104
35
36
37
38
39
40

UNIT - V
ELECTROCHEMISTRY - I

Electric Conductor - definition

A material or an object that conducts electricity is called electric conductor. It helps electric charge (electrons) move from one atom to another easily. Flow of electric charge happens when the voltage is applied across the conductor. Example: All metals are electric conductors.



Metallic	Electrolytic
Flow of electricity takes place without the decomposition of the substance.	Flow of electricity takes place with the decomposition of the substance.
Conduction is due to the flow of electrons.	Conduction is due to the flow of ions.
Conductivity decreases with temperature increase. [Kernels start vibrating. This causes hindrance.]	Conductivity increases with temperature increase. [Dissociation due to increase in temperature decreases inter-ionic attractions.]
Resistance offered by the conductor is due to vibrating kernels.	Resistance offered by the conducing electrolyte is due to inter-ionic attractions, solvent viscosity, etc...
Only physical changes take place.	Physical and chemical changes.
No movement of matter.	Movement of matter takes place.
E.g.- Metals, graphite, etc.	E.g. - Solutions of acids, bases and salts in water, fused or molten salts.

Specific conductance

The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. It is generally defined as the reciprocal of resistance of that material. SI unit of conductance is S (Siemens). **Specific conductivity**(better known as conductivity) is the measure of the ability of that material to conduct electricity. It is represented by the symbol "K". Hence, by definition,

The conductance of a material depends on the nature of the material, no. of valence electrons for a material and temperature. Metals are good conductors of electricity due to their valence electrons. We observe that the conductance of materials decreases with increase in temperature.

$$G = \frac{1}{R} \qquad K = \frac{1}{\rho}$$

$$R = \rho\frac{1}{A} \qquad G = K\,\frac{A}{l}$$

Where,

K = conductivity,

R= resistance

ρ = resistivity of the material

l = length

G= conductance

A= area of cross section

Water in its pure state is known to have very low conductivity due to the presence of hydroxyl ions. The presence of electrolytes further enhances the conductivity as they furnish their ions in the solution. The conductance of electricity by ions present in the solution is called electrolytic or ionic conductance. Specific conductivity or conductivity of an electrolytic solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with the unit area of cross-section and at a distance of unit length. The conductivity of electrolytic solutions depends on:

1. The nature and the concentration of the electrolyte added
2. The size of the ions produced and their salvation.
3. Solvent nature and viscosity.
4. Temperature.

Due to charge, concentration and size of the ions in which electrolytes dissociate or ease with which the ions move under a potential gradient, the conductivity of solutions of different electrolytes differs with the same solvent and at a given temperature. Hence we define a more common term **molar conductivity** for an electrolyte solution. The molar conductivity of a solution at a given concentration is the conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross section and distance of unit length. In general terms, it is defined as the ratio of specific conductivity and the concentration of the electrolyte. The symbol Λm denotes it.

$$\Lambda_m = \frac{K}{c}$$

Where,

K = specific conductivity

c= concentration of electrolyte.

Equivalent Conductance (ʌe)

- It is defined as the conductance (or conducting power) of all the ions(of a solution) produced by dissolving one gram equivalent of an electrolyte in a particular solution.
- We can say that the conductance of an electrolytic solution depends on the concentration of the ions present in the solution.
- It is helpful to get comparable results for different electrolytes.
- Denoted by ʌe.
- Equivalent Conductance(ʌe) is calculated from specific conductance.

Formulae:

Equivalent conductance, ʌe = **κ** × V

κ: Specific Conductance (reciprocal of resistivity)
V : Volume(in mL) containing 1gm equivalent electrolyte

Molar Conductivity or Molar Conductance

Molar conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.

It is denoted by Λ (lambda). Molar conductance is related to specific conductance (κ) as,

$$\Lambda = \frac{\kappa}{M}$$

where, M is the molar concentration.

If M is in the units of molarity i.e., moles per litre $(mol\ L^{-1})$, the Λ may be expressed as,

$$\Lambda = \frac{\kappa \times 1000}{M}$$

For the solution containing 1 gm mole of electrolyte placed between two parallel electrodes of 1 sq. cm area of cross-section and one cm apart,

$$\text{Conductance}(G) = \text{Conductivity} = \text{Molar conductivity}(\Lambda)$$

But if solution contains 1 gm mole of the electrolyte therefore, the measured conductance will be the molar conductivity. Thus,

$$\text{Molar conductivity}(\Lambda) = 100 \times \text{Conductivity}$$

In other words, $(\Lambda) = \kappa \times V$

Where V is the volume of the solution in cm^3 containing one gram mole of the electrolyte.

If M is the concentration of the solution in mole per litre, then

M mole of electrolyte is present in $1000\ cm^3$

1 mole of electrolyte is present in $= \frac{1000}{M} cm^3$ of solution

Thus, $\Lambda = \kappa \times \text{Volume in } cm^3$ containing 1 mole of electrolyte.

or $\Lambda = \frac{\kappa \times 1000}{M}$

Units of Molar Conductance: The units of molar conductance can be derived from the formula ,

$$\Lambda = \frac{\kappa \times 1000}{M}$$

The units of κ are S cm^{-1} and units of Λ are, $\Lambda = S\,cm^{-1} \times \frac{cm^3}{mol} = S\,cm^2\,mol^{-1} = S\,cm^2 mol^{-1}$

According to SI system, molar conductance is expressed as $S\,m^2 mol^{-1}$, if concentration is expressed as $mol\ m^{-3}$.

Relation between specific equivalent and molar conductance

There is a subtle difference between specific conductance and equivalent conductance.

As you might have heard before, for specific conductance is actually conductivity of a solution(for cases of electrochemistry), meaning it is the conductance of a given solution for a very special case.

Specific Conductance or conductivity is the conductance of a given solution enclosed in a cell having two electrodes of unit area and are separated by 1cm.

We know that Conductance(C)= Conductivity(K)*A/l

Thus, Conductivity or Specific Conductance(K)=Conductance*l/A

While Equivalent Conductance is also a specific case but a little different than that of the previous one.

Equivalent Conductance is the conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution.

Let Vcm^3 of solution is considered.
We can say that the equivalent conductance is directly proportional to the volume of solution considered, as more the ions, more the conductance.

Thus, Equivalent Conductance (Λ)= Equivalent Conductivity(k)*V(in cm^3)…….(1)
So, here, Equivalent Conductance is the conductance of ions present in Vcm^3 of solution containing 1gm equivalent of the electrolyte, while Equivalent Conductivity is the specific case for unit volume.

Now, to relate this equation with gmequivalent(as defined for gm equivalent), we know that Normality= No. of gm equivalents/Volume(in lit). As we have considered a solution containing 1 gm-equivalent.

Thus, Equivalent Conductance (Λ)= Equivalent Conductivity(k)*1000/Normality.
1000 is multiplied as Equivalent Conductance is defined for volume in cm^3 while Normality is defined for volume in litres.

Now, this was all about Specific Conductance and Equivalent Conductance, now coming to your question for relation between them.

With reference to used symbols for various quantities.
K=C*l/A

Multiplying with A in numerator and denominator in RHS.
K=C*V/(A^2)

If we consider the solution for unit volume.
K=C*V

So, now you should understand that specific conductance is just a concept to quantify and express conductivity of a solution, while Equivalent Conductivity is a special case of it, while considering gm-equivalents, similarly we may also have molar conductivity which is considered for moles in a solution.

So, you can directly, say that Equivalent Conductance = Specific Conductance(when considered for gm-equivalents)* Volume.

Read more on Brainly.in - https://brainly.in/question/6815393#readmore

Measuring Conductance

Two electrodes into a solution that contains dissolved ions and apply a voltage to the electrodes, the ions will move through the solution: the negative ions (anions) will move toward the positive electrode (the anode); the positive ions (cations) will move toward the negative electrode (the cathode). This simple apparatus is called a conductance cell. Figure 1 uses a schematic diagram of a conductance cell to demonstrate the relationship between the concentration of ions in solution and the amount of current that flows through the solution.

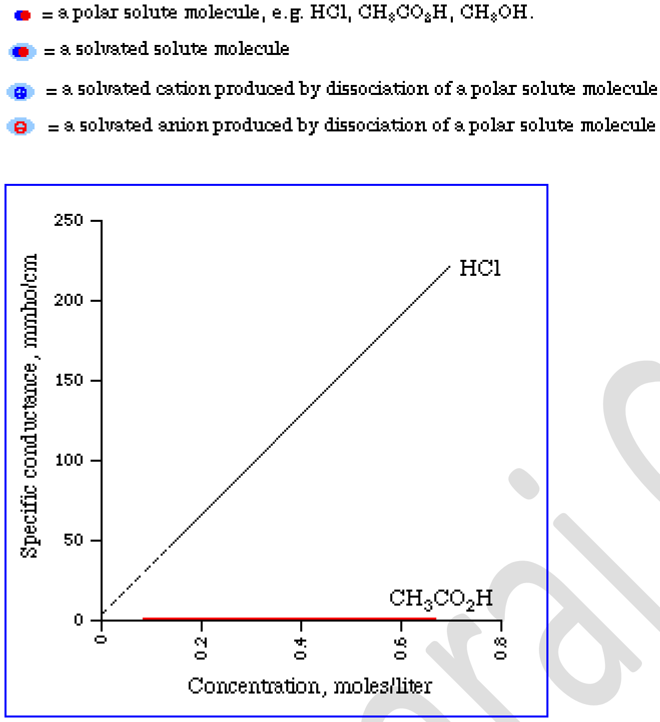
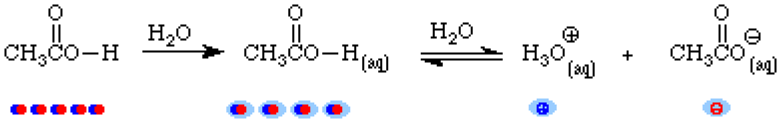


Figure 2: *All Electrolytes Are Not Created Equal*

Two features of this graph are noteworthy. First, the fact that the conductance of acetic acid is much less than that of hydrochloric acid is direct evidence that an aqueous solution of acetic acid contains fewer ions than a solution of hydrochloric acid of comparable concentration. Second, when extrapolated to 0 concentration (dashed line), the conductance of the HCl
solution does not equal 0. In other words, pure water has a small, but finite conductance.

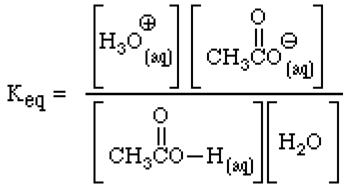
Weak Electrolytes

Scheme 1 depicts the situation that ensues when acetic acid is dissolved in water.



Scheme 1: *Dissolution and Dissociation of Acetic Acid*

The important point here is that the solution contains mostly solvated, but unionized acetic acid molecules with a few hydronium ions and acetate ions that are produced by dissociation of a few acetic acid molecules. The relationship between the numbers of hydronium ions, acetate ions, and undissociated acetic acid in solution is given by the expression



$$K_{eq} = \frac{\left[H_3O^{\oplus}_{(aq)}\right]\left[CH_3\overset{O}{\overset{\|}{C}}O^{\ominus}_{(aq)}\right]}{\left[CH_3\overset{O}{\overset{\|}{C}}O-H_{(aq)}\right]\left[H_2O\right]}$$

whereK_{eq} stands for the equilibrium constant for the dissociation of acetic acid molecules.

Conductance data of the type shown in Figure 1 allows chemists to calculate the concentrations of the hydronium ions and acetate ions in solution. Once you know that you can determine how much of the acetic acid you started with is still un-dissociated once the system comes to equilibrium. Then you can calculate K_{eq} .

Specific conductivity and cell constants

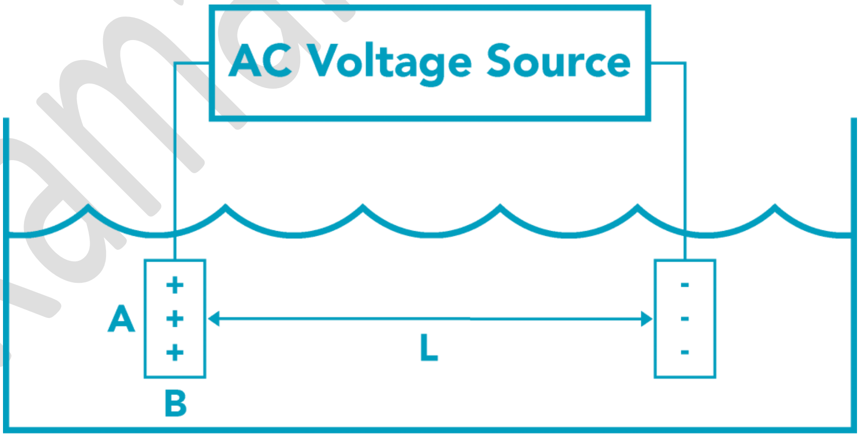
Measured conductivity is typically measured in milliSiemens (mS) or microSiemens (µS). When using a contacting conductivity sensor, conductivity cell geometry affects the conductivity reading. In order to ensure standardization of electrical conductivity measurements, units of specific conductivity are used. Specific conductivity is expressed as milliSiemens per centimeter (mS/cm) or microSiemens per centimeter (µS/cm).

What is a conductivity cell constant?

Specific conductivity compensates for variations in conductivity cell geometry by multiplying measured conductivity by a factor called the cell constant. Cell constant (k) is directly proportional to the distance separating the two conductive plates and inversely proportional to their surface area.

K = L/a, where a(area) = A x B.

Specific conductivity = Measured conductivity (G) * Cell Constant (k)



Conductivity cell constant determination

A cell constant of 1.0 will produce a measured conductivity (G) approximately equal to the specific conductivity of a solution. However, a cell constant of 1.0 is not always an appropriate choice. For example, in solutions with very low conductivity, measuring surfaces must be placed closer together in order to produce a good signal to the conductivity meter. When the path length between conducting plates is reduced, the cell constant is also reduced to 0.1 or even 0.01. Conversely, when measuring high conductivity solutions, a longer path length (higher cell constant) of 10 or 100 typically produces a more accurate reading.

Select a conductivity sensor with a cell constant that is appropriate for the conductivity range of the solution you will be measuring. Conductivity ranges of typical solutions and the optimum cell constant for each are given in the table below.

Solution	Conductivity Range	Optimum Cell Constant
Ultra pure water	0.05 µS/cm	0.01
Power plant or boiler water	0.05-1 µS/cm	0.01 or 0.1
Drinking water	150-800 µS/cm	1.0
Cooling tower water	0-5mS/cm	1.0
Wastewater effluent	0.9-9 mS/cm	1.0
Ocean water	53 mS/cm	10 (consider toroidal measurement)
29% Nitric Acid	865 mS/cm	100 (consider toroidal measurement)

Variation of conductance with dilution

Upon dilution, specific conductance or conductivity decreases while molar conductivity increases

Conductivity is the conductance of one centimeter cube of the solution. Upon diluting the solution, the concentration of ions per centimeter cube decreases and therefore, the conductivity decreases.

The increase in molar conductivity on dilution is due to the fact that it is the product of conductivity (κ) and the volume (V) of the solution containing one mole of the electrolyte.

$\Lambda = \kappa \times V$

On dilution, conductivity decreases but volume containing one mole of an electrolyte increases. The increase in volume on dilution is much more than the decrease in conductivity. As a result molar conductivity increases with dilution.

The molar conductance of strong (HCl, KCl, KNO_3) as well as weak electrolytes (CH_3COOH, NH_4OH) increase with decrease in concentration or increase in dilution.

Equivalent conductivity also increases with dilution because of increase in volume containing one gram equivalent of the electrolyte.

Variation of Molar Conductivity with Concentration for Strong and Weak Electrolytes

1) Variation of Molar Conductivity with Concentration for Strong Electrolytes

In strong electrolytes, molar conductivity increases slowly with dilution and there is a tendency for molar conductivity to approach a certain limiting value when the concentration approaches zero i.e., when the dilution is infinite. The molar conductivity when the concentration approaches zero (infinite dilution) is called **molar conductivity at infinite dilution.** It is denoted by Λ_m°

$\Lambda_m = \Lambda_m^\circ$

when C——-> 0 (at infinite dilution)

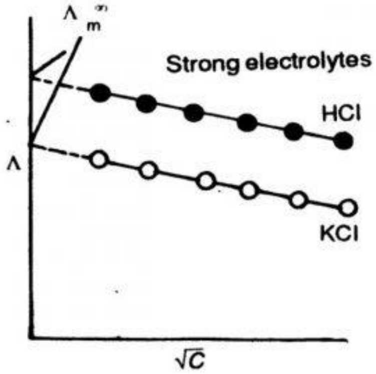
The variation of molar conductivity with concentration may be given by the expression

$\Lambda_m = \Lambda_m^\circ - AC^{1/2}$

where A is a constant and Λ° is called molar conductivity at infinite dilution.This equation is called **Debye Huckel Onsager equation** and is found to hold good at low concentrations.
The variation of molar conductivity with concentration can be studied by plotting the values of Λ_m against square root of concentration ($C^{½}$).

The variation of $\Lambda_m$with concentration, $C^{½}$ is small so that the plots can be extrapolated to zero concentration.The **intercept** gives the limiting value of molar conductivity when the concentration approaches zero, called molar conductivity at infinite dilution, Λ_m. The **slope** of the line is equal to – 'A'. The value of constant A for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation anion produced on the dissociation of the electrolyte in the solution.

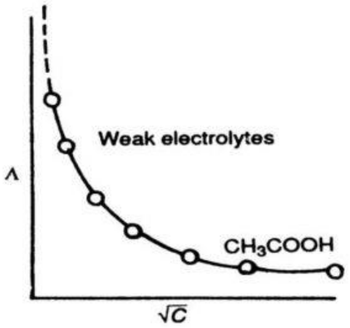
Thus NaCl is known as 1-1 electrolyte, $CaCl_2$ as 2-1 electrolytes and $MgSO_4$ as 2-2 electrolyte.



2) Variation of Molar Conductivity with Concentration for Weak Electrolytes

The weak electrolytes dissociate to a much lesser extent as compared to strrong electrolytes. Therefore, the molar conductivity is low as compare of strong electrolytes.

However, the variation of Λ_m with $C^{½}$ is very large and so much so that we cannot obtain molar conductance at infinite dilution ($\Lambda_m°$) by extrapolation of Λ_m versus $C^{½}$ plots.



Variation of Molar Conductivity with Concentration

a) Conductance behaviour of weak electrolytes

The number of ions furnished by an electrolyte in solution depends upon the degree of dissociation with dilution. With the increase in dilution, the degree of dissociation increases and as a result molar conductance increases. The limiting value of molar conductance (Λ_m) corresponds to degree of dissociation equal to 1, i.e. the whole of the electrolyte dissociates.
Thus, the degree of dissociation can be calculated at any concentration
$\alpha = \Lambda_m^c / \Lambda_m^\circ$

where α is the degree of dissociation, Λ_m^c is the molar conductance at concentration C and Λ_m° is the molar conductance at infinite dilution.

b) Conductance behaviour of strong electrolytes

For strong electrolytes, there is no increase in the number of ions with dilution because strong electrolytes are completely ionised in solution at all concentrations.

In concentrated solutions of strong electrolytes there are strong forces of attraction between the ions of opposite charges called interionic forces. Due to these interionic forces the conducting ability of the ions is less in concentrated solutions. With dilution, the ions become far apart from one another and interionic forces decrease. As a result, molar conductivity increases with dilution. When the concentration of the solution becomes very very low, the interionic attractions become negligible and the molar conductance approaches the limiting value called **molar conductance at infinite dilution**.This value is characteristic of each electrolyte.

Kohlrausch's Law

The difference of Λ° of different pairs of electrolytes having a common cation or a common anion was almost same.

Example 1 : the difference between the molar conductance of K^+ and Na^+ is 23.4 $ohm^{-1}\ cm^2\ mol^{-1}$ irrespective of the anion.

Λ° (KCl) = 149.9
Λ° (NaCl) = 126.5
Difference = Λ° (KCl) – Λ° (NaCl) = 149.9 – 126.5 = 23.4
Λ° (KNO_3) = 145
Λ° ($NaNO_3$) = 121.6
Difference = Λ° (KNO_3) – Λ° ($NaNO_3$) = 145 – 121.6 = 23.4
Λ° (KBr) = 156.6
Λ° (NaBr) = 128.2
Difference =Λ° (KBr) – Λ° (NaBr) = 156.6 – 128.2 = 23.4
$\lambda^\circ (K^+) - \lambda^\circ (Na^+) = 23.4\ S\ cm^2\ mol^{-1}$

Example 2 : The difference between the molar conductivities of chloride and nitrate ions is 4.9 $ohm^{-1}\ cm^2\ mol^{-1}$ irrespective of the cation.

Λ° (KCl) = 149.9
Λ° (KNO_3) = 145
Difference = Λ° (KCl) – Λ° (KNO_3) = 149.9 – 145 = 4.9
Λ° (NaCl) = 126.5
Λ° ($NaNO_3$) = 121.6
Difference = Λ° (NaCl) – Λ° ($NaNO_3$) = 126.5 -121.6 = 4.9
Λ° (LiCl) = 115
Λ° ($NaNO_3$) = 110.1
Difference = Λ° (LiCl) – Λ° ($NaNO_3$) = 115 -110.1 = 4.9
$\lambda^\circ (Cl^-) - \lambda^\circ (NO_3^-) = 4.9\ S\ cm^2\ mol^{-1}$

Kohlrausch's law states that, **at infinite dilution when the dissociation is complete, each ion makes a definite contribution towards molar conductivity of the electrolyte irrespective of the nature of the other ion with which it is associated.**

The molar conductivity at infinite dilution for a given salt can be expressed as the sum of the individual contributions from the ions of the electrolyte. If molar conductivity of the cation is denoted by λ°_+ and λ°_- then the law of independent migration of ions is :
$\Lambda = \nu_+ \lambda^\circ_+ + \nu_- \lambda^\circ_-$

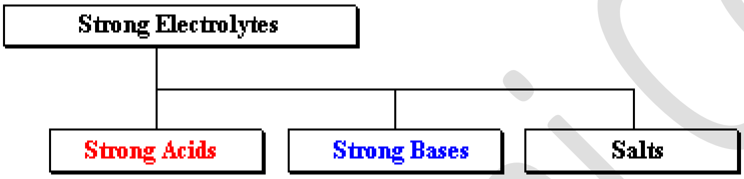
where ν_+ and ν_- are the number of cations and anions per formula unit of electrolyte (e.g.= $\nu_+ = \nu_- = 1$ for HCl, $\nu_+ = 1$ and $\nu_- = 2$ for $MgCl_2$).

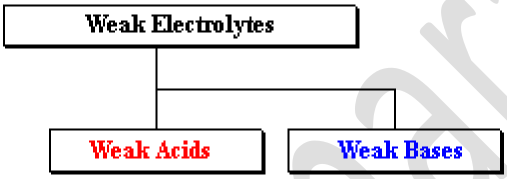
Strong and weak electrolytes.

Classifying Electrolytes

Electrolytes are substances which, when dissolved in water, break up into cations (plus-charged ions) and anions (minus-charged ions). We say they *ionize*. *Strong* electrolytes ionize completely (100%), while *weak* electrolytes ionize only partially (usually on the order of 1–10%). That is, the *principal species* in solution for strong electrolytes are ions, while the principal specie in solution for weak electrolytes is the un-ionized compound itself.

Strong electrolytes fall into three categories: *strong acids*, *strong bases*, and *salts*. (Salts are sometimes also called *ionic compounds*, but really strong bases are ionic compounds as well.) The weak electrolytes include *weak acids* and *weak bases*.





Examples of strong and weak electrolytes are given below:

Strong Electrolytes	strong acids	HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and H_2SO_4
	strong bases	NaOH, KOH, LiOH, $Ba(OH)_2$, and $Ca(OH)_2$
	salts	NaCl, KBr, $MgCl_2$, and many, many more
Weak Electrolytes	weak acids	HF, $HC_2H_3O_2$ (acetic acid), H_2CO_3 (carbonic acid), H_3PO_4 (phosphoric acid), and many more
	weak bases	NH_3 (ammonia), C_5H_5N (pyridine), and several more, all containing "N"

Six Steps for Categorizing Electrolytes

So how do we categorize compounds based on their formula? One practical method is outlined below:

Step 1 Is it one of the seven strong acids?

Step 2 Is it of the form $Metal(OH)_n$? Then it's a strong base.

Step 3 Is it of the form Metal$(X)_n$? Then it's a salt.

Step 4 Does it's formula start with 'H'? It's *probably* a weak acid.

Step 5 Does it have a nitrogen atom? It *may* be a weak base.

Step 6 None of those? Call it a nonelectrolyte.

Note that there are ambiguities here starting in Step 4. That's just the way it is. To determine whether a substance is a weak acid or weak base you have to know more than the molecular formula, especially for compounds containing carbon. (A *structural* formula, which shows the detailed connections of atoms is often necessary.)

Strong and Weak Electrolytes

Some polar molecular compounds are nonelectrolytes when they are in their pure state, but become electrolytes when they are dissolved in water. Hydrogen chloride (HCl)is a gas in its pure molecular state and is a nonelectrolyte. However, when HCl is dissolved in water, it conducts a current well because the HClmolecule ionizes into hydrogen and chloride ions.

$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$

When HClis dissolved, into water, it is called hydrochloric acid. Ionic compounds and some polar compounds are completely broken apart into ions and thus conduct a current very well. A **strong electrolyte** is a solution in which a large fraction of the dissolved solute exists as ions.

Some other polar molecular compounds become electrolytes upon being dissolved into water, but do not ionize to very great extent. Gaseous nitrous acid ionizes in solution to hydrogen ions and nitrite ions, but does so very weakly. Aqueous nitrous acid is composed of only about 5%ions and 95%intact nitrous acid molecules. A **weak electrolyte** is a solution in which only a small fraction of the dissolved solute exists as ions. The equation showing the ionization of a weak electrolyte utilizes a double arrow indicating an equilibrium between the reactants and products.

$HNO_2(g) \rightleftharpoons H^+(aq) + NO^-_2(aq)$

Migration of ions

The conductance of an electrolytic solution results from the movement of the ions it contains as they migrate toward the appropriate electrodes. But the picture we tend to have in our minds of these ions moving in a orderly, direct march toward an electrode is wildly mistaken. The thermally-induced random motions of molecules is known as *diffusion*. The term *migration* refers specifically to the movement of ions due to an externally-applied electrostatic field.

The average thermal energy at temperatures within water's liquid range (given by RT) is sufficiently large to dominate the movement of ions even in the presence of an applied electric field. This means that the ions, together with the water molecules surrounding them, are engaged in a wild dance as they are buffeted about by thermal motions (which include Brownian motion).

An external electric field to the solution, the chaotic motion of each ion is supplemented by an occasional jump in the direction dictated by the interaction between the ionic charge and the field. But this is really a surprisingly tiny effect:

It can be shown that in a typical electric field of 1 volt/cm, a given ion will experience only about one field-directed (non-random) jump for every 10^5 random jumps. This translates into an average migration velocity of roughly 10^{-7} m sec^{-1} (10^{-4} mm sec^{-1}). Given that the radius of the H_2O molecule is close to 10^{-10} m, it follows that about 1000 such jumps are required to advance beyond a single solvent molecule!

The ions migrate Independently

All ionic solutions contain at least two kinds of ions (a cation and an anion), but may contain others as well. In the late 1870's, the physicist Friedrich Kohlrausch noticed that the limiting equivalent conductivities of salts that share a common ion exhibit constant differences.

electrolyte	**Λ_0(25°C)**	**difference**	**electrolyte**	**Λ_0 (25°C)**	**difference**
KCl	149.9	34.9	HCl	426.2	
LiCl	115.0		HNO_3	421.1	4.9
KNO_3	145.0	34.9	LiCl	115.0	
$LiNO_3$	140.1		$LiNO_3$	110.1	4.9

These differences represent the differences in the conductivities of the ions that are *not* shared between the two salts. The fact that these differences are identical for two pairs of salts such as KCl/LiCl and KNO_3 /$LiNO_3$ tells us that the mobilities of the non-common ions K^+ and LI^+ are not affected by the accompanying anions.

Kohlrausch's law greatly simplifies estimates of Λ_0

This principle is known as *Kohlrausch's law of independent migration*, which states that *in the limit of infinite dilution*,

Each ionic species makes a contribution to the conductivity of the solution that depends only on the nature of that particular ion, and is independent of the other ions present.
Kohlrausch's law can be expressed as$\Lambda_0 = \Sigma\, \lambda^0_+ + \Sigma\, \lambda^0_-$

This means that we can assign a *limiting equivalent conductivity* λ_0 to each kind of ion:

cation	H_3O^+	NH_4^+	K^+	Ba^{2+}	Ag^+	Ca^{2+}	Sr^{2+}	Mg^{2+}	Na^+	Li^+
λ_0	349.98	73.57	73.49	63.61	61.87	59.47	59.43	53.93	50.89	38.66
anion	OH^-	SO_4^{2-}	Br^-	I^-	Cl^-	NO_3^-	ClO_3^-	CH_3COO^-	$C_2H_5COO^-$	$C_3H_7COO^-$
λ_0	197.60	80.71	78.41	76.86	76.30	71.80	67.29	40.83	35.79	32.57
Limiting ionic equivalent conductivities at 25°C, S $cm^{-1}eq^{-1}$										

Just as a compact table of thermodynamic data enables us to predict the chemical properties of a very large number of compounds, this compilation of equivalent conductivities of twenty different species yields reliable estimates of the of Λ_0 values for five times that number of salts.

We can now estimate weak electrolyte limiting conductivities

One useful application of Kohlrausch's law is to estimate the limiting equivalent conductivities of weak electrolytes which, as we observed above, cannot be found by extrapolation. Thus for acetic acid CH_3COOH ("HAc"), we combine the λ_0 values for H_3O^+ and CH_3COO^- given in the above table:

$\Lambda^0_{HAc} = \lambda^0_{H+} + \lambda^0_{Ac-}$

How fast do ions migrate in solution?

Movement of a migrating ion through the solution is brought about by a force exerted by the applied electric field. This force is proportional to the field strength and to the ionic charge. Calculations of the frictional drag are based on the premise that the ions are spherical (not always true) and the medium is continuous (never true) as opposed to being composed of discrete molecules. Nevertheless, the results generally seem to be realistic enough to be useful. According to Newton's law, a constant force exerted on a particle will *accelerate* it, causing it to move faster and faster unless it is restrained by an opposing force. In the case of electrolytic conductance, the opposing force is frictional drag as the ion makes its way through the medium. The magnitude of this force depends on the radius of the ion and its primary hydration shell, and on the viscosity of the solution.

Eventually these two forces come into balance and the ion assumes a constant average velocity which is reflected in the values of λ_0 tabulated in the table above.

The relation between λ_0 and the velocity (known as the *ionic mobility* μ_0) is easily derived, but we will skip the details here, and simply present the results:

Anions are conventionally assigned negative μ_0 values because they move in opposite directions to the cations; the values shown here are absolute values $|\mu_0|$. Note also that the units are cm/sec per volt/cm, hence the cm^2 term.

cation	H_3O^+	NH_4^+	K^+	Ba^{2+}	Ag^+	Ca^{2+}	Sr^{2+}	Mg^{2+}	Na^+	Li^+
μ_0	0.362	0.0762	0.0762	0.0659	0.0642	0.0616	0.0616	0.0550	0.0520	0.0388
anion	OH^-	SO_4^{2-}	Br^-	I^-	Cl^-	NO_3^-	ClO_3^-	CH_3COO^-	$C_2H_5COO^-$	$C_3H_7COO^-$
μ_0	.2050	0.0827	0.0812	0.0796	0.0791	0.0740	0.0705	0.0461	0.0424	0.0411
Absolute limiting mobilities of ions at 25°C, (cm^2 $volt^{-1}$ sec^{-1}) × 100										

As with the limiting conductivities, the trends in the mobilities can be roughly correlated with the charge and size of the ion. (Recall that negative ions tend to be larger than positive ions.)

Cations and anions carry different fractions of the current

In electrolytic conduction, ions having different charge signs move in opposite directions. Conductivity measurements give only the sum of the positive and negative ionic conductivities according to Kohlrausch's law, but they do not reveal how much of the charge is carried by each kind of ion. Unless their mobilities are the same, cations and anions do not contribute equally to the total electric current flowing through the cell.

Recall that an electric current is defined as a flow of electric charges; the current in amperes is the number of coulombs of charge moving through the cell per second. Because ionic solutions contain equal quantities of positive and negative charges, it follows that the current passing through the cell consists of positive charges moving toward the cathode, and negative charges moving toward the anode. But owing to mobility differences, cations and ions do not usually carry identical fractions of the charge.

Transference numbers are often referred to as *transport numbers*; either term is acceptable in the context of electrochemistry. The fraction of charge carried by a given kind of ion is known as the *transference number*$t_\pm$

. For a solution of a simple binary salt,

t_+ = \dfrac{\lambda_+}}{\lambda_+ + \lambda_-}

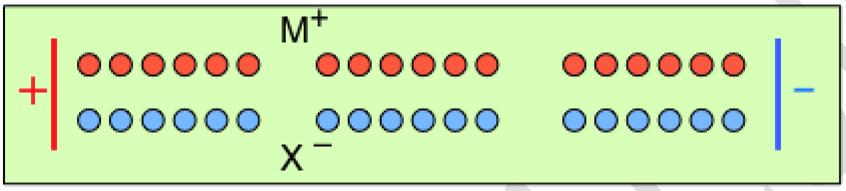
and

t_- = \dfrac{\lambda_-}}{\lambda_+ + \lambda_-}

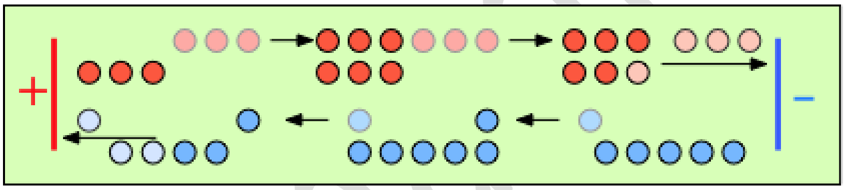
By definition,

$t_+ + t_- = 1$.(8.10.9D.1)

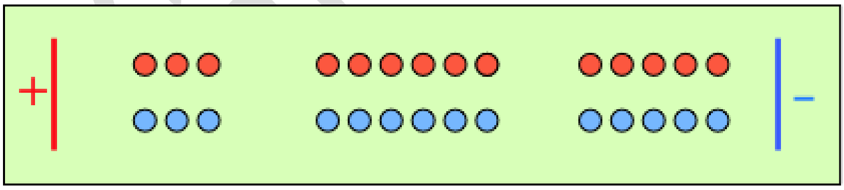
To help you visualize the effects of non-identical transference numbers, consider a solution of $M^+ X^-$ in which $t_+ = 0.75$ and $t_- = 0.25$. Let the cell be divided into three [imaginary] sections as we examine the distribution of cations and anions at three different stages of current flow.



Initially, the concentrations of M^+ and X^- are the same in all parts of the cell.

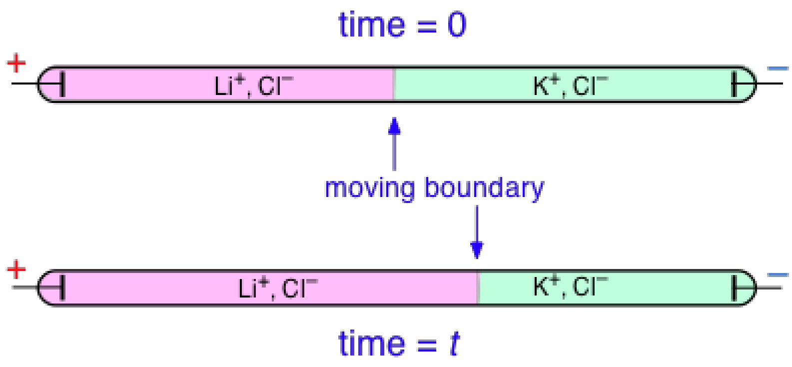


After 4 faradays of charge have passed through the cell, 3 eq of cations and 1 eq of anions have crossed any given plane parallel to the electrodes. Note that 3 anions are discharged at the anode, exactly balancing the number of cations discharged at the cathode.



In the absence of diffusion, the ratio of the ionic concentrations near the electrodes equals the ratio of their transport numbers.

Transference numbers can be determined experimentally by observing the movement of the boundary between electrolyte solutions having an ion in common, such as LiCl and KCl:



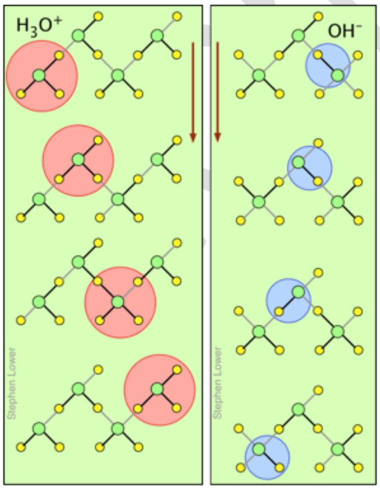
In this example, K^+ has a higher transference number than Li^+, but don't try to understand why the KCl boundary move to the left; the details of how this works are rather complicated and not important for the purposes of this this course.

H^+ and OH^- ions "migrate" without moving, and rapidly!

the hydrogen- and hydroxide ions have extraordinarily high equivalent conductivities and mobilities. This is a consequence of the fact that unlike other ions which need to bump and nudge their way through the network of hydrogen-bonded water molecules, these ions are *participants* in this network. By simply changing the H_2O partners they hydrogen-bond with, they can migrate "virtually". In effect, what migrates is the hydrogen-bonds, rather than the physical masses of the ions themselves.

This process is known as the *Grothuss Mechanism*. The shifting of the hydrogen bonds occurs when the rapid thermal motions of adjacent molecules brings a particular pair into a more favorable configuration for hydrogen bonding within the local molecular network. Bear in mind that what we refer to as "hydrogen ions" H^+*(aq)* are really *hydronium ions* H_3O^+. It has been proposed that the larger aggregates $H_5O_2^+$and $H_9O_4^+$ are important intermediates in this process.

It is remarkable that this virtual migration process was proposed by Theodor Grotthuss in 1805 — just five years after the discovery of electrolysis, and he didn't even know the correct formula for water; he thought its structure was H–O–O–H.



These two diagrams will help you visualize the process. The successive downward rows show the first few "hops" made by the virtual H^+ and OH^-ions as they move in opposite directions toward the appropriate electrodes. (Of course, the same mechanism is operative in the absence of an external electric field, in which case *all* of the hops will be in random directions.)

Ion transport number

Ion transport number, also called the transference number, is the fraction of the total electrical current carried in an electrolyte by a given ionic species *i*,

$$t_i = \frac{I_i}{I_{tot}}$$

Differences in transport number arise from differences in electrical mobility. For example, in an aqueous solution of sodium chloride, less than half of the current is carried by the positively charged sodium ions (cations) and more than half is carried by the negatively charged chloride ions (anions) because the chloride ions are able to move faster, i.e., chloride ions have higher mobility than sodium ions. The sum of the transport numbers for all of the ions in solution always equals unity.

At zero concentration, the limiting ion transport numbers may be expressed in terms of the limiting molar conductivities of the cation (λ_0^+), anion (λ_0^-), and electrolyte (Λ_0):

$$t_+ = \nu^+ \cdot \frac{\lambda_0^+}{\Lambda_0} \text{ and } t_- = \nu^- \cdot \frac{\lambda_0^-}{\Lambda_0},$$

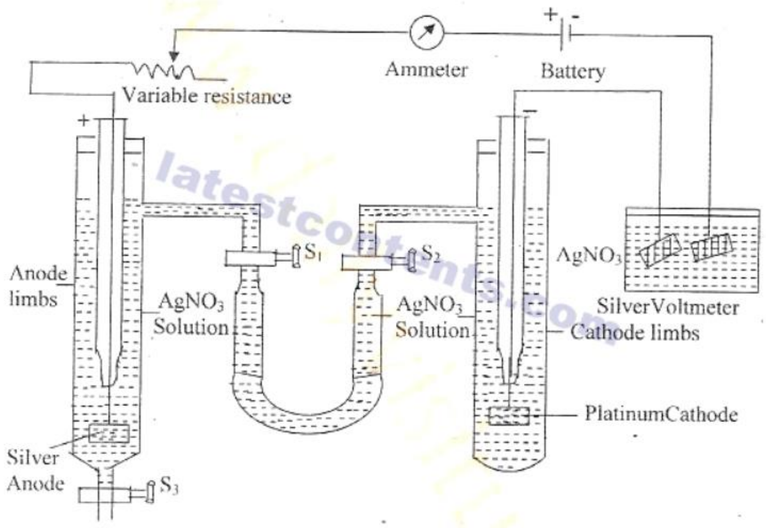
where ν^+ and ν^- re the numbers of cations and anions respectively per formula unit of electrolyte.[2] In practice the molar ionic conductivities are calculated from the measured ion transport numbers and the total molar conductivity. For the cation

$$\lambda_0^+ = t_+ \cdot \frac{\Lambda_0}{\nu^+},$$

and similarly for the anion. The sum of the cation and anion transport numbers equals 1.

Hittorf's Method for Determination of Transport Number

This method is based on the principle that the concentration changes occur around the electrodes due to the migration of ions. The apparatus used consists of a U-shaped tube, connected on one side to the "anode limb" and on the other side to the "cathode limb". The anode is made of silver and cathode is made of platinum metal. The U-tube, the anode limb and cathode limb are filled with a standard solution of Ag NO3. The apparatus is connected in series to a silver voltmeter. A steady current of about 0.01 amperes is passed for about two to three hours. After that, the stopcocks S1 and S2 are closed. The whole of the solution from anode limb is taken out through stopcock S3 in a weighed flask. The silver content of this solution is determined by Volhard's method. The weight of silver deposited in the silver voltameter is also determined.



OBSERVATION AND CALCULATION

Mass of silver deposited in silver voltameter = W grams

This mass 'W' is proportional to the total current passed.

Mass of the solution taken out from the anode limb = a grams

Mass of Ag NO$_3$ in 'a' grams of the solution (Volhard method) = b grams

Mass of water in the solution = (a – b) grams

Mass of AgNO$_3$ associated with (a–b) grams of water before Electrolysis (standard solution of AgNO$_3$) = C grams

∴ Increase in mass of AgNO$_3$ around anode after electrolysis = (b –c) grams

Formula weight of AgNO$_3$ = 108 + 14 + 48 = 170

Therefore, 170 g AgNO$_3$ = 108 grams Ag

$$1 \text{ g } AgNO_3 = \frac{108}{170}$$

$$(b\text{–}c) \text{ grams } AgNO_3 = \frac{108}{170} \times (b-c) = X \text{ grams}$$

Thus increase in mass of silver around anode after electrolysis = X grams.

If the silver ions (Ag+) had not migrated from the anode, then the increase in mass of silver would have been 'W' grams. Hence decrease in the concentration around the anode as a result of migration of Ag+ ions, will be (W-X) grams. This decrease will be proportional to the speed of Ag+ ions and the speed is proportional to the fraction of current carried by Ag+ ion. Therefore, transport number of Ag+ ions (t_{Ag+}) is given by: -

$$t_{Ag+} = \frac{\text{Fall in conc. around anode}}{\text{Total current passed}} = \frac{W-X}{W}$$

In AgNO$_3$ solution, we have: $t_{Ag+} + t_{NO3^-} = 1$

Therefore $t_{NO3^-} = 1 - t_{Ag+} = 1 - \frac{W-X}{W}$

or $t_{NO3^-} = 1 - \frac{W-X}{W}$

Thus the transport number of Ag$^+$ and NO$_3^-$ ion in the standard solution of AgNO$_3$ can be calculated.

MOVING BOUNDARY METHOD

This method is based on the direct observation of the migration of ions under the influence of an applied electric field. Let us consider Hydrochloric acid and the transport numbers of H+ and Cl ions present in HCl have to be determined. The hydrochloric acid is called the principal or experimental electrolyte. Another electrolyte containing a common ion (Cl-) called the indicator electrolyte is selected. The speed of the cation of the indicator electrolyte is selected. The speed of the cation of the indicator electrolyte should be less than that of the cation of the experimental electrolyte. For example: CdCl2 can be selected as the indicator electrolyte as the speed of Cd++ ion is less than that of H+ ions. A concentrated solution of CdCl2 is used, so that HCl solution can float on it.

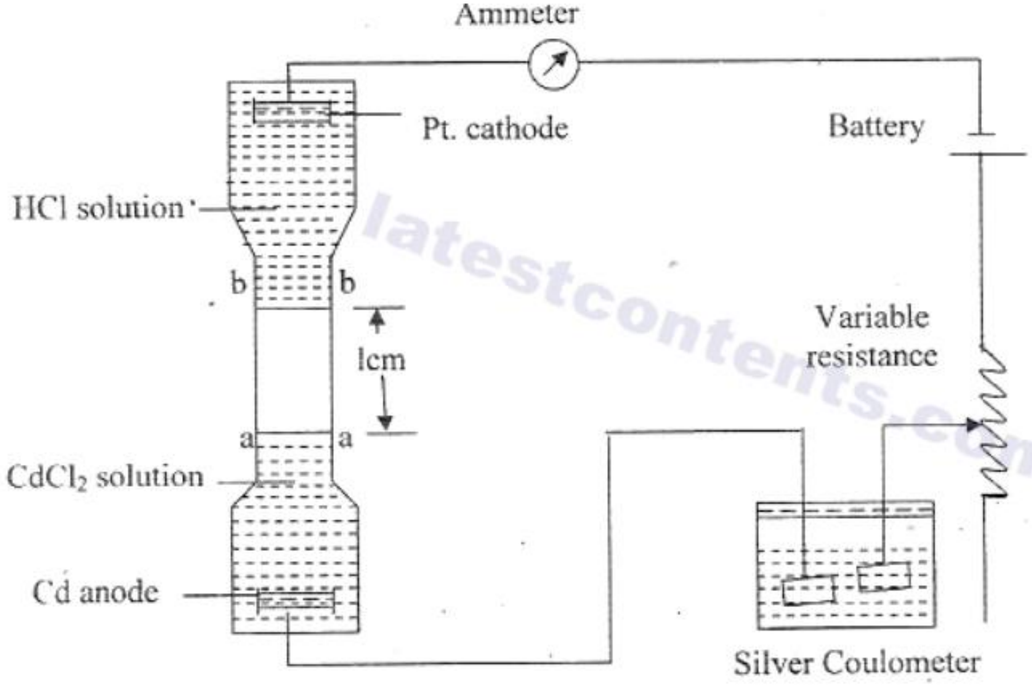


Fig.4.4. The moving boundary method of determining transport number.

The apparatus used in the moving boundary method is shown in the figure. It consists of a long vertical tube. The lower part of the tube is filled with Cd Cl$_2$ solution and the upper part is filled with HCl solution. The boundary between the two solutions is visible due to the difference in their refractive indices. The cathode made up of platinum is fitted at the top of the tube and the anode made of cadmium is placed at the bottom. A Silver coulometer is also included in the circuit and gives the quantity of electricity passed through the cell. When the current is passed through the cell, H$^+$ ions move in the upward direction towards the platinum cathode and H$_2$ gas is evolved. A slow movement of Cd^{2+} ions is also observed in the upward direction. The boundary separating the two solutions also moves from "aa" to "bb" through a distance 'l' cm. If 'A' is the area of cross section of the tube, then volume moving upward will be given by:

$$V\ cm^3 = l \times A$$

Suppose the hydrochloric acid solution contain 'C' gram equivalents of HCl per dm^3, then the conc. of H^+ ions will also be 'C' gram equivalents per dm^3 as one HCl molecule forms one H^+ ion. Hence,

$$1 \text{ dm}^3 \text{ or } 1000 \text{ cm}^3 \text{ of HCl solution} = C \text{ g .equiv. of } H^+ \text{ ions}$$

$$1 \text{ cm}^3 \text{ of HCl solution} = \frac{C}{1000}$$

$$V \text{ cm}^3 \text{ of HCl solution} = \frac{C}{1000} \times V \text{ g. Equiv. of } H^+ \text{ ions.}$$

Now 1 gram Equiv. of H+ ions carry current = 1 faraday.

$$\frac{C \times V}{1000} \text{ gram Equiv. of H+ ions carry current} = 1 \times \frac{C \times V}{1000} \text{ faraday}$$

The quantity of electric current passed through the cell as indicated by silver coulometer is equal to 'Q' faradays. The transport number of H^+ ions is given by the equation:-

$$T_{H+} = \frac{\text{Current carried by } H^+ \text{ ions}}{\text{Total current}} = \frac{C \times V}{1000} \times \frac{1}{Q}$$

Kohlrauschs law

Kohlrausch's law states that the equivalent conductivity of an electrolyte at infinite dilution is equal to the sum of the conductance's of the anions and cations. If a salt is dissolved in water, the conductivity of the solution is the sum of the conductance's of the anions and cations. The law, which depends on the independent migration of ions, was deduced experimentally by the German chemist Friedrich Kohlrausch (1840-1910).

$$\alpha = \frac{\text{Molar conductivity at a concentration c}}{\text{Molar conductivity at infinite dilution}} = \frac{\Lambda_m^c}{\Lambda_m^o}$$

Degree of dissociation of electrolyte at a given dilution is given by this example.

Kohlrausch observed certain regularities while comparing the values of limiting molar conductivities of some strong electrolytes. On the basis of his observations, Kohlrausch proposed "limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anions and cations of the electrolyte". This law is popularly known as Kohlrausch law of independent migration of ions. For example, limiting molar conductivity, Ë$_m$° of sodium chloride can be determined with the knowledge of limiting molar conductivities of sodium ion and chloride ion. Some important applications of Kohlrausch law of independent migration of ions are:

1. Kohlrausch law helps us in the determination of limiting molar conductivities for any electrolyte. Weak electrolytes have lower molar conductivities and lower degree of dissociation at higher concentrations. The graph plotted between molar conductivity and $c^{1/2}$ (where c is the concentration) is not a straight line for weak electrolytes. The molar conductivity of weak electrolyte increases steeply at lower concentrations. Therefore, limiting molar conductivity, Ë$_m$° cannot be obtained by extrapolation of molar conductivity to zero concentration. Hence, we use the Kohlrausch law of independent migration of ions for the determination of limiting molar conductivity, Ë$_m$° for weak electrolytes.

2. Kohlrausch law also helps us in determining the value of dissociation constant from the value of molar conductivity and limiting molar conductivity for a weak electrolyte at a given concentration.

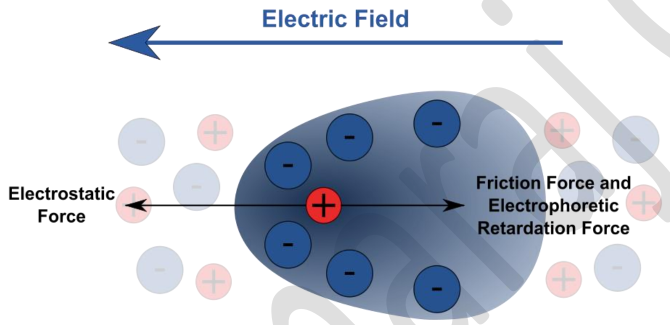
$$\alpha = \frac{\Lambda}{\ddot{E}_m{}^{o}}$$

Uses of Kohlrausch's law

- Calculation of Degree of dissociation
- Calculation of solubility of sparingly soluble salt
- Calculation of Dissociation Constant for week electrolytes
- Calculation of Molar Conductivity for week electrolytes at infinite dilution

Diffusion and ionic mobility

Many different biochemical techniques use the principles of electrophoresis to identify compounds of interest in a sample and understand interactions at the molecular and ionic level. The basic concept of the techniques uses an electric field that attracts or repels certain ions, and measurements of the mobility of the ions through the medium (Figure 1). The cations move toward the cathode, and the anions move toward the anode. Heavier or bulkier ions move more slowly through the medium. Visual patterns formed on the various media (through the use of dyes and other techniques, such as Coomassie Brilliant Blue G 250 dye) can be analyzed for useful information.



The velocity of the ion is given by the following equation:

$$v = \frac{E \times q}{f}$$

v is the velocity,

f is the coefficient of friction,

E is the applied electric field (Volts/cm), and

q is the net charge on the ion

The **coefficient of friction** (*f*) in Equation 1 is introduced due to the fact that when the ion moves through the medium, the medium exerts a frictional force on the ion that inhibits the movement of the ion. Usually the voltage applied is held constant, so the **mobility** (*η*) of the ion can be measured; it is defined as follows:

$$\eta = \frac{v}{E}$$

v is the velocity

E is the applied electric field (Volts/cm)˙

The electric field's properties determine the separation of ions, and is affected by resistance, current, and voltage.

The higher the current, the faster the migration of the ions (due to increased Coulombic attractions). Because current is affected by voltage, as the difference in potential between the electrodes increases, the rate of migration increases. The resistance is dependent on the properties of the medium; a denser or more saturated medium will retard migration, as will a longer or narrower medium. Mediums with different densities can be made from the same compound, and are quite useful for separating and identifying molecules (through molecular sieving, for example). The most common mediums are agar and polyacrylamide gels.

Different compounds have different stability conditions, and the buffer must be chosen carefully so as not to "harm" the molecules' native states. The main factors to consider when choosing a buffer are its concentration and its pH. Concentration in terms of electrophoresis buffer refers to the ionic strength of the buffer; a buffer with a higher ionic strength will conduct the current more than the sample, leading to slower migration of the molecules. For compounds that have different ionization forms, pH is a major factor in choosing a buffer. The buffer must have a pH that matches the specific ionization forms' pH range.

Walden rule

A rule which states that the product of the viscosity and the equivalent ionic conductance at infinite dilution in electrolytic solutions is a constant, independent of the solvent; it is only approximately correct.

Applications of conductance measurements

The conductance of electrolytes depends on the number of ions and their speeds. The measurements of conductance of electrolytic solutions have been utilized for determining –

a) the endpoints of acid-base titrations,
b) the endpoints of precipitation titrations;
c) the solubility of sparingly soluble salts and
d) the kinetics of reactions.

For conductometric titration experiments, a known volume of the solution to be titrated is placed in a beaker and a conductivity cell dipped into it. The conductivity cell is now connected to one end of the Wheatstone's bridge. The other solution is then added to the solution in the beaker in installments and the conductance measured after each addition. This is continued beyond a sharp change in conductance value. The conductance values are then plotted against the volumes of titrated added. In each case, the straight-line portions of the graph are extrapolated and the point at which the straight lines intersect is taken as the end pony of the titration.

In natural waters, conductivity is mostly used to approximation the concentrations of dissolved salts in the water, which can provide insights into processes affecting the water. In coastal areas, the conductivity of water might change with assimilation with saltwater, and the conductivity of water might rise when it becomes contaminated with road salt in areas with cool climates.

Common Application of conductance measurements:

- Determination of dissociation constant of weak electrolytes from conductance measurements.

- Weak electrolytes like HAc dissociation according to – Determination the solubility of a sparingly soluble salt by conductance measurement.

Water Treatment and Industrial Applications

Water treatment may be used to make water safe to drink or proper for manufacturing use. In many industrial applications, scale or corrosion might be an apprehension. Conductivity might also be used to monitor the usefulness of desalinization, which is another water conduct procedure that removes salts to make water drinkable or useable for manufacturing processes. In other industrial applications, conductivity measurements might be used to identify leaks, where the leaking water might have a superior conductivity. Conductivity might also be used to check the efficiency of rinsing procedures, where a low conductivity of water in contact with the rinsed object indicates an efficient rinse.

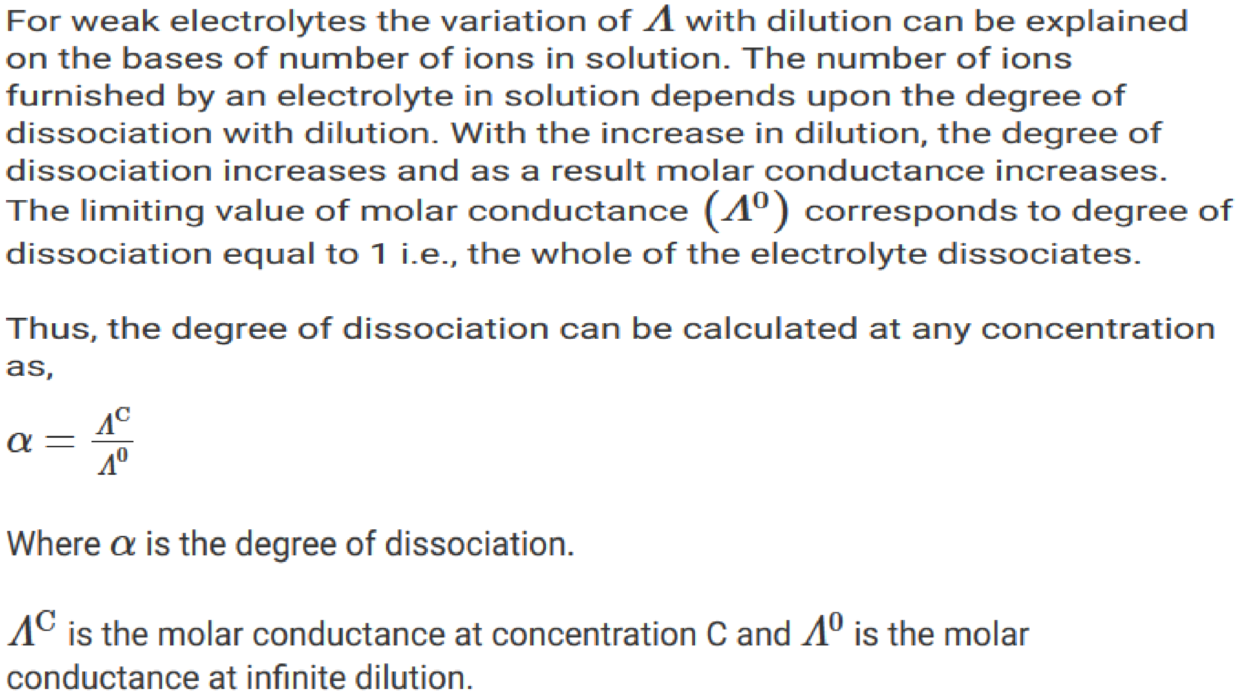
Agricultural and Hydroponics Applications

For irrigation, the salinity of the water is a significant factor. If the salinity is too high, salts will build up in the soil as the water evaporates which might demean soil eminence and inhibit plant growth.

Conductivity can also be used to observe nutrient concentrations in liquid fertilizers. Comparable to fertilizer application, conductivity is used in hydroponics to monitor the concentrations of nutrient solutions. If the conductivity gets too high, indicating a nutrient concentration at toxic levels, plants might be debilitated or die. Low conductivities can designate insufficient nutrient supply. Conductivity monitoring can be used as a component of mechanized nutrient supply systems.

Conductance offers a very simple and convenient mean for determining the solubility of a sparingly soluble salt such as AgCl, etc. dissolved to a very small extent. That is why these salts are called sparingly soluble salts.

Degree of dissociation of weak electrolytes



For weak electrolytes the variation of Λ with dilution can be explained on the bases of number of ions in solution. The number of ions furnished by an electrolyte in solution depends upon the degree of dissociation with dilution. With the increase in dilution, the degree of dissociation increases and as a result molar conductance increases. The limiting value of molar conductance (Λ^0) corresponds to degree of dissociation equal to 1 i.e., the whole of the electrolyte dissociates.

Thus, the degree of dissociation can be calculated at any concentration as,

$$\alpha = \frac{\Lambda^C}{\Lambda^0}$$

Where α is the degree of dissociation.

Λ^C is the molar conductance at concentration C and Λ^0 is the molar conductance at infinite dilution.

The degree of dissociation of a weak electrolyte is proportional to the inverse square root of the concentration, or the square root of the dilution

$$a = \sqrt{\frac{K_d}{c_0}}$$

Determination of Solubility of Sparingly Soluble Salts

Salts like $AgCl$, $BaSO_4$, $CaCO_3$, Ag_2CrO_4, $PbSO_4$, PbS, $Fe(OH)_3$ etc. are ordinarily regarded as sparingly soluble and have a very small but definite solubility in water. The solubility of such sparingly soluble salts is obtained by determining the specific conductivity (κ) of a saturated salt solution. The molar conductivity at such high dilution can practically be taken as $\wedge_m^\infty$, i.e. for sparingly soluble salts,

$$\wedge_m^\infty = \kappa . \mathbf{V} \qquad (15)$$

Where, V is the volume in cm^3 containing 1 mole of salt while $\wedge_m^\infty$, can be calculated using Kohlraush's law.

Substituting the values of κ and $\wedge_m^\infty$ in eq. 15; below the value of V can be calculated:

$$\mathbf{V} = \wedge_m^\infty / \kappa \approx (\nu_+ \wedge_+ + \nu_- \wedge_-) / \kappa \qquad (16)$$

But Vcm^3 of saturated solution contains = 1 mole of salt

1000 cm^3 of saturated solution contains= 1000 / V mole of salt

Hence, solubility of salt, S = 1000/V M

= 1000/V x M. Wt. = g/L

Determination of ionic product of water

With the help of specific conductivity of water, the ionic product of water can be determined. The ionization of water may be represented as,

$$\mathbf{H_2O} \rightleftharpoons \mathbf{H^+ + OH^-}$$

The product of the concentrations of H^+ and OH^- ions expressed in mol/L is called ionic product of water and is represented by K_w.

$$[\mathbf{H^+}]\ [\mathbf{OH^-}] = \mathbf{K_w}$$

The measured specific conductivity of the purest form of water is 0.055×10^{-6} S cm^{-1}. The molar conductance is given by

$$\Lambda_m = K_v \times 18 \qquad (17)$$

Thus, $= 0.055 \times 10^{-6} \times 18$

$$= 0.990 \times 10^{-6}\ \mathrm{Scm^2mol^{-1}}$$

The molar conductance of water at infinite dilution can be obtained by

$$\Lambda_m^{\infty}\ (H_2O) = \Lambda\ (H^+) + \Lambda\ \ (OH^-)$$

Therefore, $\Lambda_\infty\ (H_2O) = 349.8 + 198.5 = 548.30\ \mathrm{Scm^2mol^{-1}}$

and for water, $\alpha\ \ = \Lambda_m / \Lambda_\infty$

$$= 0.055 \times 10^{-3} \times 18/\ 548.3$$

$$C_H^{\ +} = C_{OH}^{\ -} = 0.055 \times 10^{-3} \times 18/\ 548.3$$

(Concentration of water = 1000/18 = 55.55 M

$C_H^{\ +} = C_{OH}^{\ -} = \alpha \times 55.55 \times 10^{-9}$

$= 1.806 \times 55.55 = 1.003 \times 10^{-7}$

$Kw = (1.003 \times 10^{-7})$

Debye - Huckel - Onsager equation

The modern treatment of the concept of the influence of the attractive forces between ions on electrolyte conductance was studied by Debye and Huckel and its extension by Onsager andFalkenhagen. The asymmetry of ionic atmosphere due to time of relaxation and electrophoretic effect ′ tend to retard the motion of ions in solutions. By considering these two factors tthey proposed an equation known as -Debye - Huckel – Onsager conductance equation are the equivalent conductances at a given mm concentration C and at infinite dilution, respectively. 'e' is tthe dielectric constant, n is the viscosity of the medium and T is the temperature in absolute scale.

$$\Lambda_m = \Lambda_m^{\circ} - \left[\frac{82.4}{(\epsilon T)^{1/2}\eta} + \frac{8.20 \times 10^5}{(\epsilon T)^{3/2}} \Lambda_m^{\circ} \right] \sqrt{C}$$

where Λ_m and Λ_m°

The only interactions the theory considers are the electrostatic interactions between ions. These interactions are much stronger than those between uncharged molecules, and they die off more slowly with distance. If the positions of ions in an electrolyte solution were completely random, the net effect of electrostatic ion- ion interactions would be zero, because each cation–cation or anion–anion repulsion would be balanced by a cation–anion attraction. The positions are not random, however: each cation has a surplus of anions in its immediate environment, and each anion has a surplus of neighboring cations. Each ion therefore has a net attractive interaction with the surrounding ion atmosphere. The result for a cation species at low electrolyte molality is a decrease of μ_+ compared to the cation at same molality in the absence of ion–ion interactions, meaning that the single-ion activity coefficient γ_+ becomes less than 1 as the electrolyte molality is increased beyond the ideal-dilute range. Similarly, γ_- also becomes less than 1.

According to the Debye–Hückel theory, the single-ion activity coefficient γ_i of ion i in a solution of one or more electrolytes is given by

$$\ln \gamma_i = -\frac{A_{\mathrm{DH}} z_i^2 \sqrt{I_m}}{1 + B_{\mathrm{DH}} a \sqrt{I_m}}$$

where

- $z_i =$ the charge number of ion i ($+1$, -2, etc.);
- $I_m =$ the **ionic strength** of the solution on a molality basis, defined by $I_m \overset{\text{def}}{=} \frac{1}{2} \sum_{\text{all ions}} m_j z_j^2$
- A_{DH} and B_{DH} are defined functions of the kind of solvent and the temperature;
- a is an adjustable parameter, equal to the mean effective distance of closest approach of other ions in the solution to one of the i ions.

The definitions of the quantities A_{DH} and B_{DH} appearing in Eq. 10.4.1 are

$$A_{\mathrm{DH}} \overset{\text{def}}{=} \left(N_{\mathrm{A}}^2 e^3 / 8\pi\right) \left(2\rho_{\mathrm{A}}^*\right)^{1/2} \left(\epsilon_{\mathrm{r}} \epsilon_0 RT\right)^{-3/2}$$

$$B_{\mathrm{DH}} \overset{\text{def}}{=} N_{\mathrm{A}} e \left(2\rho_{\mathrm{A}}^*\right)^{1/2} \left(\epsilon_{\mathrm{r}} \epsilon_0 RT\right)^{-1/2}$$

where N_{A} is the Avogadro constant, e is the elementary charge (the charge of a proton), ρ_{A}^* and ϵ_{r} are the density and relative permittivity (dielectric constant) of the solvent, and ϵ_0 is the electric constant (or permittivity of vacuum).

When the solvent is water at $25\,^{\circ}\mathrm{C}$, the quantities A_{DH} and B_{DH} have the values

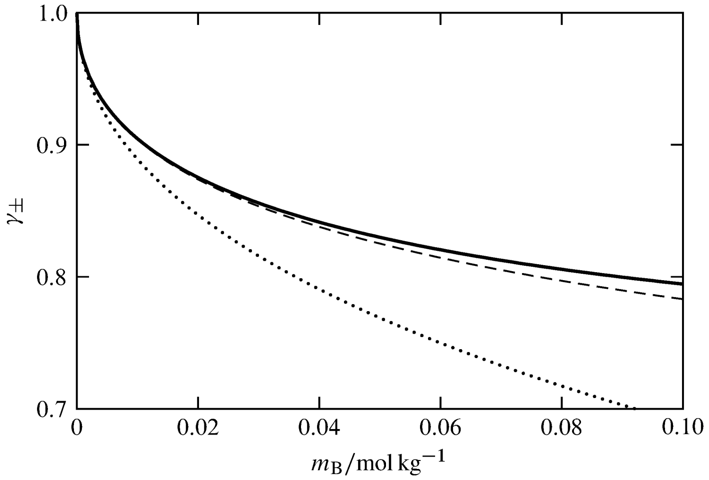
$$A_{\mathrm{DH}} = 1.1744\,\mathrm{kg}^{1/2}\,\mathrm{mol}^{-1/2}$$

$$B_{\mathrm{DH}} = 3.285 \times 10^9\,\mathrm{m}^{-1}\,\mathrm{kg}^{1/2}\,\mathrm{mol}^{-1/2}$$

the electroneutrality condition $\nu_+ z_+ = \nu_- z_-$, we obtain the following expression for the logarithm of the mean ionic activity coefficient of an electrolyte solute:

$$\ln \gamma_\pm = -\frac{A_{\mathrm{DH}} \left|z_+ z_-\right| \sqrt{I_m}}{1 + B_{\mathrm{DH}} a \sqrt{I_m}}$$

In this equation, z_+ and z_- are the charge numbers of the cation and anion of the solute. Since the right side of Eq. is negative at finite solute molalities, and zero at infinite dilution, the theory predicts that $\gamma_\pm$ is less than 1 at finite solute molalities and approaches 1 at infinite dilution.



As the molalities of all solutes become small it becomes

$$\ln \gamma_{\pm} = -A_{DH}\,|z_+ z_-|\,\sqrt{I_m}$$

VERIFICATION OF DEBYE-HÜCKEL-ONSAGER EQUATION FOR STRONG ELECTROLYTES

The conductance behavior of strong electrolytes has been given by the

Debye-Hückel-Onsager equation $\lambda_c = \lambda_o - (A + B\,\lambda_o)\sqrt{c}$,

where λ_c is the equivalent conductivity at concentration c ,

λ_o is the equivalent conductivity at infinite dilution,

A and B are the Debye – Hückel – Onsager coefficients. At 25 °C ,

the values are $A = 60.2$, and $B = 0.229$.

A plot of λ_c (y - *axis*) **against** $\sqrt{c}$ (x - *axis*) should be linear,

with a slope = $-(A + B\,\lambda_o)$.

The intercept on the y-axis would give λ_o .

Hence, λ_o **can be obtained by extrapolating the graph to** ***zero***

Wien effect

The Wien effect is the experimentally-observed increase in ionic mobility or conductivity of electrolytes at very high gradient of electrical potential.[1] A theoretical explanation has been proposed by Lars Onsager.

A related phenomenon is known as the Second Wien Effect or the dissociation field effect, and it involves increased dissociation constants of weak acids at high electrical gradients.[3] The dissociation of weak chemical bases is unaffected.

The effects are important at very high electrical fields (10^8 – 10^9 V/m), like those observed in electrical double layers at interfaces or at the surfaces of electrodes in electrochemistry.

More generally, the electric field effect (directly, through space rather than through chemical bonds) on chemical behavior of systems (e.g., on reaction rates) is known as the field effect or the direct effect

Debye–Falkenhagen effect

The increase in the conductivity of an electrolyte solution when the applied voltage has a very high frequency is known as Debye–Falkenhagen effect.[1][2]Impedance measurements on water-p-dioxane and the methanol-toluene systems have confirmed Falkenhagen's predictions made in 1929