
Physical Chemistry I

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Bachelor Course
Water: Chemistry, Analysis and Microbiology

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Literature: P.W. Atkins Physical Chemistry / Physikalische Chemie
 T. Engel and P. Reid Physical Chemistry / Physikalische Chemie

 G.K. Vemulapalli Physical Chemistry

I. Introduction

In the universe we find all kinds of „objects“, very large objects like the sun, earth and moon, medium-size objects like a chair, an engine or an animal, small objects like bacteria and viruses and very small objects like electrons, atoms and molecules. All larger objects are composed of atomic particles. On a microscopic scale these atomic particles interact with each other and can give rise to something like a chemical bond in a molecule or a hydrogen bond between water molecules. In addition to atomic particles electric and magnetic fields exist which can interact with these atomic particles. Radiation like visible light or X-rays, for instance, can be described as rapidly varying electric and magnetic fields (electromagnetic waves) which propagate in space with a very high speed, the light velocity c , ca. 300.000 km/s (this speed is dependent on the medium in which the wave propagates, the fastest speed is found when the wave propagates in vacuum).

Physicists, chemists and biologists have developed a large number of theories to describe properties of living and dead objects and the process in which these objects are involved. From a physical point of view there exist however a few almost universal theories on which all other theories must be based.

- *Classical or Newtonian mechanics* describes the motion of large objects, like for instance planets or bullets, extremely well.
- *Quantum mechanics* is needed to describe the properties of atomic particles and of processes in which such particles are involved. On such a microscopical scale classical mechanics does not work. Quantum mechanics was developed in 1920-1930 and functions well for the description of the behaviour of atomic particles.
- *Relativity Theory* describes processes in which particles that move at very high speeds (comparable to the speed of light) are involved. Although this seems very far from daily life, do not forget that electrons in atoms seem to move at such speeds. The quantum mechanics description of molecules therefore sometimes needs a relativistic correction.
- The *electromagnetic theory* (EM theory) describes the interaction of electric and magnetic fields with microscopic objects(electrons, atoms, molecules,...) and with macroscopic objects (radio or radar wave antennas). Since light is an electromagnetic wave (a propagation of periodic electric and magnetic fields) the EM theory in combination with

quantum mechanics is also needed to describe phenomena like the absorption, emission or diffraction of light by matter.

- *Thermodynamics* was originally the theory for the description of the flow of heat and energy between macroscopic machines and their surrounding (especially useful for the development of the steam engine in 18...) but it has been developed into a general theory for the description of physical, chemical and biological processes. *Classical or phenomenological thermodynamics* describes macroscopical objects without referring to their atomic or molecular structure (the earlier investigators probably had no notion of molecules) and is based on several, often very ingenious, experiments from which general axiomatic laws were derived. In later times a thermodynamic theory was developed which describes matter as an ensemble of very many microscopical particles, each of which follows a quantummechanical description. In view of the large number of microscopical particles in an ensemble statistical methods are applied to deal with such large ensembles, therefore this branch of thermodynamics is called *Statistical Thermodynamics*.

Roughly speaking physical chemistry (the „physics of molecules“) can be divided into a description of the molecular structure of matter and the consequences thereof for the chemical or biological processes in which the molecules are involved, and into a macroscopical description of matter for which the knowledge of the precise molecular structure is not very relevant. The first approach would need quantum mechanics, the second approach is the approach of classical thermodynamics.

In this lecture we will start with the second approach, but we will try to make a relation to the first approach whenever possible.

Classical thermodynamics is based on a number of axioms (thermodynamic „laws“) which result from very many laboratory and „Gedanken“-experiments. The strength and the beauty of classical thermodynamics is that we can describe certain processes without knowing the details of the process and the structure of the components that take part in these processes. As an example, consider the daily life experience that when you put cheese and bread in a refrigerator, everyone knows that after a while both have attained the same temperature, although the molecular structures of cheese and bread are very different.

Thermodynamics is built up like mathematics with strict rules and definitions (for instance, we have to define what the meaning of temperature is before we can for instance say that the temperature of cheese and bread is the same). We therefore start with a list of definitions.

II. Definitions

As described above, thermodynamics tries to describe macroscopical objects or structures or organizations almost without knowledge about the details of the internal structure or composition. Such objects are called *systems*. Because the notion of a system is so general, also the definition has to be very general and, at first look, the definition seems to be unnecessary abstract. The advantage of this general definition is that you can apply thermodynamic theory to a large number of phenomena. Important is that the abstract definition of a system automatically implies the definition of the surrounding of the system. Everything in the universe that does not belong to the system is called the *surrounding*.

System = Part of the universe that one wants to describe and that can be separated from its environment.

A system could be a reaction vessel or a biological cell or an engine or the earth or a container with gas. For the discussion in the first chapters it is easy to think of the system as a cylinder filled with gas and closed by a piston. Properties of the gas like the volume can then be changed by exerting pressure on the piston.

The system and its surroundings may exchange *energy* and/or *matter*.

To visualize the exchange of energy between the system and its surroundings think of the gas cylinder. By applying pressure to the piston we (we = part of the surrounding) do work on the system. As a result of the work done on the system the energy of the system must have been increased.

For the exchange of matter take the example of a biological cell. The cell wall separates the cell from its surroundings but this wall is open for certain substances to enter or leave the cell.

The following general situations can be distinguished:

Closed system	: no exchange of energy or matter between system and surroundings
Open system	: exchange of energy and matter between system and surroundings is possible
Isolated system	: no exchange of energy between system and surroundings
Thermally insulated system	: no heat exchange between system and surroundings, an isolated system is also a thermally insulated system, the reverse is not true.

The state of a system: state variables.

The state of a system is characterized by values of certain properties. Think again of our cylinder with gas as the system. The gas has a certain volume V (in m^3), temperature T (for the unit see below) and pressure p in Pascal ($1 \text{ Pa} = 1 \text{ N/m}^2$, $1 \text{ bar} = 10^5 \text{ Pa}$, $1 \text{ atm} = 101325 \text{ Pa}$). These properties describe the state of the system and are called *state variables*. One can distinguish intensive variables whose values do not change when the system is enlarged:

intensive variables : $p, T, \text{density } \rho, \dots$ (the density is the mass per volume in units kg/m^3)

and extensive variables, whose values change with the size of the system:

extensive variables : V , the energy of the system E (in units Joule), the amount of the substance n expressed in mol,

Most systems contain more than one substance and a mol number n_i can be defined for every substance i .

There is always a relation between the temperature, the volume, the pressure and the amount of substance, this relation $F(p,V,T,n) = 0$ is called the *equation of state*. As we will see later, this relation is particularly simple for gases at low pressure (ideal gases).

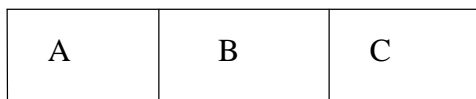
A system is in an *equilibrium state* when all the state variables are independent of time. A system usually is not in an equilibrium state, which means that one or more variables are changing in time. Sometimes it looks as if a system is in equilibrium, while many variables are constant in the time. In winter the room may be heated and the room temperature may be constant in time but higher than the outside temperature. This is called a *stationary state*. To check whether a system is in a stationary or in an equilibrium state, make it a closed system ("disconnect" the system from its surroundings). When the system variables stay constant in time, the system was in an equilibrium state, if not it was in a stationary state.

Process

A system may undergo processes that cause some state variables to change with time. For instance we can take our gas in the cylinder and raise the outside pressure on the piston. The state of the gas will change in that the internal pressure of the gas will increase and the volume decrease. An important difference is made between reversible and irreversible processes. This difference will be discussed later.

Temperature

The concept of temperature follows from the zero'th law of thermodynamics. This law states that when a system A is in thermal equilibrium with a system B (that means that when we bring A in thermal contact with B both A and B do not change) and B is in thermal equilibrium with C, that then also A is in thermal equilibrium with C.



A, B and C can be very different systems, for instance a cylinder with gas, a mercury thermometer and a block of ice. The fact that when the systems are brought into thermal contact, the state of either of the systems does not change, in spite of the fact that the composition of each system is very different, means that they have some property in common. This property is called the temperature. Although the precise definition of temperature is not trivial, we will not discuss it here. We assume that everyone has a practical feeling for the concept of temperature. The assignment of a value to the temperature of a certain system is rather arbitrary. Several temperature scales exist, the familiar Celcius scale compares the length of a mercury column when it is in thermal contact with melting ice (0°) with the

expanded length when it is in contact with boiling water (100° C). In the SI unit system (SI=Systeme Internationale) the temperature is expressed in Kelvins (K, not “degree” Kelvin), the *absolute temperature*. The absolute temperature can be expressed in the temperature according to the Celcius scale by the equation:

$$T \text{ (in K)} = t \text{ (in C)} + 273.15$$

The absolute lowest temperature that can be reached is 0 K.

The states of matter

We spoke already about a gas in a cilinder. In this case the system is a gas in which the particles are more or less free to move in every direction. Therefore a gas, if it is contained in a container, will completely fill the container. Usually the density of a gas is relatively low compared to the other forms in which matter can be found: liquids and solids. A liquid in a container does not have to fill the container completely. When not, there always is a surface between the liquid and the gas or vapour above it. The particles which form the liquid, usually molecules, can also move freely but now the density is so much higher than in a gas that collisions with neighboring particles occur every few ps (1 ps = 10⁻¹²s). The interparticle interactions are therefore very strong. Gas and liquids have in common that the long-range order is very low. We will see later that, for instance, for water there is a short-lived short-range order. Also in solids the interparticle interactions usually are very strong. Solids can be found in a highly ordered state, *crystals*, or in an unordered state, the *amorphous state*. Usually the translational mobility of the particles, atoms or molecules, in solids is very low. In many solids built of molecules, organic solids, however, the molecules show varying degrees of rotational freedom. In addition, certain functional groups may show a high rotational mobility, e.g. it is known that methyl groups rotate fast about their threefold symmetry axis even at low temperatures (20 K).

Because of the very weak interparticle interactions gases are much easier to describe than liquids or solids. For that reason we start with a description of the properties of gases.

III. The properties of gases

III. a. Perfect gases

The most simple state of matter is a gas. A gas consists of particles (atoms or molecules) which are free to move, except that the particles may collide with each other and with the wall if the gas is in a container. Between the particles there is empty space! The pressure on the walls of the container arises from the collisions of the gas particles with the wall. This implies that the pressure must be fluctuating in time, but because there are so many particles, 1 mol contains 6.02208×10^{23} particles, from a macroscopical point of view the pressure p is constant in time as long as the state of the gas does not change.

For a gas consisting of one type of particles (for instance H_2 for a hydrogen gas) the state variables are: volume V , temperature T , pressure p and amount (=number of moles) n . As mentioned above there must be a relation between these state variables, the equation of state. For gases there exist several different equations of state, depending on how accurate one wants to describe the gas. The most simple form is:

$$pV = nRT \quad (1)$$

where $R = 8.31451 \text{ JK}^{-1}\text{mol}^{-1}$ is a constant equal for all gases (the gas constant) and T has to be expressed in Kelvin (K).

This equation of state describes gases when the pressure is so low that collisions between the particles are very unlikely. Such a gas, where the particles do not interact, is called a *perfect or ideal* gas.

From the perfect gas equation (1) it is immediately seen that for perfect gases at constant temperature T and mole number n the product pV is constant (Boyle's law), that at constant p and n the quotient V/T is constant (Charles's law) and that for p and T constant the ratio V/n must be constant (Avogadro's principle). Fig. 1 shows the gas equation in graphical form. The points on the surface correspond to states of the perfect gas.

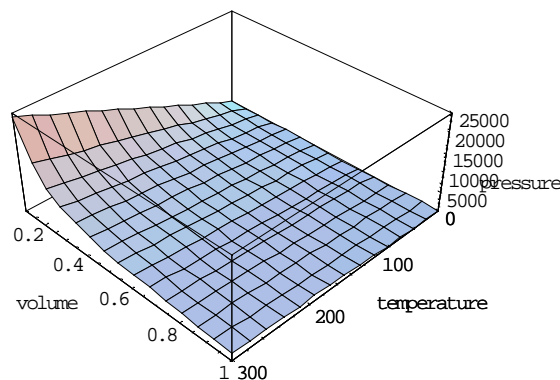


Fig. 1. The perfect gas equation in three dimensions

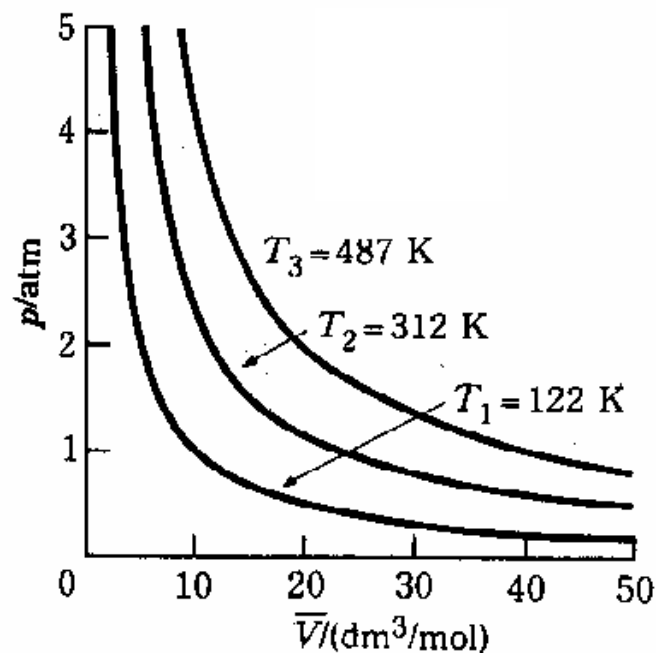


Fig. 2. The perfect gas equation with $T = \text{constant}$ (isotherms)

In many situations we deal with mixtures of gases, for instance air consists of mainly nitrogen and oxygen. Later we will also discuss mixtures of liquids and everyone knows that in a mixture of oil and water, the oil floats on the water. Oil and water separate themselves, they demix. This apparently does not happen for a mixture of nitrogen and oxygen, otherwise we would have a problem. We will later show that as a general rule two gases always mix.

For a mixture of two perfect gases in a volume V there is a very useful relation. When one realises that in a perfect gas the particles do not collide nor interact, the total pressure p of a mixture of two perfect gases results from the independent collisions of the two types of particles with the wall. The pressures from the individual gases are called *partial pressure* p_A and p_B and Dalton's law states for the total pressure p :

$$p = p_A + p_B \quad (2)$$

Therefore, for each component in the mixture we must have the relation:

$$p_A V = n_A RT \quad \text{and} \quad p_B V = n_B RT \quad (3)$$

A mixture of A and B with amounts n_A and n_B is a binary mixture, three components lead to a ternary mixture.

III. b. Motion of gas molecules

As mentioned already in a gas the particles (atoms or molecules) are very free to move and they will do so because one can prove (statistical thermodynamics) that the average energy per particle available for translational motions (kinetic energy = $\frac{1}{2}mv^2$) is $(3/2) kT$, where k is the Boltzmann constant ($k = 1.38066 \times 10^{-23} \text{ JK}^{-1}$). This shows that one can expect that the average speed of the particles in a gas increases with temperature.

The average kinetic energy of the particles can be expressed as:

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}kT$$

or:

$$\frac{1}{2}mN_A\langle v^2 \rangle = \frac{3}{2}kN_A T$$

or:

$$\frac{1}{2}M\langle v^2 \rangle = \frac{3}{2}RT$$

or:

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3RT}{M}} \quad (4)$$

Here the left hand side of the equation is the root mean square velocity ($\langle v^2 \rangle$ means the (velocity)², averaged over all particles). M in eq. (4) is the molar mass, the mass of one mole of the gas particles. For CO_2 ($M=44 \times 10^{-3} \text{ kg/mol}$) at 298 K the average speed according to eq. (4) is 411 ms^{-1} .

Eq. (4) is an expression for the average speed of the particles, some are faster, others are slower. The division between slow and fast is temporary, a fast particle may slow down because of collisions with other particles. There really is a distribution of speeds.

The *distribution function* can be calculated (Maxwell distribution):

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 \exp \left[-\frac{Mv^2}{2RT} \right] \quad (5)$$

The function is plotted in fig. 3 for different temperatures, the higher the temperature the higher the average speed and the broader the distribution. The area under the curves must remain constant.

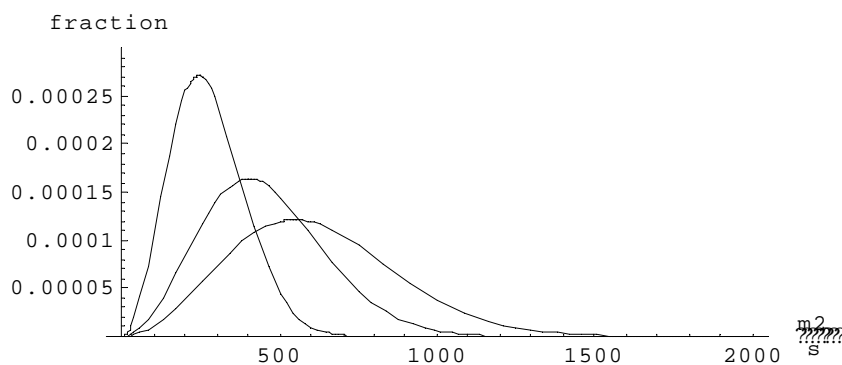


Fig. 3. The distribution of molecular speeds for N_2 (molar mass $28.02 \times 10^{-3} \text{ kg/mol}$) at 100, 273 and 500 K.

III. c. Real Gases

The difference between perfect gases and real gases is that for real gases the particles can interact with each other when their interparticle distance becomes of the order of magnitude of their radii. Depending on their distance they attract or repulse each other. Attractive forces work at relatively large distance, repulsive forces act only when the particles come so close that their electron clouds interpenetrate. These interactions are particularly important for high pressures. A complete understanding of the forces between molecules (or atoms) is part of the quantummechanical description of matter. In this thermodynamic picture it suffices to know that atomic particles are composed of electrically charged particles (negatively charged electrons and positively charged atomic nuclei). When two atomic particles approach each other, these charges interact with each other. At first they usually attract but when they come very close, so that the electron clouds of different atoms almost penetrate, the repulsive force becomes very strong, much stronger than the attractive forces. An approximate equation which describes the potential energy for the attraction and repulsion is the Lennard-Jones equation:

$$V = 4\alpha \left\{ \left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right\} \quad (6)$$

The distance dependence of this energy is shown in fig. 4. The parameters α and r_0 represent the depth of the energy well (where V has a minimum) and the distance where $V=0$, respectively.

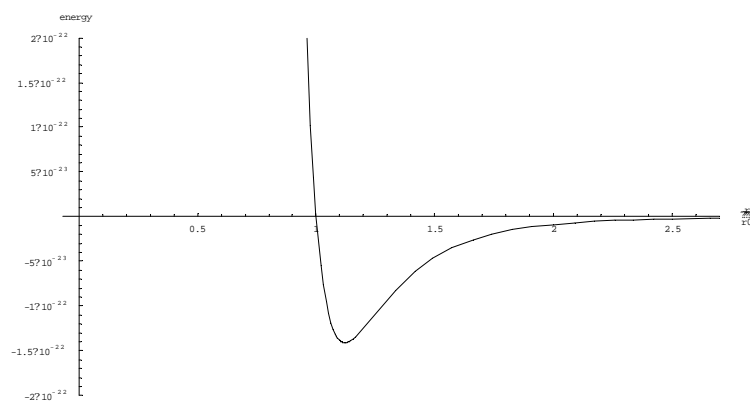


Fig. 4. The potential energy of two atoms as a function of their distance, according to eq. (6)

At this point it is good to look at the behaviour of a real gas when we increase the pressure on the piston of our gas cylinder. In fig. 5 the pV -diagram (isotherms) of a certain gas is shown. At relatively low temperatures at a certain volume of the gas the pressure does not raise upon further compression. This is represented in fig. 5 by a horizontal line. What happens is that the gas liquefies, liquid and gas coexist in the cylinder in equilibrium and are separated by a clear surface. By lowering the volume more and more liquid is produced until at the end of

the horizontal line all gas is transformed into liquid. Since the compressibility of a liquid is very low, the pressure raises fast when the volume is further reduced.

At the critical temperature T_c or above the visible separation into gas and liquid does not appear, above the critical temperature liquid does not form. Nevertheless the density of the gas above the critical temperature can be higher than that of the liquid.

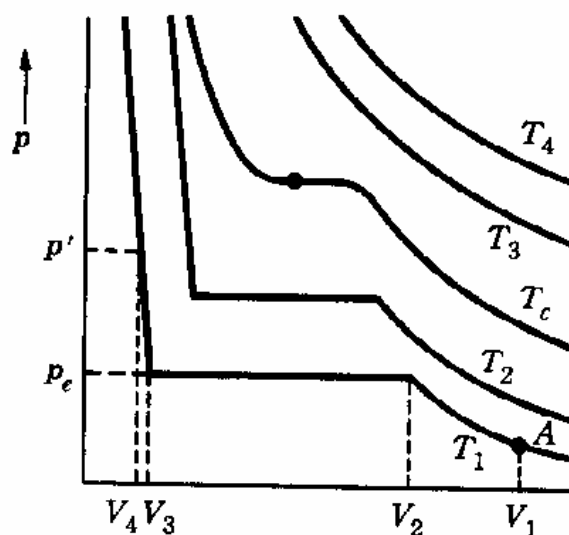


Fig. 5. The pV-diagram of real gases

Due to the interactions between the particles the equation of state for perfect gases (eq. 1) is no longer correct for real gases. But, as we mentioned already, the lower the pressure the more a real gas resembles an ideal gas, this suggests that we can construct an equation of state as follows:

$$p \frac{V}{n} = pV_m = RT(1 + B'p + C'p^2 + \dots) \quad (7)$$

or alternatively:

$$p \frac{V}{n} = pV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right) \quad (8)$$

These equations are two versions of the virial equation of state, the coefficients B' , C' , B and C are *virial coefficients*, which may be temperature dependent. Once they are determined for a certain gas, eq. (7) or (8) can be applied for every combination of pressure, volume and temperature. The second, third,.... terms in the parentheses of eq. (7) or (8) are correction terms to the ideal gas equation and become important for high pressures.

The disadvantage of using eq. (7) or (8) for the description of real gases is of course that the virial coefficients have to be known. There exists another equation, which is less accurate but contains less parameters, the *van der Waals equation*:

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \quad (9)$$

A comparison of this equation and the ideal gas equation (1) shows that (i) the volume available to the molecules in (9) is smaller than V by the volume of the molecules themselves (nb) and (ii) due to the attracting forces between the molecules the pressure is lowered by an amount proportional to a .

IV. The first Law of Thermodynamics

IV. a. The first Law

As defined above we separate the universe into a system and its surroundings. The system has properties which are described by the state variables. A very important property of the system is its total energy (expressed for instance in Joule/mol), which we call U . This internal energy of the system can be changed by the transfer of energy between system and surroundings, for instance because of the transfer of energy in the form of heat q or by applying work to the system: to compress the gas in a cylinder we (the surrounding) have to perform work on the system. Due to this work w the internal energy of the system is increased. Experience from many experiments during many centuries has shown that energy does not disappear. Therefore the exact amount of energy that is transferred from the surrounding into the system, must exactly equal to the change ΔU of the internal energy of the system:

$$\Delta U = q + w \quad (10)$$

This is the first law of thermodynamics and it is important to realise that this law is based on experience, it is an axiom. We assume that this law is always true and that means that eq. (10) is also true when the amount of exchanged energy is very small, infinitely small. Such infinitely small amounts in mathematics are denoted by the differential sign d , therefore eq. (10) can also be written in a differential form as:

$$dU = dq + dw \quad (11)$$

Eq. (10) and (11) also express that heat and work are equivalent forms of energy. When an engine does work w , the system = engine must receive energy from the outside (q) and/or its internal energy decreases by ΔU . No engine can do work without consuming some form of energy (no perpetuum mobile of the first kind).

Equations (10) and (11) allow the following conclusions:

- (i) The internal energy of a closed system remains constant
- (ii) When the system is thermally isolated (q or $dq=0$), the internal energy can only change by work ($dU = dw$).

By the first law three important state variables have been introduced, U , q and w .

IV. b. The internal energy U

When we assume that we mainly consider systems composed of molecules the internal energy represent the energy of all these molecules. Molecules can store energy as they have different degrees of freedom: they can translate in space (*translational energy*), the molecule as a whole or some part of the molecules (e.g. a methyl group) can rotate (*rotational energy*), the electrons in the molecule can be excited into higher orbitals (*electron energy*), the nuclei in a molecule can execute vibrations (*vibrational energy*) and the interaction energy between molecules can be changed. All these energies together form the internal energy U .

IV. c. Work w

Work can be applied to a system in various ways. For our discussion the work done to compress or expand a gas (“volume” work) is important, this is the work that has to be done on a system when we change the volume of the system. Again our cylinder with piston is a nice example, for the compression of the gas in the cylinder we have to apply work. The amount of work certainly depends on the pressure p we have to exert on the piston and on the change of the volume ΔV (or in differential form dV) we accomplish:

$$w = -p\Delta V \quad \text{or} \quad dw = -pdV \quad (12)$$

The minus sign expresses that for a decrease of the volume (ΔV and dV negative, compression) we have to do positive work.

The two expressions (12) are related, while:

$$w = \int_I^{II} dw = -\int_I^{II} pdV \quad (13)$$

Volume work is certainly not the only form of work, one can distinguish mechanical and electric work. To change the surface of a droplet or of a film from area A to $A + dA$ work has to be done against the surface tension γ :

$$dw = \gamma dA \quad (14)$$

Mechanical work is always the product of a force K and a displacement ds :

To displace a mass over a distance ds : $dw = Kds$

To raise a mass over a height dh : $dw = Kdh$

Electrical work is done when electrical charges are moved or changed in an electric potential field:

To change the charge of a particle in a potential field ϕ from Q to $Q + dQ$: $dw = \phi dQ$ (15)

To move an electrical charge Q from a potential ϕ to $\phi + d\phi$: $dw = Qd\phi$ (16)

IV. d. Heat q

Heat is one of the forms of energy and it can flow into or out of a system. A copper rod, for instance, can be heated on one side by a flame. This input of heat raises the temperature of the system. The temperature raise dT for a given amount of heat dq depends on the *heat capacity* C of the system:

$$dq = CdT$$

The heat dq in general is also used to make the system expand (the copper rod becomes longer, actually the volume increases). So heat can be used to raise the temperature (increase of the internal energy U) and/or increase the volume (expansion work).

Two special situations can occur:

- All of the heat is used to raise the temperature by keeping the volume constant:
 $dq = C_v dT$
- When the pressure of the system is kept constant, the applied heat is used for expansion and temperature raise: $dq = C_p dT$

When the same system is heated with the same amount dq , once at constant volume and once at constant pressure, the resulting temperature raises $(dT)_V$ and $(dT)_p$, respectively, are not equal:

$$(dT)_V > (dT)_p$$

while at constant volume all energy is used to raise the temperature and at constant pressure only part of the energy is used for expansion. With:

$$C_v (dT)_V = C_p (dT)_p$$

$$C_v < C_p \tag{17}$$

We can now derive a useful relation between C_v and the internal energy U :

$$dU = dq + dw = dq - pdV \quad \text{when only volume work is considered}$$

$$dU = dq = C_v dT \quad \text{if we assume } dV = 0 \text{ (constant volume)}$$

and then:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V \tag{18}$$

Equation (18) can be considered as the *definition* of the heat capacity C_v .

IV. e. State functions

So far we have seen many state variables, p , V , T , U which describe the state of the system. An important general distinction between state variables can be made: the value of some variables depend only on the *present* state of the system and of others on the *path* the system has reached the present state. The temperature of a system, for instance, describes the state of the system and is independent of the path over which the system has reached this state. From one temperature measurement of a system it can not be determined if the system was before at a lower, the same or a higher temperature. The energy therefore is a *state function*. When we look, however, at our definition of volume work, eq. (13):

$$w = \int_I^{II} dw = -\int_I^{II} p dV \tag{13}$$

it is immediately clear from fig. 6 that the work w depends on the path the system has gone between state I and state II, while the integral is equal to the area beneath the curve in the p - V diagram.

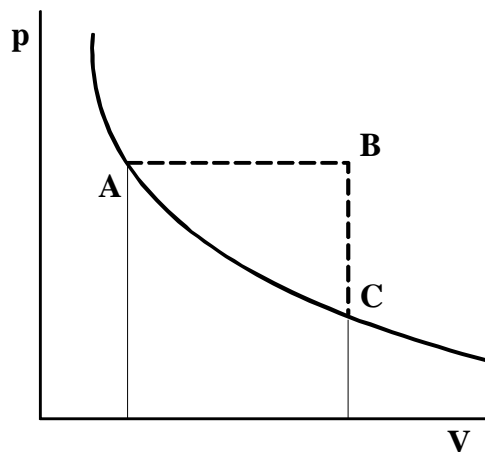


Fig. 6 The (negative) work w that has to be done to change the state of a system from A to C, according to eq. 13 equals the area beneath the curve of the pathway and is therefore different when the path is via an isotherm A-C or via the path A-B-C

As a consequence state variables can be distinguished in *state functions* (e.g. T, U,.....) and *path functions* like work or heat. There is a mathematical way to decide whether a state variable is a state function or a path function, see intermezzo I.

Intermezzo I: Exact and inexact differentials.

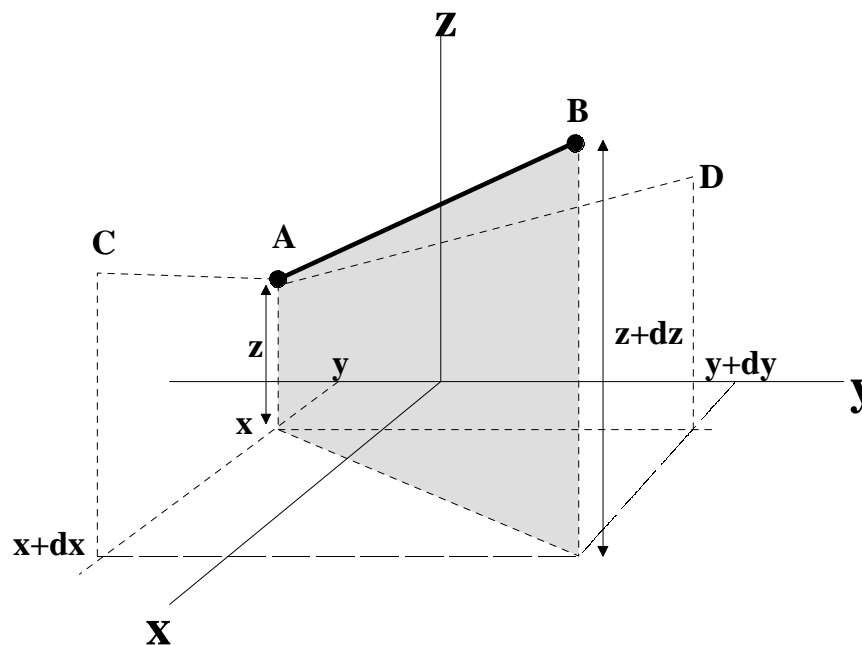


Fig. I.1 A geometrical representation of a function $F(x,y)$ in two points: A with coordinates x and y , and B with coordinates $x+dx$ and $y+dy$

Let us consider a function of two variables: $z=F(x,y)$, this function represent a surface in the (x,y,z) -coordinate system (fig. 7). In point A with coordinates x,y,z the value of the function is z ; in point B with coordinates $x+dx,y+dy,z+dz$ the function has the value $z+dz$. When dx and dy are both infinitesimally small, then also dz is infinitesimally small. In that case the surface between A and B can be considered to be a straight plane and the increase in height, when going from A to B, is the sum of the increase in height $(dz)_y$ when going from A to C, parallel to the x -axis, and the increase of z going from A to D, $(dz)_x$:

$$dz = (dz)_y + (dz)_x$$

The increases in z along the x and y axes are: $(dz)_y = \left(\frac{\partial z}{\partial x}\right)_y dx$ and $(dz)_x = \left(\frac{\partial z}{\partial y}\right)_x dy$,

and therefore:
$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad (I.1)$$

We now investigate the integral $\int_A^D dz$ for two different path ways in the x,y -plane (fig. 8):

A-B-D and A-C-D.

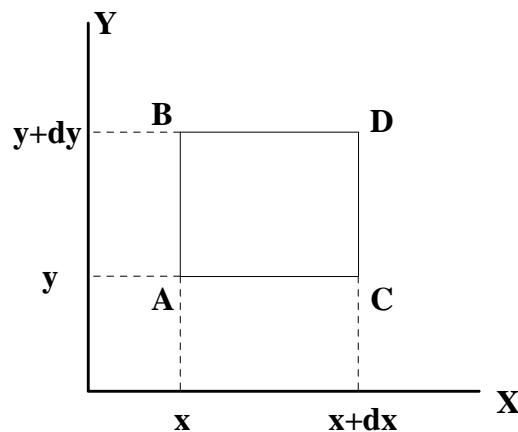


Fig. I.2

Path 1:

$$\int_A^D dz = \int_A^D \left\{ \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \right\} = \int_A^B \left(\frac{\partial z}{\partial y}\right)_x dy + \int_B^D \left(\frac{\partial z}{\partial x}\right)_{y+dy} dx = \int_A^D \left\{ \left(\frac{\partial z}{\partial y}\right)_x dy + \left(\frac{\partial z}{\partial x}\right)_{y+dy} dx \right\}$$

Path 2:

$$\int_A^D dz = \int_A^D \left\{ \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \right\} = \int_A^C \left(\frac{\partial z}{\partial x}\right)_y dx + \int_C^D \left(\frac{\partial z}{\partial y}\right)_{x+dx} dy = \int_A^D \left\{ \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_{x+dx} dy \right\}$$

The two integrals are identical when: $\left(\frac{\partial z}{\partial y}\right)_x dy + \left(\frac{\partial z}{\partial x}\right)_{y+dy} dx = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_{x+dx} dy$,

or when:
$$\left\{ \left(\frac{\partial z}{\partial y} \right)_{x+dx} - \left(\frac{\partial z}{\partial y} \right)_x \right\} dy = \left\{ \left(\frac{\partial z}{\partial x} \right)_{y+dy} - \left(\frac{\partial z}{\partial x} \right)_y \right\} dx. \quad (\text{I.2})$$

With the definitions for differentiation:

$$\frac{\left(\frac{\partial z}{\partial y} \right)_{x+dx} - \left(\frac{\partial z}{\partial y} \right)_x}{dx} = \frac{\partial}{\partial x} \frac{\partial z}{\partial y} = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and} \quad \frac{\left(\frac{\partial z}{\partial x} \right)_{y+dy} - \left(\frac{\partial z}{\partial x} \right)_y}{dy} = \frac{\partial}{\partial y} \frac{\partial z}{\partial x} = \frac{\partial^2 z}{\partial y \partial x},$$

eq. (I.2) changes into:
$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x} \quad (\text{I.3})$$

In general one can prove, that the integral $\int_A^D dz$ is independent of the path A – D when dz can be written as:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad (\text{I.1})$$

and the condition (I.3) is fulfilled.

In that case dz in expression (I.1) is called the exact or complete differential and in thermodynamics **z is a state function.**

When condition (I.3) is not fulfilled, dz in (I.1) is the inexact or incomplete integral and **z will be a path function.**

For an exact differential the cyclic integral: $\oint dz$ must be zero!

IV. f. Enthalpy

In IV. d. we found that $C_v = \left(\frac{\partial U}{\partial T} \right)_v$ and we also saw that there is a heat capacity C_p . We can ask ourselves would there be a variable H with which we can make a definition for C_p as:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (\text{19})$$

When we define $H = U + pV$,

we find by differentiation

$$\begin{aligned} dH &= dU + pdV + Vdp = (\text{if we consider only volume work}) \\ &= dq - pdV + pdV + Vdp = dq + Vdp \end{aligned}$$

with $(dq)_p = C_p dT$

$$dH = dq, \quad \text{when } dp = 0$$

$$dH = C_p dT \tag{20}$$

or $C_p = \left(\frac{\partial H}{\partial T} \right)_p$

$$H = U + pV \equiv \textit{Enthalpy}$$

The enthalpy is a form of energy and therefore an extensive variable. Is H also a state function? Using the recipe of Intermezzo I we find that the product pV is a state function and while U also is a state function, H is a state function.

$$\begin{aligned} d(pV) &= pdV + Vdp \\ &\quad \downarrow \quad \quad \downarrow \\ \frac{\partial p}{\partial p} &= 1 \quad \frac{\partial V}{\partial V} = 1 \end{aligned}$$

The enthalpy plays an important role in chemistry while many chemical processes run at a constant pressure. We now have two equivalent expressions for the first law:

$$dU = dq - pdV \qquad dH = dq + Vdp$$

The usefulness of the second expression becomes clear when we look at how the expressions change at constant pressure :

$$dU \neq dq \quad \text{for } p = \text{constant} \qquad dH = dq \quad \text{for } dp = 0$$

IV. g. Thermochemistry

At constant pressure the heat input into the system equals the change in enthalpy ΔH of the system and not the change of the internal energy ΔU . Therefore, for every process at constant pressure where heat is supplied to the system or furnished by the system the amount of this energy can be expressed as an enthalpy change. There are many physical or chemical changes of a system which can be described by an enthalpy change. To mention a few:

Melting	melt enthalpy $\Delta_m H$
Sublimation:.	sublimation enthalpy $\Delta_s H$
Chemical reaction:	reaction enthalpy $\Delta_r H$
Adsorption:	adsorption enthalpy $\Delta_a H$

Combustion: combustion enthalpy $\Delta_c H$

Usually enthalpy changes are reported for processes under a set of standard conditions. The standard enthalpy change $\Delta H^\ominus(T)$ is defined for a process where all species are in their standard state:

The standard state of a substance is the thermodynamically most stable state at the specified temperature T and at a pressure of 1 bar = 10^5 Pascal.

Example: $\text{C}(\text{solid, graphite}) + \text{O}_2(\text{gas}) \rightarrow \text{CO}_2(\text{gas}) \quad \Delta_r H^\ominus(298 \text{ K}) = -393.5 \text{ kJ/mol}$

At 298 K the stable form of carbon is graphite and for O_2 and CO_2 the gas state.

For a chemical reaction the standard reaction enthalpy can be positive or negative:

Endothermic reaction : $\Delta_r H > 0$ The reaction needs energy:
 If isothermal process \rightarrow Heat flows into the system
 If adiabatic process \rightarrow The temperature decreases

Exothermic reaction : $\Delta_r H < 0$ The reaction produces energy:
 Isothermal process \rightarrow The reaction produces heat
 Adiabatic process \rightarrow The temperature increases

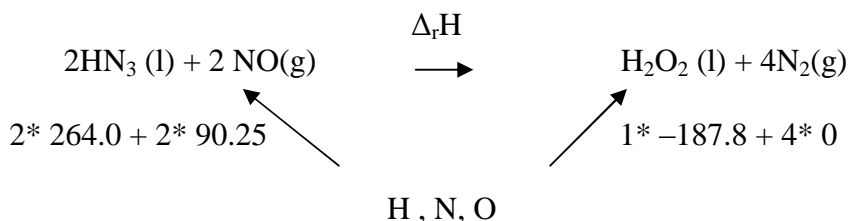
A reaction enthalpy can be calculated from the formation enthalpies of the compounds involved. The formation enthalpy is the enthalpy needed to build a compound from its elements:

Example: $2\text{HN}_3(\text{l}) + 2\text{NO}(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) + 4\text{N}_2(\text{g})$

The compounds consist of the following elements: H, N, O. The standard formation enthalpies at $T=298 \text{ K}$ to build these compounds from the elements are:

$\text{HN}_3(\text{l})$	264.0 kJ/mol
$\text{NO}(\text{g})$	90.25
$\text{H}_2\text{O}_2(\text{l})$	-187.8
$4\text{N}_2(\text{g})$	0

We can construct the following triangle:



Since energy is a state function, independent of the path, we have the following equality:
 $2 \cdot 264.0 + 2 \cdot 90.25 + \Delta_r H^\ominus(298 \text{ K}) = -187.8 + 4 \cdot 0$ or $\Delta_r H^\ominus(298 \text{ K}) = -896.3 \text{ kJ/mol}$.

A comparable situation is found when an overall reaction can be written as a series of reactions. Hess' law states that the overall reaction enthalpy is the sum of the reaction enthalpies of the individual reactions. This is also a consequence of the first law of thermodynamics.

	Δ _r H in kJ/mol
Na (s) + H ₂ O (l) → NaOH (s) + ½H ₂ (g)	-139,78
½H ₂ (g) + ½Cl ₂ (g) → HCl(g)	-92,31
HCl(g) + NaOH(s) → NaCl(s) + H ₂ O(l)	-179,06
<div style="display: flex; justify-content: space-between;"> Na(s) + ½Cl₂(g) → NaCl(s) Δ_rH = -411,15 kJ/mol </div>	

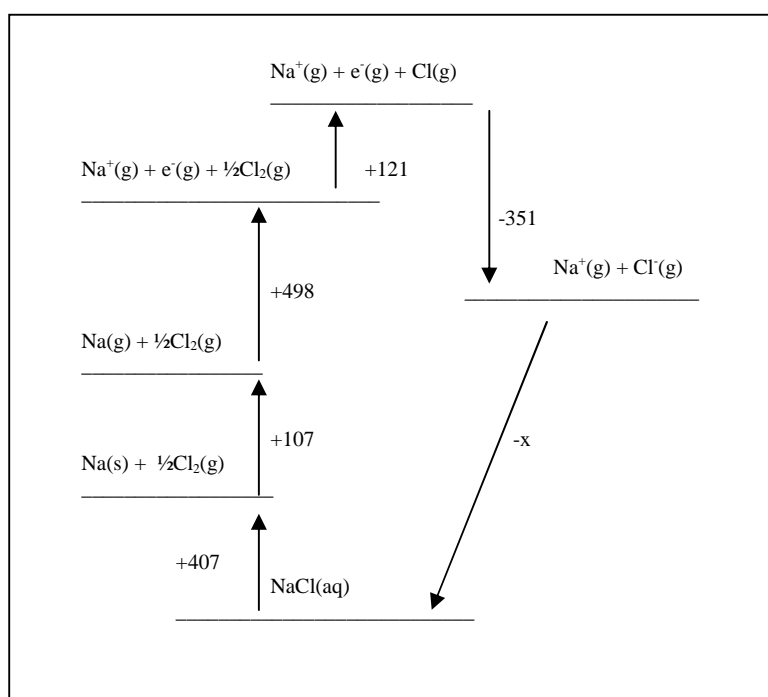


Fig. 7 A thermochemical cycle to determine the standard hydration enthalpy of Na⁺(g) and Cl⁻(g) in water.

Related to this law are the so called *thermochemical cycles*.

Let us suppose we want to know the standard enthalpy of hydration Δ_{hydr}H⁰(298 K) of Na⁺ and Cl⁻ ions in water. The cycle can be built from individual steps, as shown in fig. 7:

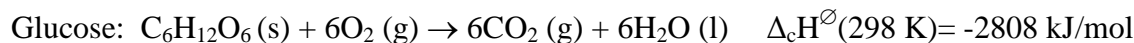
The cycle is built from the following individual reactions:

- | | | |
|--|---|--------|
| (1) Na(s) + ½ Cl ₂ (g) → NaCl(aq) | Δ _r H ⁰ (298 K) = - 407 | kJ/mol |
| (2) Na(s) → Na(g) | Δ _s H ⁰ (298 K) = 107 | kJ/mol |
| (3) Na(g) → Na ⁺ (g) + e ⁻ (g) | Δ _i H ⁰ (298 K) = 498 | kJ/mol |
| (4) ½ Cl ₂ (g) → Cl(g) | Δ _{dis} H ⁰ (298 K) = 121 | kJ/mol |
| (5) Cl(g) + e ⁻ (g) → Cl ⁻ (g) | Δ _{eg} H ⁰ (298 K) = -351 | kJ/mol |

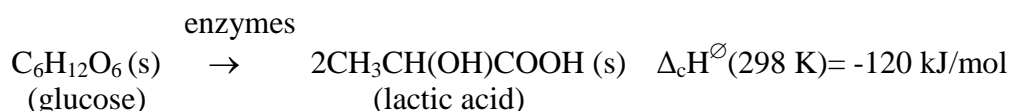
The hydration enthalpy can then be calculated since energy is conserved:

$$\Delta_{\text{hydr}}H^\ominus(298\text{ K}) = -407 - 107 - 498 - 121 + 351 = -782\text{ kJ/mol}$$

The combustion enthalpy $\Delta_c H$ is the enthalpy for the oxidation of a substance to CO_2 and H_2O . For instance:



The anaerobic fermentation of glucose brings much less energy:



In general reaction enthalpies are temperature dependent. Therefore if we find values for enthalpy changes in a handbook at a given temperature T_1 , we must be able to calculate these values for the wanted temperature T_2 .

Since reaction enthalpies usually are reported for a single temperature, we must be able to calculate the reaction enthalpies at an other temperature.

To find the temperature dependence of the enthalpy integrate eq. (20):

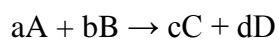
$$dH = C_p dT \quad (20)$$

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT$$

When the temperature change $T_2 - T_1$ is not large, we often can make the approximation that the C_p 's are independent of the temperature. Then the integral can be easily solved and we find:

$$H(T_2) - H(T_1) = C_p (T_2 - T_1) \quad (21)$$

When eq. (21) is correct, it is correct for the formation enthalpy of each component involved in a reaction:



$$\Delta_r H(T_1) = -a\Delta_{fA} H(T_1) - b\Delta_{fB} H(T_1) + c\Delta_{fC} H(T_1) + d\Delta_{fD} H(T_1)$$

$$\Delta_r H(T_2) = -a\Delta_{fA} H(T_2) - b\Delta_{fB} H(T_2) + c\Delta_{fC} H(T_2) + d\Delta_{fD} H(T_2)$$

$$\begin{aligned} \Delta_r H(T_2) - \Delta_r H(T_1) = & -a\{\Delta_{fA} H(T_2) - \Delta_{fA} H(T_1)\} - b\{\Delta_{fB} H(T_2) - \Delta_{fB} H(T_1)\} \\ & + c\{\Delta_{fC} H(T_2) - \Delta_{fC} H(T_1)\} + d\{\Delta_{fD} H(T_2) - \Delta_{fD} H(T_1)\} \end{aligned}$$

Using eq. (21):

$$\Delta_r H(T_2) - \Delta_r H(T_1) = -a\{C_{pA}(T_2 - T_1)\} - b\{C_{pB}(T_2 - T_1)\} + c\{C_{pC}(T_2 - T_1)\} + d\{C_{pD}(T_2 - T_1)\} = \Delta_r C_p(T_2 - T_1)$$

where $\Delta_r C_p = -aC_{pA} - bC_{pB} + cC_{pC} + dC_{pD}$

For a general reaction, written as:

$$0 = \sum_J \nu_J J \quad (\text{the stoichiometric coefficients } \nu_J \text{ are negative for educts and positive for products})$$

$$\Delta_r C_p = \sum_J \nu_J C_{pJ} \quad (22)$$

Also the energy involved at phase transitions at constant pressure (melting, vaporization, sublimation) can be expressed in enthalpy:



Above we calculated the change in enthalpy, what would be the change of the internal energy? At 100°C and 1 bar the volume of 1 mol H₂O(l) is 18 cm³, of the gas it is 30.000 cm³. Then:

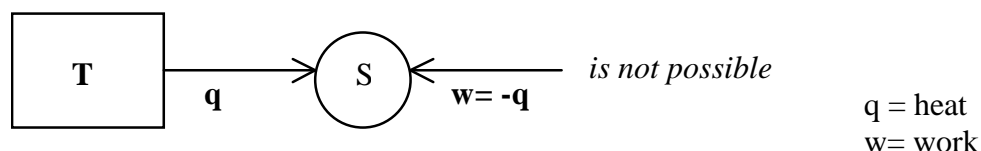
$$\begin{aligned} \Delta U_{\text{vap}}^\ominus(373 \text{ K}) &= \Delta H_{\text{vap}}^\ominus(373 \text{ K}) - \Delta(pV) = \Delta H_{\text{vap}}^\ominus(373 \text{ K}) - \Delta(nRT) = \\ &= \Delta H_{\text{vap}}^\ominus(373 \text{ K}) - RT\Delta(n) = 40.7 - 3.1 = 37.6 \text{ kJ/mol} \end{aligned}$$

Here we neglected the molar volume of the liquid and assumed that the vapour is an ideal gas.

V. The Second Law of Thermodynamics

The second law, which, just as the First Law, is based on many experiments in the past and must be considered as an axiom, can be formulated in several ways. Traditionally the following two formulations are used.

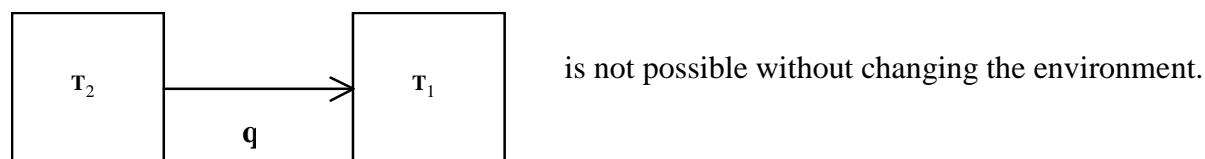
1. (After Kelvin) : It is impossible to *completely* transform heat from a reservoir into mechanical work. Schematically:



(As before, we use the sign convention, that when the internal energy of a system increases by heat input q or work w done on the system, this heat or work is taken positive. If the internal energy decreases, the energy input is negative).

2. (After Clausius): Without changing the surrounding it is impossible to transfer heat (energy) from a reservoir with temperature T_2 to a reservoir with temperature T_1 if $T_2 < T_1$.

Schematically:



These two formulations lead to a formulation, which is most important for chemical thermodynamics:

3. a. There exists a state function S , called the entropy.
- b. When a system changes through a process from state I to II, the relation between the change of the entropy, ΔS or dS , of this system and the heat exchanged between the system and its environment depends on the type of process:

$$I \rightarrow II \text{ reversibel: } \Delta S_{\text{System}}^{\text{reversibel}} = \int_I^{II} dS = \int_I^{II} \frac{dq}{T}, \quad (23)$$

$$I \rightarrow II \text{ irreversibel: } \Delta S_{\text{System}}^{\text{irreversibel}} = \int_I^{II} dS > \int_I^{II} \frac{dq}{T}, \quad (24)$$

$$\text{or combined: } \Delta S_{\text{System}} \geq \int_I^{II} \frac{dq}{T} \text{ or in differential form } dS \geq \frac{dq}{T} \quad (25)$$

$$\Delta S \geq \int_I^{II} \frac{dq}{T}; \quad \text{when } T = \text{constant: } \Delta S \geq \frac{1}{T} \int_I^{II} dq = \frac{q}{T} \quad (26)$$

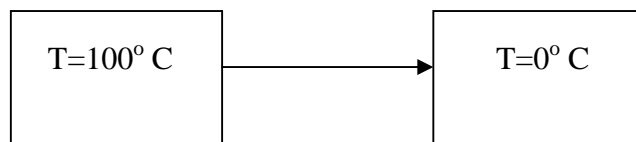
At first sight, this inequality (26), called after Clausius, seems to be in contradiction with the formulation 3. a, which implies that the entropy, being a state function, should be independent of the path or type of process (reversible or irreversible):

$$\Delta S_{\text{System}}^{\text{reversible}} = \Delta S_{\text{System}}^{\text{irreversible}} \quad (27)$$

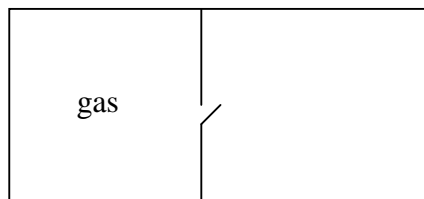
It is important to realize, however, that the amount of involved heat dq in eqs. (23) and (24) is not the same for reversible and irreversible processes.

To get a better understanding what entropy really is, let us look at the following two processes:

Process 1.



Process 2.



In the first example two heat reservoirs, at different temperatures, are brought into thermal contact. Everyone knows that after a while the two reservoirs reach an equilibrium at the same temperature, depending on the heat capacities, somewhere between 0° and 100° C.

In the second example at first a gas fills the left half of a volume and the right half is empty (vacuum). After opening a valve between the two halves the gas fills both halves at the same pressure. Both processes have in common that:

- the process is spontaneous in one direction; the opposite process will never be observed,
- the total energy change is zero (the same processes will take place, when the two heat reservoirs or the total volume would be a closed system, for which the first law tells that the energy must be conserved).

The question is, what force drives these spontaneous processes? Clearly, it is not the energy, there must be another variable: *the entropy*. By looking at the two processes discussed above, we see that in the first example energy that at first was concentrated in the high temperature reservoir, spontaneously distributes itself over both reservoirs. The second process shows that matter concentrated in a relative small volume has the tendency to distribute itself over a larger volume (when it can!). Entropy describes that energy and matter tend to distribute over as many degrees of freedom as is possible. Entropy is often said to be a measure of disorder, the higher the disorder, the higher the entropy. Order and disorder do not have a meaning in

thermodynamics. In statistical thermodynamics it can be shown that the entropy is related to the number of states accessible to the system. In our above example of the gas that distributes spontaneously over the total volume when a valve between the two halves is opened, the gas molecules get access to positions in the empty half volume.

Entropy is a measure of disorder when disorder is somehow defined as the number of states available to the system. This idea can be further clarified by the following often mentioned example. Let us suppose there are two professors A and B. In the office of professor A books and papers are lying in a seemingly random way all over the place. In professor B's office all books are in book shelves and papers are stored in an orderly way. At first sight you would say that the disorder in Prof. A's office is much higher than in the office of Prof. B. However, when you visit both offices regularly and find Prof. B rearranging his books and papers all the time, while the position of books and papers in the office of Prof. A do not change with time, the entropy of the office of Prof. B is higher than that of the office of Prof. A, while in Prof. B's office the books and papers sample more positions than in Prof. A's office. In the sense of entropy the disorder in Prof. B's office is higher than in Prof. A's office!

For some very simple systems and simple process we can calculate how much the entropy changes, but first we will discuss some consequences of eqs. (25) and (26):

$$\Delta S_{\text{System}} \geq \int_1^{\text{II}} \frac{dq}{T}$$

For a closed system $dq = 0$ and $\Delta S_{\text{System}} \geq 0$: the entropy of a closed system increases when in the system an irreversible process takes place. The entropy of a closed system can never decrease!

A system and its surroundings form together a closed system (according to the definition of surrounding, outside the surroundings there is nothing!). Consequently:

Reversible process in the system: $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$ or $\Delta S_{\text{surrounding}} = -\Delta S_{\text{system}}$

Irreversible process : $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ or $\Delta S_{\text{surrounding}} > -\Delta S_{\text{system}}$

The change of the entropy of the system is independent of the type of process (while S is a state function, see also eq. (27)), the change in entropy of the surroundings, however, depends on the process.

Entropy is the only variable that can be used to decide in what direction time changes. When we agree that the universe is a closed system, the entropy of the universe steadily increases. By measuring the entropy of the universe at two different times, we can in principle decide at which time the universe is older.

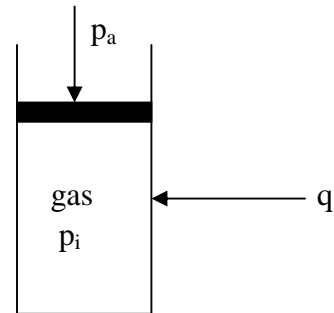
VI. Changes of the entropy

VI. 1. Isothermal expansion of an ideal gas

We consider a gas in a cylinder closed by a piston under pressure p . When we only consider volume work, the first law states:

$$dU = dq - p_a dV$$

When the gas is ideal, the atoms or molecules do not interact (Ch. III. a.) and the internal energy does not change when we compress or expand the gas: $dU=0$. Further we expand the gas under reversible conditions, i.e. in such a way that always $p_a = p_i$.



$$dq = p_a dV$$

$$q_{rev} = \int_{V_1}^{V_2} p_a dV = \int_{V_1}^{V_2} p_i dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln\left(\frac{V_2}{V_1}\right)$$

where we used the fact that the gas is ideal and the temperature is constant.

$$\Delta S_{gas} = \frac{q_{rev}}{T} = nR \ln\left(\frac{V_2}{V_1}\right) \quad (28)$$

Eq. (28) shows that the entropy of a gas increases when it is expanded.

Since S is a state function, the above equation is also correct when the expansion would be via an irreversible path. Conclusion:

Reversible expansion : $\Delta S_{gas} + \Delta S_{surrounding} = 0$; $\Delta S_{surrounding} = -nR \ln\left(\frac{V_2}{V_1}\right)$

Irreversible : $\Delta S_{gas} + \Delta S_{surrounding} > 0$; $\Delta S_{surrounding} > -nR \ln\left(\frac{V_2}{V_1}\right)$

As already discussed in the previous chapter, the entropy change of the system is independent of the path of the process, the entropy change of the surrounding depends on the path!

VI. 2. The entropy change when a substance is heated

When a substance with heat capacity C_p is heated at constant pressure, the change in temperature is proportional to the heat input (Chapter IV. d):

$$dq = C_p dT$$

The change of the entropy of the system does not depend on the reversibility or irreversibility

of the process, therefore we can assume that it is reversible. Then:

$$\Delta S = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_p dT}{T} \approx C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln\left(\frac{T_2}{T_1}\right) \quad (29)$$

where it has been assumed that over the temperature range $T_2 - T_1$ the heat capacity is independent of the temperature. We can change eq. (29) into:

$$S(T) - S(0) = \int_0^T \frac{C_p dT}{T} \quad (30)$$

where $S(0)$ is the entropy at the temperature 0 K. When $S(0)$ would be known, eq. (30) would allow the calculation of the entropy at a higher temperature T . The entropy at 0 K will be discussed in one of the following chapters. First we calculate what happens when between 0 K and temperature T a phase transition occurs.

VI. 2. The entropy change at a phase transition

A phase transition (melting, boiling) at the temperature T_m or T_b is accompanied by a transfer of heat between the substance (system) and the surrounding. At constant pressure this heat equals the transition enthalpy ($\Delta_m H$ or $\Delta_v H$). Therefore:

$$\Delta S = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = \frac{\Delta_m H}{T_m} \quad (31)$$

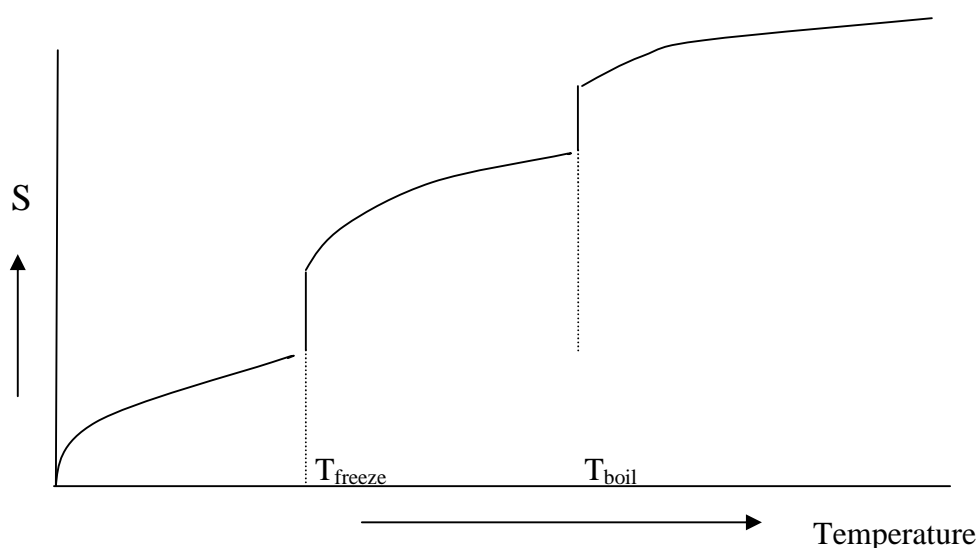


Fig. 8. The increase of the entropy as a function of temperature

By combining eqs. (30) and (31) we are able to calculate the entropy difference $S(T) - S(0)$ of a substance at an arbitrary temperature T , at least when the heat capacity at every temperature is known:

$$S(T) = S(0) + \int_0^{T_m} \frac{C_p dT}{T} + \frac{\Delta_m H}{T_m} + \int_{T_m}^{T_v} \frac{C_p dT}{T} + \frac{\Delta_v H}{T_m} + \int_{T_v}^T \frac{C_p dT}{T} \quad (32)$$

The change of the entropy with temperature is sketched in fig. 8.

VII. The third law

We saw that to calculate the entropy at an arbitrary temperature T (eq. 32) we need to know the entropy at 0 Kelvin. Without going into too much detail, we simply use the following interpretation of the third law:

The entropy of a perfect crystal at 0 Kelvin is zero.

Actually, the third law only claims that the entropies of all perfect crystals at $T=0$ are equal, but it is convenient to take the value $S(0)=0$. The difficult part of the above statement is the notion of a perfect crystal. When we would have a crystal with defects (a defect could be that at some lattice points an atom is missing). This “disorder” (see the discussion on entropy and disorder) raises the entropy and therefore the entropy of an imperfect crystal at 0 K can not be equal to 0. In this respect it is of interest to look at the crystal structure of ice: fig. 9.

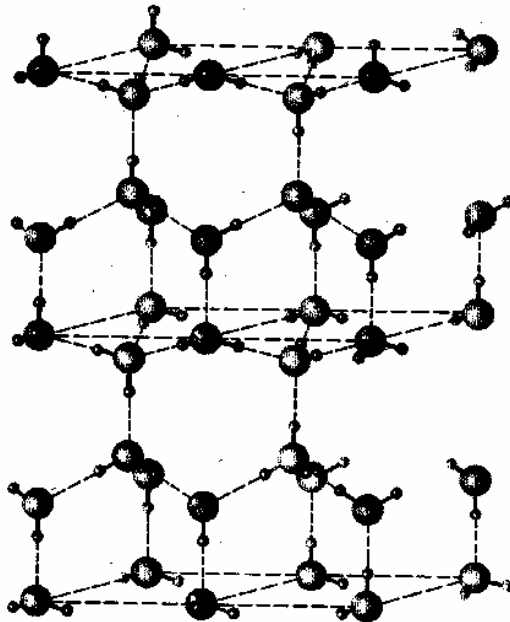


Fig. 9 The structure of ice. Each oxygen is surrounded by four other oxygens in a regular tetrahedron. Each oxygen bonds to two hydrogens by short hydrogen bonds and to two other hydrogens by long hydrogen bonds (from: L. Pauling, General Chemistry).

In the structure of ice (we will see later that at high pressures there are other ice structures, this structure is that of ice at normal pressure) each oxygen bonds to four other oxygens by four hydrogen bonds. Two of these hydrogen bonds are short, two are long. Even at 0 K it is not determined which hydrogen bonds are short and which are long. This „disorder“ contributes to a residual entropy $S(0)$ of 3.4 J/Kmol.

Just as for the other thermodynamic variables, one defines standard entropies:

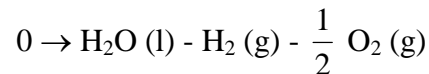
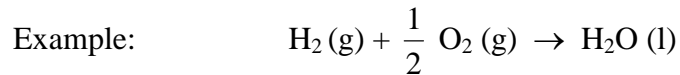
$$S^{\ominus}(T) = \text{standard entropy at standard conditions at temperature } T.$$

$$\Delta_r S^\ominus = \text{standard reaction entropy}$$

Chemical reaction : $0 = \sum_J \nu_J J$

J = educts and products, ν_J positive for products, negative für educts.

$$\Delta_r S^\ominus = \sum_J \nu_J S_J^\ominus$$



$$\Delta_r S^\ominus = 69,9 - 130,7 - \frac{1}{2} 205,1 = -163,4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Although $\Delta_r S^\ominus < 0$ the reaction is spontaneous because the entropy of the surrounding increases strongly due to the highly exothermal reaction:

:

$$\Delta S_{\text{surrounding}} = \Delta_r H^\ominus / T = 2220000 / 298 = 7449 \text{ J/mol.K}$$

and :

$$\Delta S_{\text{total}} = \Delta_r S^\ominus + \Delta S_{\text{surrounding}} = -163 + 7449 = 7286 \text{ J/mol.K} > 0$$

VIII. Free Energy and Free Enthalpy

VIII. 1 Introduction of F and G

In the previous chapters we have seen that we can predict whether a chemical reaction runs spontaneously or not. The recipe was to calculate the entropy change of the system and of the surrounding. When the total entropy change was positive the reaction would spontaneously go. In this chapter we introduce two new state functions with which it is somewhat easier to decide whether a reaction goes spontaneously or not. We do this in the following schematic way:

Assumption: only volume work

$dU = dq - p dV$ $\text{with } dV = 0$ $dU = dq$	\Leftarrow first law \Rightarrow	$dH = dq + V dp$ $\text{with } dp = 0$ $dH = dq$
Clausius' inequality $dS_{\text{System}} \geq \frac{dq}{T}$		
$dS \geq \frac{dU}{T}$ $T dS \geq dU$ $dU - T dS \leq 0$		$dS \geq \frac{dH}{T}$ $T dS \geq dH$ $dH - T dS \leq 0$
$d(U - T S) \leq 0$ $(dF)_{V,T} \leq 0$	\Leftarrow if T = constant \Rightarrow (33)	$d(H - T S) \leq 0$ $(dG)_{p,T} \leq 0$
$F = U - TS = \text{Free Energy}$ $(\text{IUPAC : A = Helmholtz Energy})$		$G = H - TS = \text{Free Enthalpy}$ $(\text{IUPAC: G = Gibbs-Energy})$

F and G are functions of state, because U, H and (TS) are functions of state.

Eq. (33) shows that at constant volume V and temperature T the change in free energy *of the system* is negative for irreversible (*spontaneous*) processes and = 0 for reversible processes. Eq. (34) shows that at constant pressure p and temperature T the change in free enthalpy *of the system* is negative for irreversible processes and = 0 for reversible processes.

Now we can use the free energy F and the free enthalpy G of the system to decide whether a process goes spontaneously or not and we do not have to consider the entropy change of the system + surrounding. However, it is important to realize that the eqs. (33) and (34) are only valid for V, T constant, respectively p, T constant. In case of the entropy we did not have such a limitation.

According to the definition of G we can write:

$$\begin{array}{ccc}
 \Delta G = \Delta H & - & T \Delta S \quad \text{if } T = \text{constant} \\
 \downarrow & & \downarrow \\
 \text{energy-} & & \text{entropy-} \\
 \text{contribution} & & \text{contribution}
 \end{array} \quad (35)$$

and this shows that a spontaneous process for which $\Delta G < 0$ not only can occur when $\Delta H < 0$ (exothermic) and $\Delta S > 0$, but also when:

$$\begin{array}{ll} \Delta S < 0 & \text{and } \Delta H < T \Delta S \quad (\text{highly exothermic process}) \\ \text{or } \Delta H > 0 & \text{and } T \Delta S > \Delta H \quad (\text{spontaneous endothermic reaction!}) \end{array}$$

VIII. 2 Free Energy, Free Enthalpy and work

In the same schematic way as before we can derive very useful relations between F and G and the maximum amount of work a system can deliver.

$$dU = dq + dw$$

$$dw = dU - dq$$

$$T dS \geq dq$$

$$dw \geq dU - T dS$$

$$-dw \leq T dS - dU$$

dw = work done on the system

$dw' = -dw$ = work done by the system

$$dw' \leq T dS - dU$$

$$dw' \leq -dF \quad (T = \text{constant})$$

The maximum amount of work a system can deliver, is obtained for a reversible process and is equal to $-dF$ ($T = \text{constant}$)

$$dw'_{\text{max}} = -dU + TdS$$

The internal energy U can not completely be used for work when dS is positive

dU → „ordered“ stored energy

TdS → „disordered“, non usable energy

$$dH = dU + p dV + V dp$$

$$dH = dq + dw + p dV + V dp$$

$$T dS \geq dq$$

$$dH \leq T dS + dw + p dV + V dp$$

$$dw = dw_a - p dV$$

dw_a = all work that is not volume work

$$dH \leq T dS + dw_a + V dp$$

$$dH - T dS \leq dw_a + V dp$$

$$\underline{p, T = \text{constant}}$$

$$dG \leq dw_a$$

$dw_a' = -dw_a$ = work done by the system

$$dw_a' \leq -dG$$

The maximum non-volume work that a system can deliver is obtained for a reversible process and is equal to $-dG$ ($p, T = \text{constant}$)

VIII. 3 Free Energy and rubber elasticity

Maybe entropy is still an abstract idea, therefore a little “experiment” to show that entropy is so real you can feel it! We first make a combination of the first and second law:

$$\begin{aligned} dU &= dq + dw = TdS + dw && \text{(is true if the process is reversible)} \\ dU &= TdS + dw && \text{(must be true also for irreversible processes while U is a} \\ &&& \text{function of state).} \end{aligned}$$

When we stretch a rubber band from length l to a length $l+dl$ by applying a force K we have to do stretching work Kdl and possibly volume work $-pdV$. The internal energy U changes:

$$dU = TdS + Kdl - pdV$$

In good approximation the volume of a rubber band does not change upon stretching, $dV=0$. With:

$$dF = dU - TdS \quad (\text{if } T = \text{constant})$$

one finds:

$$dF = Kdl,$$

$$\text{or: } \left(\frac{\partial F}{\partial l} \right)_{V,T} = K$$



polymer chain:

The above equation means that the force K we have to apply to stretch the rubber band at constant temperature and volume equals the derivative of the Free Energy with respect to the length of the band.

$$\left(\frac{\partial F}{\partial l} \right)_{V,T} = \left(\frac{\partial U}{\partial l} \right)_{V,T} - T \left(\frac{\partial S}{\partial l} \right)_{V,T} = K \quad (36)$$

Energy Entropy
elasticity elasticity

Eq. (36) shows that part of the force K we have to apply to stretch a rubber band is due to the change of the entropy with the length of the band (for most rubbery systems the entropy part is the main part, rubbers for which the energetic part is zero are called ideal rubbers). This change of the entropy comes about while upon stretching the polymer molecules are forced to change their form from a more chaotic (coiled form) to a more regular stretched form.

Let us consider the experiment when a weight hangs on a rubber band and the temperature of the rubber is increased. What will happen to the length of the rubber band?

The right side of eq. (36), the force K , does not change with temperature because it is equal to the mass of the weight multiplied with the gravity factor g . Where we are looking for is the partial derivative:

$$\left(\frac{\partial l}{\partial T}\right)_K$$

To derive the sign of this derivative we use two mathematical relations:

a. For a function z , which depends on two independent variables x and y , $z = z(x, y)$, one has the cyclic rule ("Kettenregel"):

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

For the function $l = l(K, T)$ this implies:

$$\left(\frac{\partial K}{\partial T}\right)_l \left(\frac{\partial T}{\partial l}\right)_K \left(\frac{\partial l}{\partial K}\right)_T = -1 \quad \text{or} \quad \left(\frac{\partial l}{\partial T}\right)_K = \frac{1}{\left(\frac{\partial T}{\partial l}\right)_K} = -\left(\frac{\partial K}{\partial T}\right)_l \left(\frac{\partial l}{\partial K}\right)_T \quad (37)$$

We immediately see that the second term on the right side $\left(\frac{\partial l}{\partial K}\right)_T > 0$, the length at constant temperature will increase with increasing force K .

b. The derivative $\left(\frac{\partial K}{\partial T}\right)_l$ in (37) can be rewritten using the fact that the free energy F is a state function:

$$dF = dU - TdS - SdT = TdS + Kdl - TdS - SdT = Kdl - SdT$$

and

$$\left(\frac{\partial K}{\partial T}\right)_l = -\left(\frac{\partial S}{\partial l}\right)_T \quad (\text{Schwarz equation}) \quad (38)$$

The entropy will decrease with increasing length l because the molecules become more ordered when the band is stretched, therefore $\left(\frac{\partial K}{\partial T}\right)_l$ in eq. (38) is positive, which means that

$\left(\frac{\partial l}{\partial T}\right)_K$ in eq. (37) must be negative, the length of the rubber band will decrease at increasing temperature.

I. IX. The fundamental equations and the chemical potential

IX.1 The fundamental equations

When the only work we consider is volume work, we can write the following equations, *the fundamental equations*, which combine the statements of the First and Second Law of Thermodynamics.

$$dU = dq - pdV \rightarrow dU = TdS - pdV \quad (38)$$

(the = sign instead of the ? sign can be used here because U is a state function, whose value should be independent of the path, reversible or irreversible).

Then:

$$dH = dU + pdV + Vdp \rightarrow dH = TdS + Vdp \quad (39)$$

$$dF = dU - TdS - SdT \rightarrow dF = -SdT - pdV \quad (40)$$

$$dG = dH - TdS = SdT \rightarrow dG = Vdp - SdT \quad (41)$$

IX.2 The chemical potential

U, H, F and G are extensive variables, this implies that their values should also depend on the amounts (mols) of the substances in the system:

$$G = G(p, T, n_A, n_B, \dots, n_N)$$

Or:

$$dG = \left(\frac{\partial G}{\partial p} \right)_{T, n_i} dp + \left(\frac{\partial G}{\partial T} \right)_{p, n_i} dT + \left(\frac{\partial G}{\partial n_A} \right)_{p, T, n_i} dn_A + \dots + \left(\frac{\partial G}{\partial n_N} \right)_{p, T, n_i} dn_N \quad (42)$$

(in the partial derivatives n_i means that all n are to be kept constant, except the n involved in the differentiation)

This can also be written as:

$$dG = \left(\frac{\partial G}{\partial p} \right)_{T, n_i} dp + \left(\frac{\partial G}{\partial T} \right)_{p, n_i} dT + \sum_j \left(\frac{\partial G}{\partial n_j} \right)_{p, T, n_i} dn_j \quad (43)$$

A comparison between eqs. (41) and (43) shows that the coefficients of dp and dT in eq. (43) must be:

$$\left(\frac{\partial G}{\partial p} \right)_{T, n_i} = V \quad \left(\frac{\partial G}{\partial T} \right)_{p, n_i} = -S$$

The coefficients of the differential dn_j in eq. (43) are defined as the chemical potential μ_j of the substance j:

$$\left(\frac{\partial G}{\partial n_j} \right)_{p,T,n_i} = \mu_j \quad (44)$$

Combining eqs. (43) and (44) we find an important equation, which is often called the

fundamental equation of chemical thermodynamics:

$$dG = Vdp - SdT + \sum_j \mu_j dn_j \quad (45)$$

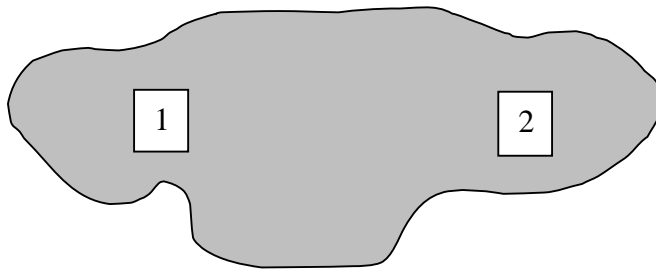
The fundamental equations (38) – (40) can also be written in the form of eq. (45), but we will not need them. The fundamental equations (38)-(41) are correct as long as the amounts of the substances are constant: $dn_j=0$.

The chemical potential μ for a single component system with n mol substance is very simple, while:

$$G = n\bar{G} \quad \text{and} \quad \mu = \left(\frac{\partial G}{\partial n} \right)_{p,T} = \bar{G}, \quad (46)$$

where \bar{G} is the Free Enthalpy of 1 mol of the substance, the molar Free Enthalpy.

To show why the chemical potential is so important, we consider a N-component system. We suppose that in this system the chemical potential of any component is the same everywhere in the system, except for component I, which differs at site 1 and 2: $\mu_i(1) > \mu_i(2)$



When we bring at constant p and T an amount dn_i of the substance i from site 1 to site 2 the resulting change of the free enthalpy is negative:

$$dG = -\mu_i(1)dn_i + \mu_i(2)dn_i = (\mu_i(2) - \mu_i(1))dn_i < 0$$

Therefore such a transport of substance i from a site with high chemical potential to a site with lower chemical potential is a spontaneous process! This process will continue until in equilibrium the chemical potential for each component of the system is the same everywhere in the system. Thermodynamics does not say, however, how fast this process goes. It could take an infinitely long time.

The conclusion is:

For a system in equilibrium the chemical potential for every substance is the same everywhere in the system, independent of the phase (the definition of phase comes later).

For instance when at ca. 273 K and 1 bar ice and water are in equilibrium, then the chemical potential of H₂O is the same in ice and water. At temperatures below 273K at 1 bar the chemical potential of ice is lower than that of water, therefore at this temperature water should freeze. At room temperature and 1 bar the chemical potential of graphite is lower than that of diamond. Graphite at these conditions is thermodynamically more stable than diamond. The transition from diamond to graphite, however, is infinitely slow and therefore will not be observable. So thermodynamics tells in what direction a process should go but not how fast!

IX. 3 The chemical potential of an ideal gas

By comparing eqs. (41) and (46) we find for a constant temperature:

$$d\mu = \bar{V}dp$$

By using the equation of state for an ideal gas $p\bar{V} = RT$ this can be rewritten as:

$$d\mu = \frac{RT}{p} dp$$

which after integration from pressure p_A to p_E gives:

$$\mu(p_E) - \mu(p_A) = RT \int_{p_A}^{p_E} \frac{dp}{p} = RT \ln\left(\frac{p_E}{p_A}\right)$$

By choosing a special starting pressure (standard pressure) $p_A = p^\ominus = 1 \text{ bar} = 10^5 \text{ Pa}$ (Pascal), the above expression becomes:

$$\mu(p, T) = \mu^\ominus(T) + RT \ln\left(\frac{p}{p^\ominus}\right) \quad (47)$$

II. X. Mixtures

X.1 General

In most real cases a system consists of many different substances and can be considered to be mixtures of many components. Mixtures can also consist of more than one phase, for instance the mixture in a bottle of beer consists of a liquid phase and a gas phase. The liquid phase contains at least two components, water and ethanol, the gas phase is also a mixture of water vapour and ethanol vapour. The thermodynamics of the previous chapter can be perfectly well applied to the description of mixtures. To keep things simple we discuss only mixtures of two components A and B, binary mixtures. The composition of a binary mixture is defined by the mole numbers n_A and n_B . We frequently will work with the mole fractions x_A and x_B :

$$x_A = \frac{n_A}{n_A + n_B} \quad x_B = \frac{n_B}{n_A + n_B} \quad n = n_A + n_B \quad x_A + x_B = 1$$

Another definition we need is the volume of 1 mole of A and B (*molar volume*), these volumes in general are not equal:

$$\text{Molar volume of A} = \bar{V}_A^*; \text{ molar volume of B} = \bar{V}_B^*$$

The cross indicates that it is the volume of *pure* A or B.

X. 2. Partial molar quantities

As an introduction to the description of the free enthalpy of a mixture we first describe what happens to the total volume V of a mixture when we add n_A moles of A (volume = $n_A \bar{V}_A^*$) to n_B moles of B (volume = $n_B \bar{V}_B^*$):

$$V \neq n_A \bar{V}_A^* + n_B \bar{V}_B^*$$

The reason is that the interaction between A and B molecules may differ from the interactions between A molecules or the interaction between B molecules. As an example let us add 1 mole water to a very large amount (say 1000 moles) of water and to a large amount of ethanol (also 1000 moles ethanol). In both cases the volume of the mixture increases by ΔV :

$$\begin{array}{ll} 1 \text{ mole water to 1000 moles of water} & \rightarrow \Delta V = 18 \text{ cm}^3 \\ 1 \text{ mole water to 1000 moles of ethanol} & \rightarrow \Delta V = 14 \text{ cm}^3 \end{array}$$

The reason for the difference is that in the first case every added water molecule is surrounded by other, identical water molecules. In the second case statistically the added water molecule is surrounded by ethanol molecule only. Due to a difference in the intermolecular interaction water – ethanol the density around the water molecules in the ethanol – water mixture is higher than in the water – water mixture.

This means that the volume of 1 mole water depends on the type and amount of the other component in the mixture. In the pure liquid 1 mole of A has a volume equal to the molar volume \bar{V}_A^* , for a mixture we define the volume of 1 mole A as the *partial molar volume* \bar{V}_A .

Mathematically the partial molar volume is defined as the increase of the total volume dV of a mixture when dn_A mole of A is added to the A+B mixture at constant pressure, temperature and amount of B:

$$\bar{V}_A = \left(\frac{\partial V}{\partial n_A} \right)_{p, T, n_B} \quad (48)$$

Here a partial derivative has to be used while a partial molar volume is not only a function of p and T , but also a function of the composition of the mixture (as shown in fig. 10 for the water – ethanol mixture).

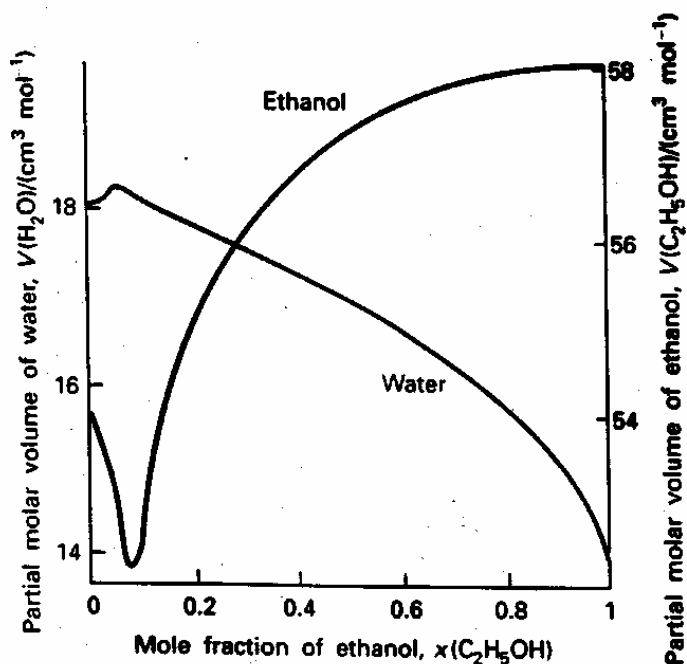


Fig. 10. Partial molar volume of water and ethanol as a function of the composition of a water – ethanol mixture

So now we have a molar volume \bar{V}_A^* for the pure substance A defined as:

$$\bar{V}_A^* = \left(\frac{\partial V}{\partial n} \right)_{p, T}$$

and a partial molar volume for the component A in a A+B mixture defined according to eq. (48).

When we consider the total volume V of a mixture as a function of n_A and n_B , we can write for the differential dV :

$$dV = \left(\frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B = \bar{V}_A dn_A + \bar{V}_B dn_B \quad (49)$$

Eq. (49) is a differential equation that can be integrated:

$$V = n_A \bar{V}_A + n_B \bar{V}_B \quad (50)$$

The result eq. (50) is surprising because it looks as if one can integrate eq. (49) by assuming that \bar{V}_A and \bar{V}_B are independent of n_A and n_B , which is certainly not the case (see for instance fig. 10). The proof that eq. (50) can be obtained by integration of eq. (49) will be given in Appendix I.

For the free enthalpy G we have a similar expression:

$$dG = \left(\frac{\partial G}{\partial n_A} \right)_{p,T,n_B} dn_A + \left(\frac{\partial G}{\partial n_B} \right)_{p,T,n_A} dn_B = \bar{G}_A dn_A + \bar{G}_B dn_B = \mu_A dn_A + \mu_B dn_B \quad (51)$$

which we can integrate to:

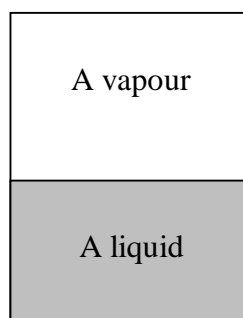
$$G = \mu_A dn_A + \mu_B dn_B \quad (p,T=\text{constant}) \quad (52)$$

Eq. (51) shows that the chemical potential can also be viewed as a partial molar entity. Remember that just as \bar{V}_A and \bar{V}_B also μ_A and μ_B are functions of n_A and n_B , or better x_A !

X. 3. Binary mixture in two phases.

Before we can describe the chemical potential in a liquid mixture, we must have an expression for the chemical potential of a component in a liquid phase. We can obtain such a relation by considering a pure liquid A in equilibrium with its vapour in a closed system (fig. 11).

Fig. 11



We assume that the vapour can be described as an ideal gas with pressure p_A^* . Applying eq. (47) we have for the chemical potential of the gas:

$$\mu_A^*(g) = \mu^\ominus + RT \ln \left(\frac{p_A^*}{p^\ominus} \right)$$

Now we use the fact that in equilibrium the chemical potential of A in the liquid state equals the chemical potential of A in the gas phase:

$$\mu_A^*(l) = \mu_A^*(g) = \mu^\ominus + RT \ln \left(\frac{p_A^*}{p^\ominus} \right) \quad (53)$$

Now we look at the binary mixture A+B in two phases, fig. 12:

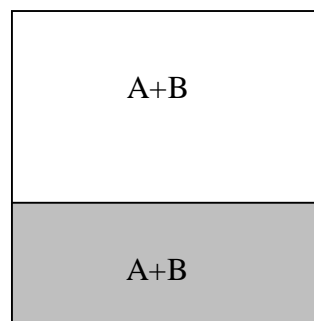


Fig.12

We can apply eq. (53) also to this situation when we replace p_A^* by the partial pressure of A in the gas mixture p_A (we remove the star while now we discuss a mixture!):

$$\mu_A(g) = \mu^\ominus + RT \ln \left(\frac{p_A}{p^\ominus} \right) \quad (54)$$

By combining eqs. (53) and (54) we can write:

$$\mu_A(l) = \mu_A^*(l) + RT \ln \left(\frac{p_A}{p_A^*} \right) \quad (55)$$

With equation (55) we got an expression for the chemical potential of a component in a fluid mixture and it shows that *the presence of a second component A in the mixture A+B lowers the chemical potential of A!*

Eq. (55) for A and a similar expression for B is still not so convenient for a liquid mixture while it depends on the partial pressure in the corresponding vapour. We would like to have an expression without parameters with depend on the vapour composition of the mixture.

The following equations are correct for every possible composition of the mixture:

$$\mu_A(l) = \mu_A^*(l) + RT \ln \left(\frac{p_A}{p_A^*} \right) \quad \mu_B(l) = \mu_B^*(l) + RT \ln \left(\frac{p_B}{p_B^*} \right) \quad (55)$$

Now we first consider some special mixtures:

- A. the mixture is *ideal*, that means that the molecular interaction between A molecules, A-A, is equal to that interaction between B molecules, B-B, and between A and B molecules, A-B. In an ideal gas these interactions are zero, in an ideal liquid mixture these interactions of course can not be zero but are equal. An ideal mixture is formed only when the molecules are very similar, for instance benzene and toluene. In the case of an ideal mixture:

$$p_A = x_A p_A^* \quad \text{and} \quad p_B = x_B p_B^* \quad (\text{Raoult's law}) \quad (56)$$

which changes eq. (55) into:

$$\mu_A(l) = \mu_A^*(l) + RT \ln(x_A) \quad \mu_B(l) = \mu_B^*(l) + RT \ln(x_B) \quad (57)$$

- B. A special situation for two dissimilar molecules which do not form an ideal mixture (or solution) is found when the solution is very dilute. In such an *ideal-dilute solution* (N.B. an ideal-dilute solution is less ideal than an ideal solution!) both the solvent molecules A and the solute molecules B statistically are surrounded exclusively by A molecules, the probability that two neighbouring molecules are both of the B type is very small. For the A molecules this means that the situation is like in an ideal mixture:

$$\mu_A(l) = \mu_A^*(l) + RT \ln(x_A) \quad (\text{Raoult's law}) \quad (58)$$

For the solute molecules B this is different, here we write $x_B = \frac{p_B}{K_B}$ (Henry's law)

and:

$$\mu_B(l) = \mu_B^*(l) + RT \ln\left(\frac{K_B x_B}{p_B^*}\right) = \mu_B^*(l) + RT \ln\left(\frac{K_B}{p_B^*}\right) + RT \ln(x_B) = \mu_B^+(l) + RT \ln(x_B) \quad (59)$$

Here K_B , the Henry constant, is a constant with the dimension of pressure and which depends on B only; μ_B^+ is the chemical potential of B in a (hypothetical) mixture with for which the partial pressure is K_B .

- C. For a real solution, not ideally diluted, only equations (55) are correct and here the expressions for the chemical potentials are rewritten by replacing x_A and x_B in eqs. (58) and (59) by the activities a_A and a_B :

$$\mu_A(l) = \mu_A^*(l) + RT \ln(a_A) \quad \text{and} \quad \mu_B(l) = \mu_B^+(l) + RT \ln(a_B)$$

These activities are numbers like a mole fraction. The activities can also be introduced via the molality (mole/kg solvent).

X. 4. A mixture of two liquids

We consider a binary mixture of n_A mole of A and n_B mole of B, $n = n_A + n_B$. Using eq. (52):

$$G = \mu_A dn_A + \mu_B dn_B$$

we can now calculate the total Free Enthalpy G_B before (pure substances A and B) and after mixing G_M :

$$\begin{aligned} G_B &= n_A \mu_A^* + n_B \mu_B^* \\ G_M &= n_A \mu_A + n_B \mu_B \end{aligned} \quad (60)$$

The difference is the Free Enthalpy of mixing $\Delta_M G$ and for an ideal mixture we can apply eq. (57):

$$\Delta_M G = G_M - G_B = n_A RT \ln x_A + n_B RT \ln x_B = nRT(x_A \ln x_A + x_B \ln x_B) \quad (61)$$

For a mixture x_A and x_B are both smaller than 1, which makes $\Delta_M G$ negative. This implies that the mixing process for an ideal mixture, at constant p and T , is always spontaneous for every composition! Components which are so similar that they form an ideal mixture, always mix. As the mixing Free Enthalpy is the sum of an energy and an entropy term:

$$\Delta_M G = \Delta_M H - T\Delta_M S \quad (\text{at constant temperature})$$

From eq. (45) we have:

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_{p, n_A, n_B} \quad \text{and consequently also} \quad \Delta_M S = -\left(\frac{\partial(\Delta_M G)}{\partial T}\right)_{p, x_A, x_B}; \text{ we find:} \\ \Delta_M S &= -nR(x_A \ln x_A + x_B \ln x_B) \end{aligned} \quad (62)$$

The mixing entropy is positive, which also shows that the mixing process must be spontaneous. Combining eqs. (61) and (62) shows that for an ideal mixing process $\Delta_M H=0$ (that is while all intermolecular interactions are equal). The mixing of an ideal mixture is completely driven by the entropy!

For many mixtures the mixing free enthalpy is not negative (or the mixing entropy is not positive). Then also $\Delta_M H$ is not equal to zero:

$$\begin{aligned} \Delta_M H &= H_E \\ \Delta_M S &= S_E - nR(x_A \ln x_A + x_B \ln x_B) \\ \Delta_M G &= G_E + nRT(x_A \ln x_A + x_B \ln x_B) \end{aligned}$$

where the new parameters are the excess parameters, whose values indicate how much the real mixture deviate from an ideal mixture. When $\Delta_M G > 0$ the two components do not mix (for instance oil and water for most compositions). When they have been somehow brought together, they spontaneously demix. It is found that for most substances the question whether they mix, depends on the relative concentrations and p and T . This can be indicated in a *phase diagram*, as will be discussed in Chapter XII.

III. XI. Colligative Properties

XI.1. Boiling point elevation and freezing point depression

Most physical properties of a pure solvent change when a solute is dissolved (density, viscosity,.....). While the change of, for example, the viscosity depends on the molecule that has been dissolved, the change of some properties is independent of the type of molecule. These changes only depend on the amount of the dissolved molecules. Such properties are called colligative properties. Examples are the change of the freezing and boiling temperatures and osmosis.

Using eqs. (45) and (46) we find for the chemical potential of a pure substance:

$$d\mu = \bar{V}dp - \bar{S}dT$$

where \bar{V} and \bar{S} are molar quantities. At a constant pressure p we find:

$$\left(\frac{\partial\mu}{\partial T}\right)_p = -\bar{S} \quad (63)$$

Eq. (63) and fig. 8 allow us to draw the function $\mu=\mu(T)$, see fig. 13.

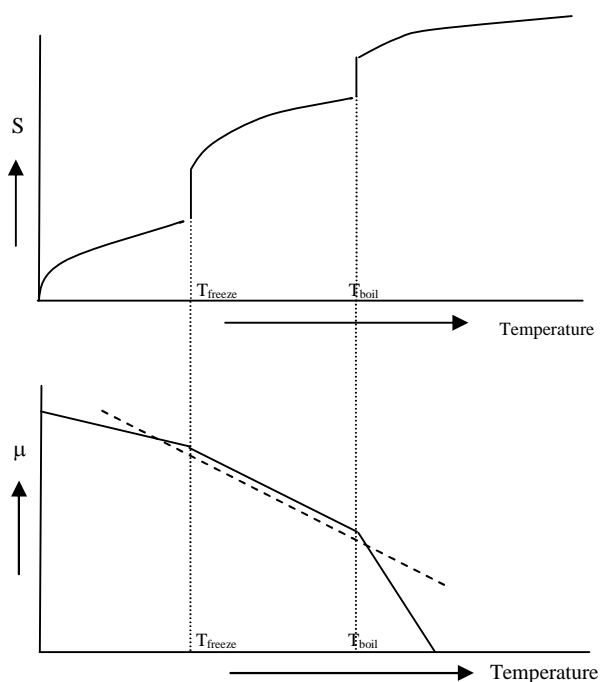


Fig. 13. The dependence of μ on T can be constructed via eq. (63) from the dependence of S on temperature. In the lower figure the gross simplification has been made that S linearly increases with the temperature, in reality the dependence of μ on T should follow curved lines. Crucial here is, however, the change in slope at the freezing and boiling point.

XI. 2 Boiling point elevation

When a compound B is dissolved in the solvent A the chemical potential of the solvent changes:

$$\mu_A(l) = \mu_A^*(l) + RT \ln x_A \quad (\text{assumption the solution is ideal or ideally diluted})$$

Since $x_A = 1 - x_B < 1$ the chemical potential of A has decreased relative to that of the pure liquid. When we assume for simplicity that the partial pressure of the solute is zero and that the solute and solvent do not mix in the solid state, then only the curve of μ in the liquid phase changes, as indicated in fig. 13 by the dashed line. From this figure it is immediately clear that the boiling temperature has increased and the freezing point depressed.

The changes in freezing and boiling point can be calculated using expressions for the chemical potential. For the equilibrium of the vapour A (the vapour consists only of A when we assume that B has no vapour pressure) with the mixture A+B:

$$\mu_A^*(g) = \mu_A(l) \quad \text{and}$$

$$\mu_A(l) = \mu_A^*(l) + RT \ln x_A \quad \text{follows:}$$

$$\ln x_A = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\bar{G}_A(g) - \bar{G}_A(l)}{RT} = \frac{\Delta \bar{G}_A(T)}{RT} \quad (64)$$

where $\Delta \bar{G}_A$ is the vaporisation free enthalpy of A.

By differentiation of eq. (64) we get:

$$\frac{d}{dT}(\ln x_A) = \frac{1}{R} \frac{d}{dT} \left(\frac{\Delta \bar{G}_A(T)}{T} \right) \quad (65)$$

The reason to write eq. (64) in the clumsy form of eq. (65) is that we know how to differentiate the terms in eq. (65).

Intermezzo: the Gibbs-Helmholtz equation.

$$dG = Vdp - Sdt \quad (41)$$

$$\left(\frac{\partial G}{\partial T} \right)_p = -S \quad (66)$$

$$G = H - TS \quad \rightarrow \quad -S = \frac{G - H}{T}$$

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

$$\frac{\partial}{\partial T} \left(\frac{G}{T} \right) = \frac{T \frac{\partial G}{\partial T} - G}{T^2} = \frac{1}{T} \left(\frac{G - H}{T} \right) - \frac{G}{T^2} = -\frac{H}{T^2} \quad (67)$$

Eq. (67) is correct for any free enthalpy, therefore also for the vaporisation enthalpy:

$$\frac{\partial}{\partial T} \left(\frac{\Delta \bar{G}_A}{T} \right) = \frac{\partial}{\partial T} \left(\frac{\bar{G}_A(g) - \bar{G}_A(l)}{T} \right) = -\frac{\bar{H}_A(g)}{T^2} + \frac{\bar{H}_A(l)}{T^2} = -\frac{\Delta \bar{H}_A}{T^2} \quad (68)$$

By insertion of eq. (68) into eq. (65) we find:

$$d(\ln x_A) = -\frac{\Delta \bar{H}_A}{RT^2} dT$$

and integrating:

$$\int_1^{x_A} d(\ln x_A) = -\int_{T_{boil}^*}^{T_{boil}} \frac{\Delta \bar{H}_A}{RT^2} dT \quad (69)$$

Here T_{boil}^* is the boiling temperature of the pure liquid A and T_{boil} the boiling temperature of the solution ($T_{boil} > T_{boil}^*$). When we assume that the vaporisation enthalpy $\Delta \bar{H}_A$ does not depend on the temperature over the temperature range $T_{boil} - T_{boil}^* = \delta T_{boil} \ll T_{boil}^*$, then:

$$\ln x_A = -\frac{\Delta \bar{H}_A}{R} \int_{T_{boil}^*}^{T_{boil}} \frac{dT}{T^2} = -\frac{\Delta \bar{H}_A}{R} \left(-\frac{1}{T_{boil}} + \frac{1}{T_{boil}^*} \right) = -\frac{\Delta \bar{H}_A}{R} \left(\frac{T_{boil} - T_{boil}^*}{T_{boil} T_{boil}^*} \right) \approx -\frac{\Delta \bar{H}_A}{R} \frac{\delta T_{boil}}{T_{boil}^*} \quad (70)$$

The last step we have to make is to relate x_A to the amount of dissolved species x_B :

$$\ln x_A = \ln(1 - x_B) \approx -x_B \text{ when } x_B \ll 1.$$

The change in boiling temperature of the solvent due to dissolving B is then:

$$\delta T_{boil} = \frac{RT_{boil}^*}{\Delta \bar{H}_A} x_B \quad (71)$$

The change in boiling temperature of A only depends on the amount B, *not on the type of molecule B* and further on the vaporisation enthalpy of the solvent.

XI. 3. Freezing point depression

In a completely analogous way the freezing temperature depression can be calculated, with the result:

$$\delta T_{freeze} = \frac{RT_{freeze}^*}{\Delta \bar{H}_A} x_B \quad (72)$$

XI. 4. Osmosis

Osmosis is found when the transport of solvent and solute molecules into a certain enclosed volume is different. Many osmosis effects are found in biology, for instance for a cell for which the cell wall acts as a selective membrane. To describe the effect in a thermodynamic way we consider a volume with solvent A and solute B separated from the pure solvent A by a semi-permeable membrane, see fig.14. Experimentally it is found that the solution in the compartment raises to a higher level than the level of the pure solvent. This causes an extra pressure, the osmotic pressure, on the solution of:

$$\pi = \rho gh$$

where ρ is the density of the solution, g the acceleration due to gravity and h the difference in liquid levels.

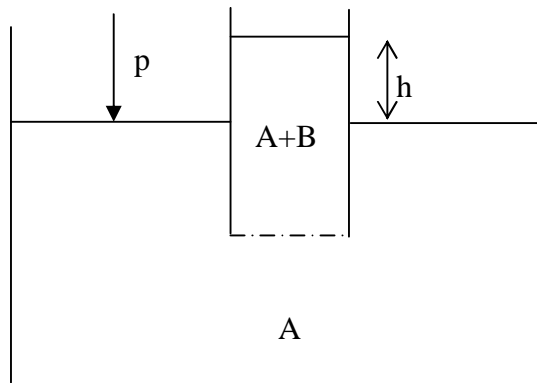


Fig. 14. Osmosis; the semi-permeable membrane (dashed line) allows the transport of solvent molecules A but not of the solute B.

In equilibrium the chemical potential of A at the same height is the same in the pure solvent at pressure p and in the solution at pressure $p+\pi$:

$$\mu_A^*(p) = \mu(p+\pi) = \mu_A^*(p+\pi) + RT \ln x_A \quad (73)$$

$$\mu_A^*(p+\pi) = \mu_A^*(p) + \int_p^{p+\pi} \bar{V}_A^* dp \quad (74)$$

where \bar{V}_A^* is the molar volume of A.

By combining the eqs. (73) and (74) we find:

$$-RT \ln x_A = \int_p^{p+\pi} \bar{V}_A^* dp$$

or:
$$RT x_B = \bar{V}_A^* \pi \quad (75)$$

obtained by using:

$$-RT \ln x_A = -RT \ln(1 - x_B) \approx RT x_B \quad (x_B \ll 1)$$

$$\int_p^{p+\pi} \bar{V}_A^* dp \approx \bar{V}_A^* \pi \quad (\text{if } \bar{V}_A^* \text{ independent of pressure between } p \text{ and } p + \pi)$$

In the compartment with volume V we have n_A mole A and n_B mole B; with $n_B \ll n_A$ we have the following equations:

$$x_B \approx \frac{n_B}{n_A} \quad (76)$$

$$n_A \bar{V}_A^* \approx V$$

By combination of the eqs. (75) and (76) we find the van 't Hoff equation for ideal solutions:

$$\pi V = n_B RT$$

or:

$$\frac{\pi}{[B]} = RT$$

where $[B]$ is the concentration of B in mol per liter. For real solutions a virial equation can be assumed to exist:

$$\frac{\pi}{[B]} = RT(1 + B[B] + C[B]^2 + \dots)$$

Also the osmotic pressure π is not dependent on the type of molecule B, it only depends on the amount of B!

