C33J - CHEMICAL THERMODYNAMICS

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CONTENTS

I. CONSERVATION OF ENERGY: THE FIRST LAW

The First Law of Thermodynamics is simply a statement of the law of conservation of energy, which follows from the basic principles of mechanics and electrodynamics.
The law applies to *closed* systems, i.e. for a given amount of matter, and is usually expressed in the form of an energy balance equation:

$$dU = đq + đw$$

which pertains to an arbitrary small change (indicated by the symbols d and $đ$) in the state of the system. The system may be a gas or liquid contained in a vessel (cylinder) which is closed at one end by a movable piston. The meanings of the symbols are as follows:
dU represents a small change in the *internal energy U*, which is the sum of kinetic and potential energies due to molecular interactions and should, strictly speaking, also include the effects of external fields, like the potential energy in the Earth's gravitational field. This latter contribution is usually neglected in applications to Chemistry, when we are dealing with relatively small systems. The SI unit for energy is the *Joule* (J, 1 J = 1 Newton meter = 1 Nm). Although the quantity U by itself has no absolute significance, due to the arbitrary choice of the zero level of energy for a given amount of matter, energy *differences* do have an absolute, unambiguous meaning.
$đq$ is a small amount of *heat supplied to* the system, and may thus be positive or negative. Heat is the *flow* of internal energy down a temperature gradient.
$đw$ denotes *work* performed *on* the system. Unlike the heat term, the work term can assume many different forms, depending on the type of action to which the system is subjected. Here, we will be mainly concerned with the work done by applying an external pressure p_{ext} (unit $Nm^{-2} = Pa$) which causes a change in volume dV. The amount of work done on the system is then $đw = -p_{ext}dV$, where the $-$ sign is added because $dV < 0$ for compression, when $đw$ should be positive.
Depending on the circumstances, other work terms must be added. For example, if the system contains an interface between two bulk phases (e.g. liquid and vapour), or if bubbles or droplets are present, a change in surface area, dA, gives rise to a change in U equal to γdA where γ is the *surface tension*.
Electrochemistry provides an example of a system, the galvanic cell, which can exchange *electrical work* with its surroundings. The corresponding work term in the energy balance is then $-EdQ$ where E is the cell EMF and dQ is a small quantity of charge that is passed through the cell and external circuit.
In this course we will only be concerned with "pV-work", however, in which case the First Law reads as

$$dU = đq - p_{ext}dV$$

dV will be > 0 or < 0, depending on whether the internal pressure, p_{int}, of the system is higher or lower than p_{ext}, respectively. In particular, if $p_{ext} = p_{int} \equiv p$, the piston will not move spontaneously but may be displaced *reversibly*. A reversible process is one that can be retraced completely without effecting any permanent change in the surroundings.
This concept will be further elaborated as we come to discuss the Second Law (Ch. 2).

The quantities *U, p, V* introduced above are examples of so-called "functions of state" or "state variables". Another very important one is the *absolute temperature T* (in *K*). These variables generally belong to either one of two categories: (1) *Extensive* functions of state, those that are proportional to the size or quantity (e.g. the number of moles, *n*) of a system or substance , for example *U* and *V*; and (2) *Intensive* functions of state like *T* and *p*, which are independent of system size. Also, the *molar volume* $\overline{V} = V / n$ and *molar energy* $\overline{U} = U / n$ are to be regarded as intensive variables.

Furthermore, for any substance that is uniform in composition and physical properties, it has been established empirically that the macroscopic state of the system is uniquely determined by specifying *two* intensive variables, e.g. *T* and *p*, so that we can write

$$U = n\overline{U}(T, p) \text{ and } V = n\overline{V}(T, p)$$

The expression for $\overline{V}$ as a function of *T* and *p* for a pure substance has special significance: it is called the *equation of state*. Examples include the Boyle-Gay Lussac equation of state for an ideal gas (approximated by all real gases for high enough *T* and sufficiently low *p*):

$$V / n = \overline{V} = RT / p$$

and the more sophisticated Van der Waals equation:

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

which includes the effects of finite size of the molecules (through *b*) and attractive (dispersion) forces (via $a / \overline{V}^2$) and correctly predicts the liquid/vapour phase transition. From the ideal gas model it furthermore follows that $\overline{U}$ depends *exclusively* on *T* (i.e. it is independent of *p*):

$$\overline{U} = \overline{U}(T) \qquad \text{(ideal gas)}$$

An equation of state may be conveniently represented in a *pV*-diagram where, for each *T*, the *p-V* relationship describes a curve, called an *isotherm* (for a given quantity *n* of the substance). In addition, the *pV*-diagram can be used to represent a *reversible change* of a system. Each point (*V,p*) corresponds to definite values of both *T* and *U*. For a finite change of state, going from say *A* to *B* along the curve indicated in the figure, the net amount of *pV*-work is equal to the area under the curve:

$$w = \int_A^B đw_{rev} = -\int_{V_A}^{V_B} pdV = +\int_{V_B}^{V_A} pdV$$

Clearly, the value of *w* depends on the path leading from *A* to *B*, i.e. *w* is *not* a function of state! This is why we used the symbol *đw*, and not *dw*, in the energy balance equation.
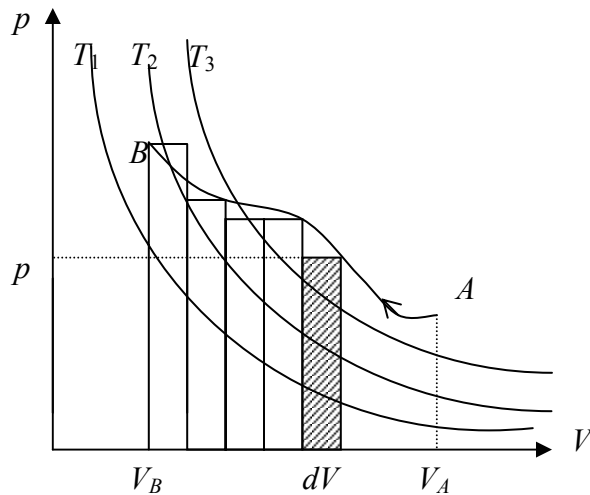
In mathematical jargon, a quantity such as dU is known as a *complete* or *exact* differential, expressing the fact that any change in U, in this case $\Delta U = U_B - U_A$, depends *only* on the initial and final states, *not* on the path connecting them or upon whether the process is reversible or not.

For the above process the First Law can be stated as

$$\Delta U = q + w$$

from which it is evident that q, like w, is a path-dependent quantity (hence the notation $đq$ used earlier).

It frequently occurs that a process (e.g. a chemical reaction) takes place at constant pressure p (when the piston is free to move). In that case, $w = -p\Delta V$ and $\Delta U = q - p\Delta V$ or, equivalently,

$$(\Delta H)_p = q$$

defining the *enthalpy* (or "heat content") H as

$$H = U + pV$$

(*N.B.*: A thermodynamic quantity appearing as a subscript, like p in the above formula, always indicates that it is held constant for the change under consideration).

From its definition it is obvious that H is an extensive function of state.

In many applications it is desirable to have a way of describing the effect of heat added *reversibly* to a (chemically inert) system upon its temperature. A useful quantity in this regard is the *heat capacity*,C, defined as

$$C = đq_{rev}/dT$$

(*molar* heat capacity, $\overline{C}$, when referred to 1 mol).

Clearly, this definition is ambiguous since dq_{rev} depends on the conditions under which it is supplied. The most common cases are V = constant ($\therefore dV = 0$) and p = constant. The first gives rise to the *isochoric heat capacity*, C_V:

$$C_V = \frac{dq_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$

(the symbol ∂ is used here because U depends on more than one variable, and it is differentiated with respect to one of these, T, while the other, V, is kept fixed). The second condition leads to the *isobaric heat capacity, C_p*:

$$C_p = \frac{dq_p}{dT} = \left(\frac{dU + pdV}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

For an *ideal gas*, $\overline{U} = \overline{U}(T)$ and $p\overline{V} = RT$, hence $\overline{H}(T) = \overline{U}(T) + RT$ and therefore

$$\overline{C}_p = \frac{d\overline{H}}{dT} = \frac{d\overline{U}}{dT} + R = \overline{C}_V + R$$

In general, however, $\overline{C}_V$ and $\overline{C}_p$ will be dependent on both T and p.

Let us now consider a special and very important class of processes, *viz.*, those where the initial and final states are identical, so-called *cyclic processes*. A reversible cyclic process for a pure substance may be represented in a pV-diagram by a closed loop, C. Clearly, $\Delta U = \oint_C dU = 0$ for such a process, hence $q_{rev} = -w_{rev}$, where w_{rev} = area enclosed by C; $w_{rev} > 0$ if C is traversed in counter-clockwise sense (the cross-hatched area does not contribute since it is swept out twice in opposite directions).
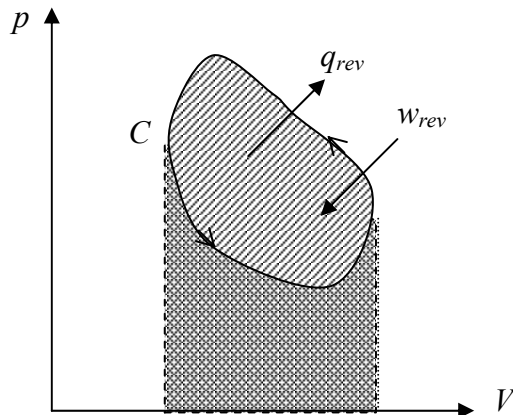
Of course, the result $\oint_C dX = 0$, for any function of state X, like U or H, is true for *any* cyclic process, no matter how complex or practically unfeasible. In particular, during certain stages of the process chemical reactions may proceed to a given extent. The mixture before reaction will be denoted by R, after reaction by P. Pressure and temperature throughout the reaction are maintained at p and T, respectively. The heat of reaction is $q_{rxn}(T, p) = \Delta H_{rxn}(T, p)$ (since p = constant). At a slightly higher temperature $T + dT$, but at the same p, it is equal to $q_{rxn}(T + dT, p) = \Delta H_{rxn}(T + dT, p)$.

Next, consider the isobaric thermodynamic cycle shown below.
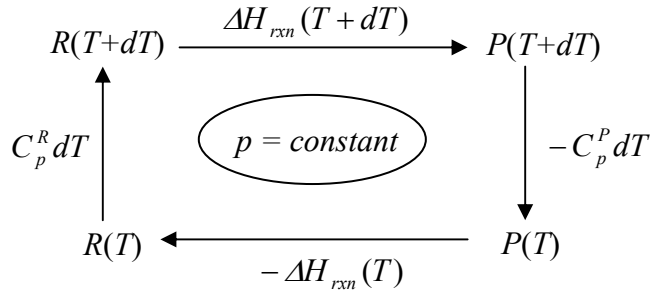
The isobaric heat capacities of the mixture before and after reaction are C_p^R and C_p^P, respectively. Then, since $\oint (dH)_p = 0$ (which is basically one statement of *Hess' law*),

$$-\Delta H_{rxn}(T, p) + C_p^R dT + \Delta H_{rxn}(T + dT, p) - C_p^P dT = 0$$

This rearranges to

$$\left(\frac{\partial \Delta H_{rxn}}{\partial T} \right)_p = C_p^P - C_p^R \equiv \Delta C_p$$

This expression relates the temperature coefficient of the heat of reaction to the difference between the heat capacities of reactants and products. It is known as *Kirchhoff's equation* (*N.B.*: The equation can be obtained more quickly if we take the temperature derivative of $\Delta H_{rxn} = H^P - H^R$ and use the formula for C_p).

II. SPONTANEOUS PROCESSES: THE SECOND LAW AND ENTROPY.

II.1 Entropy.

From our everyday experience we know that most, if not all, processes in Nature are spontaneous and irreversible, e.g. chemical reactions proceed in one direction, heat only flows from high to low temperature but never in the opposite direction, even though this would not violate the First Law. Another example is the so-called *Joule expansion*, where

a gas is initially confined to one of two bulbs that are connected by means of a capillary equipped with a valve. The other bulb is evacuated. When the valve is opened, the gas
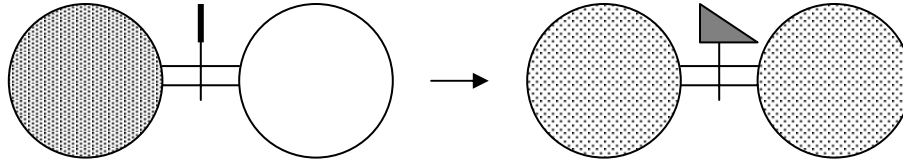
will distribute itself evenly between the bulbs. No external work is done in the process and if the bulbs are thermally insulated then U will be constant. If furthermore the gas behaves ideally, T will remain constant as well, since $U = U(T)$ in that case. The reverse process will never happen spontaneously, however. Phenomena like these show a universal trend toward increased randomisation, or dissipation, of energy. It is the purpose of the Second Law of Thermodynamics to express this tendency in a unifying, quantitative manner.

Many different statements of the Second Law have been put forward, all of them essentially equivalent. For example, Lord Kelvin postulated that

*"No process is possible whose **sole result** is the conversion of heat (from a **single** source) to an equivalent amount of useful work"*

Work can of course always be converted to heat, for example in the form of frictional losses, but Kelvin's statement tells us that it is impossible to retrieve this heat and convert it back entirely to work. In the following we shall see that this simple fact of experience captures the essence of the unidirectional character of all spontaneous processes that occur in Nature.

To understand the consequences of the Second Law we shall investigate in detail one particular cyclic process known as the *Carnot cycle*. A Carnot cycle consists of four reversible steps: two isothermal and two adiabatic strokes carried out by a simple heat engine.

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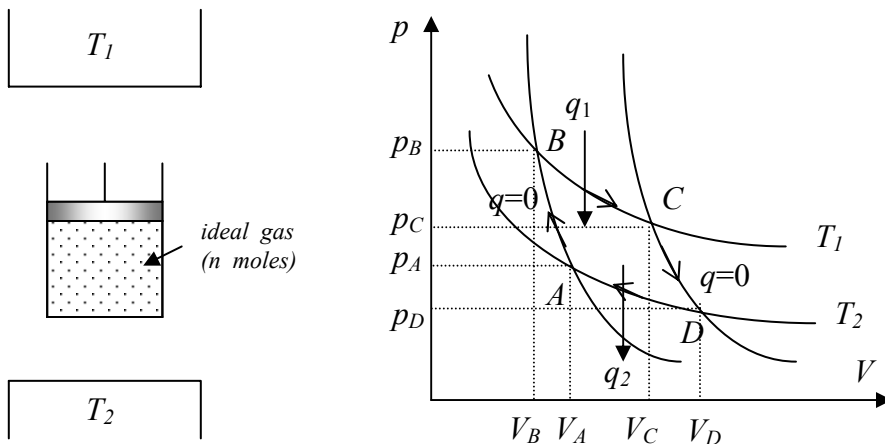
It requires therefore two heat reservoirs (thermostats of "infinite" heat capacity) of temperatures T_1 and T_2, with $T_1 > T_2$, and a cylinder containing the working substance which will be assumed to be n moles of a perfect gas.

The process can be represented in a pV-diagram, as shown. Suppose the cycle starts at point A (temperature = T_2), where the cylinder is not connected to either T_1 or T_2. The gas is then slowly and adiabatically compressed until its temperature reaches T_1, at which point it is brought in thermal contact with reservoir T_1. Then follows a reversible isothermal expansion along BC, during which heat q_1 is absorbed from the reservoir, and an adiabatic expansion along CD. At that point, contact is made with reservoir T_2 and during the subsequent isothermal compression back to point A, heat $-q_2$ is lost by the gas and absorbed by the reservoir. According to the First Law, the amount of pV work, w, performed by the gas on the surroundings (which could be used to lift a weight, for example) must be equal to $q_1 + q_2$. Of course, this cycle could also be reversed in which case w, q_1 and q_2 would get opposite signs (refrigeration cycle!).

Remember that along an isotherm the internal energy of a perfect gas is constant so that any heat absorbed (evolved) should exactly match the pV work done (absorbed). Thus,

$$q_1 = \int_{V_B}^{V_C} pdV = nRT_1 \int_{V_B}^{V_C} \frac{dV}{V} = nRT_1 \ln\left(\frac{V_C}{V_B}\right)$$

and similarly

$$q_2 = -nRT_2 \ln\left(\frac{V_D}{V_A}\right) \qquad (<0)$$

To find the relationship between V_D / V_A and V_C / V_B we need to digress a little on the mathematical properties of the adiabatics in the pV-diagram.

To this end, consider an infinitesimal adiabatic compression or expansion of the gas. Since $đq = 0$, $dU = -pdV$. At the same time, this change brings about a change in temperature, dT, which is related to dU by a formula that was derived earlier: $dU = C_V dT$.

At each point in the pV-diagram, $pV = nRT$, so that small, simultaneous changes in p, V and T will be interrelated by the equation

$$pdV + Vdp = nRdT$$

Substituting $dT = dU / C_V = -pdV / C_V$ gives

$$pdV + Vdp = -\frac{nR}{C_V} pdV$$

or, equivalently,

$$Vdp = -\left(1 + \frac{nR}{C_V}\right)pdV = -\left(\frac{C_V + nR}{C_V}\right)pdV = -\frac{C_p}{C_V}pdV \equiv -\gamma pdV ,$$

defining $\gamma = C_p / C_V$.

Comparing the first and last members of the above equation gives, after dividing both sides by pV,

$\frac{dp}{p} = -\gamma \frac{dV}{V}$, so that $d \ln p = d \ln V^{-\gamma}$, or $d \ln(pV^{\gamma}) = 0$.

Thus, along a *reversible* adiabatic,

$$pV^{\gamma} = constant$$

Since γ is obviously > 1, adiabatics are always "steeper" than isotherms, for which $pV = constant$. The equation for an adiabatic in the case of a perfect gas can now be used to write

$$p_A V_A^{\gamma} = p_B V_B^{\gamma} \quad \text{and} \quad p_D V_D^{\gamma} = p_C V_C^{\gamma}$$

Dividing the first equation by the second yields

$$\frac{p_A}{p_D}\left(\frac{V_A}{V_D}\right)^{\gamma} = \frac{p_B}{p_C}\left(\frac{V_B}{V_C}\right)^{\gamma}$$

Note that A and D lie on the same isotherm, and so do B and C, so that $p_A / p_D = V_D / V_A$ and $p_B / p_C = V_C / V_B$. Hence

$$\left(\frac{V_A}{V_D}\right)^{\gamma-1} = \left(\frac{V_B}{V_C}\right)^{\gamma-1}$$

or $V_D / V_A = V_C / V_B$.

Returning to the expressions for q_1 and q_2 we see that the logarithmic factors are in fact equal, and we conclude that

$$\frac{q_1}{T_1} = -\frac{q_2}{T_2}$$

for perfect gases. This result is known as the *Carnot-Clausius theorem*.

Now consider a body, no longer an ideal gas, undergoing an arbitrary cyclic process which is not necessarily reversible. The body is a closed system that may possess any degree of complexity, but will henceforth be regarded as a "black box" to keep the

argument as general as possible. It is not always feasible to represent this process in a pV-diagram, even if the cycle is reversible, as different forms of work may be involved.

Imagine that the heat absorbed or ejected during the various stages of the cycle is supplied or drained off by an auxiliary Carnot engine containing an ideal gas as working substance. This engine operates *reversibly* between the body and a large heat reservoir at temperature T_0 and carries out a very large number of infinitesimal Carnot cycles until the main cycle C is completed. One of these infinitesimal cycles is depicted symbolically in the figure below.
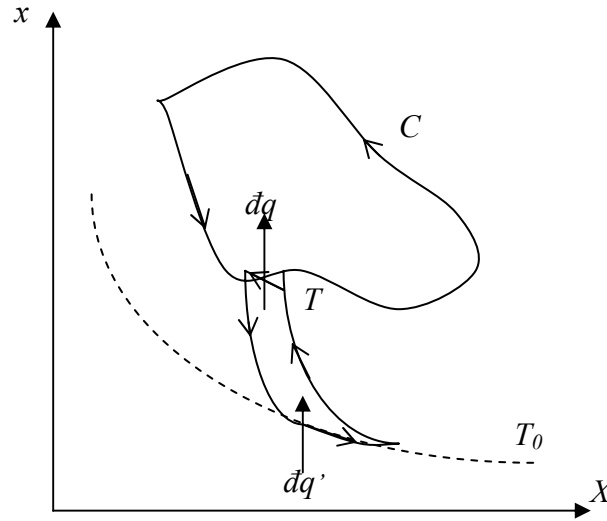
For each such cycle, $đq' = T_0 đq/T$ if T is the momentary, local temperature at which heat $đq$ is absorbed by the body (which is not necessarily uniform in temperature). Upon completion of the main cycle C the total amount of heat dispensed by the reservoir equals

$$\oint_C dq' = T_0 \oint_C \frac{dq}{T}$$

According to the First Law, since both the body and the Carnot engine will have returned to their respective original states after completion of the cycle C, the net amount of work performed in the main cycle and the Carnot cycles together should be equal to

$$w = \oint_C dq + \oint_C (dq' - dq) = \oint_C dq'$$

that is, w equals the net amount of heat *absorbed from* the reservoir.

But then the Second Law demands that $\oint_C dq'$ cannot be positive, and hence

$$\oint_C \frac{dq}{T} \leq 0 \quad \text{for } \textit{any} \text{ cyclic process}$$

In particular, if C is a *reversible* cycle, driving the process backwards would lead to the additional requirement $\oint_C dq/T \geq 0$. Both conditions can only be met simultaneously if

$$\oint_C \frac{dq_{rev}}{T} = 0 \text{ for } \textit{any reversible cycle}$$

Note that this implies that the Carnot-Clausius theorem is valid for *all* Carnot cycles, *irrespective of the nature of the working substance*.
The above property is the hallmark of a function of state with exact differential

$$dS = \frac{dq_{rev}}{T}$$

This new function of state, S, is called the *entropy* of the system. It is an *extensive* quantity, expressed in $J\,K^{-1}$.
The difference in the entropy of a system between two states A and B can thus be calculated by considering *any* reversible path connecting them and evaluating the integral

$$S_B - S_A = \int_A^B dS = \int_A^B \frac{dq_{rev}}{T}$$

An important corollary is the following:
For a *reversible* change in a *closed* system the First Law can now be reformulated as

$$dU = TdS + dw_{rev}$$

If only pV work can be exchanged with the surroundings, this becomes

$$dU = TdS - pdV$$

The heat capacities C_V and C_p can likewise be written in "entropy form", as follows:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \text{ and } C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

For an *irreversible* cycle, on the other hand, it is evidently true that

$$\oint_C \frac{dq}{T} < 0$$

Assume that some cycle C consists of an irreversible process leading from A to B (see figure, dashed line) followed by a reversible process leading from B back to A. Then
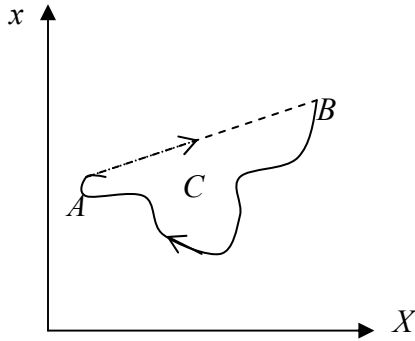
$$\oint_C \frac{dq}{T} = \int_A^B \frac{dq_{irrev}}{T} + \int_B^A \frac{dq_{rev}}{T} < 0$$

which is equivalent to

$$S_B - S_A = \int_A^B \frac{dq_{rev}}{T} > \int_A^B \frac{dq_{irrev}}{T}$$

If *A* and *B* are infinitesimally close, this result can be formulated as

$$dS > \frac{dq_{irrev}}{T}$$

Summarising, we have shown that, in general,

$$dS \geq \frac{dq}{T}$$

where the equality only holds for a small reversible change and the inequality for an irreversible change of state in a material body (R. Clausius, 1865).
In particular, for an *adiabatic* change ($dq = 0$), $dS \geq 0$.
This last result always applies when we are dealing with a (closed) system in combination with its surroundings, with which it can exchange heat and work. This constitutes an isolated system, with constant total energy $U_t = U + U_{surr}$ and total volume $V_t = V + V_{surr}$. The entire system is thought of as being enclosed by an insulating rigid wall. A change in the total entropy $S_t = S + S_{surr}$ then always has to obey the inequality

$$\left(\Delta S_t \right)_{U_t, V_t} \geq 0$$

The Second Law may now be stated as follows:

During a spontaneous process, the total entropy of an isolated system increases. It remains constant for reversible changes of state.

In fact, any isolated system will spontaneously evolve in such a way that its entropy continuously increases, until it reaches the *maximum possible* value compatible with the given constraints (U_t, V_t constant). In this final state of maximum entropy the system is in *thermodynamic equilibrium* and no further observable changes will occur.
A process is *reversible* if, and only if, it consists of a continuous sequence of equilibrium states during which the system plus its surroundings maintain a constant entropy value.
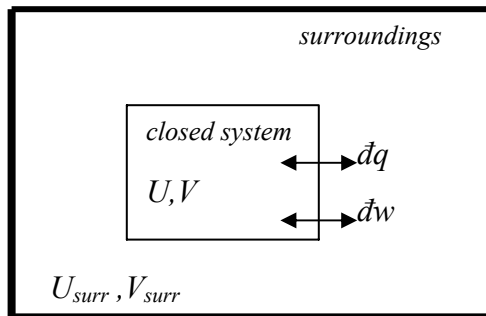

On a philosophical note, the above statement can be understood to imply that *entropy gives direction to time*, in the sense that past states of the Universe (an isolated system!) are distinguished from later ones by their lower entropy. But, paradoxically perhaps, time itself does not figure explicitly in thermodynamic relationships!
Kelvin's formulation of the Second Law indicates that the irreversibility essentially comes about as a result of work being dissipated, or wasted, as heat. For this reason the Second Law is sometimes paraphrased as the "law of degradation of energy".
Since S is a state variable, it is always possible, in principle at least, to calculate the net entropy change accompanying an irreversible process by constructing an alternative route between initial and final states. The first part of this alternative process is entirely reversible (with $\Delta S_t = 0$), and is followed by a completely irreversible step in which (some of the) work produced in the first step is dissipated directly as heat at some temperature T, thus $\Delta S_t = w_{diss}/T$. This procedure will be illustrated by explicitly calculating the entropy increase in two irreversible changes that have been mentioned previously, *viz.* the Joule expansion and spontaneous heat transfer.

(i)   Joule expansion.

n moles of a supposedly ideal gas are confined to one compartment (volume V_i) of a rigid vessel (volume V_f) by a partition. The other compartment is empty. After removing the partition, the gas expands spontaneously, uniformly filling the vessel. T remains constant, without the need for heat exchange with the surroundings. To calculate the accompanying increase in S_t ("universal entropy"), imagine the partition being replaced by a piston while T is maintained through a thermal contact with an auxiliary heat reservoir. The gas is thus allowed to expand reversibly and isothermally.
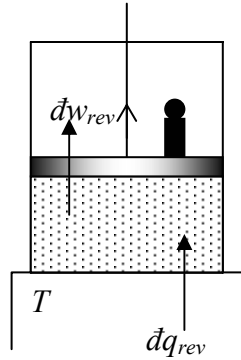
Since U remains constant (because T does), $dU = 0$ and $đq_{rev} = -đw_{rev} = pdV$. Overall,

$$q_{rev} = \int_{V_i}^{V_f} pdV = nRT \ln\left(\frac{V_f}{V_i}\right) = -w_{rev}$$

The same amount of heat was lost by the reservoir at the same T, so in this first step the *total* entropy change is zero: $\Delta S + \Delta S_{reservoir} = \dfrac{q_{rev}}{T} - \dfrac{q_{rev}}{T} = 0$,as for any reversible process in an isolated system (gas + reservoir + the object on which the work is done, e.g. a weight that is lifted). Now the gas has reached the same final state as in the spontaneous expansion process, but the heat reservoir has lost a quantity of heat q_{rev} while an equivalent amount of work has been done (lifting a weight). To reach the same final state as in the spontaneous process, the energy of the weight must be dissipated as heat and delivered to the reservoir, generating an amount of entropy equal to

$$\Delta S_t = \frac{w_{diss}}{T} = nR \ln\left(\frac{V_f}{V_i}\right) > 0$$

This is of course also equal to the entropy change ΔS of the gas itself, since the surroundings were not involved in the spontaneous expansion.

(ii) Heat transfer

Two bodies with different temperatures T_1 and T_2 $(T_1 > T_2)$ are temporarily brought in contact as a result of which heat q is transferred between them, presumably flowing from T_1 to T_2. The resulting increase in universal entropy, ΔS_t, can be calculated by using an auxiliary, reversibly operating, Carnot engine which extracts the heat q from "heat reservoir" T_1, and delivers heat $q' = \dfrac{T_2}{T_1} q$ at "heat reservoir" T_2. During this process, no change in entropy occurs. After completion of the cycle, the working substance of the

Carnot engine returns to its original state and need not be considered further.
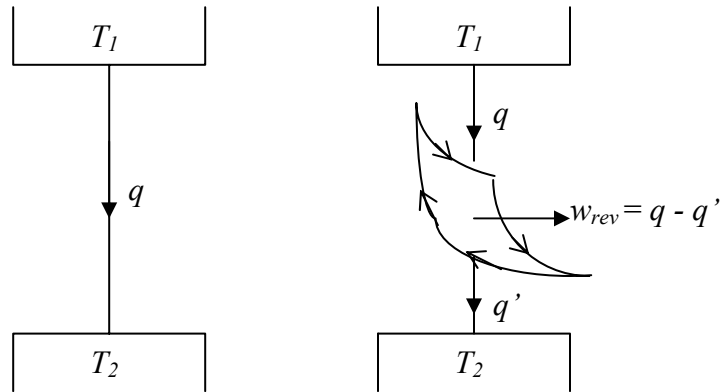
The difference $q - q' = q\left(1 - \dfrac{T_2}{T_1}\right)$ has been converted into work, e.g. a weight has been raised, and to get to the final state of the spontaneous heat flow process this energy should be dissipated at T_2, producing an amount of entropy

$$\Delta S_t = \frac{w_{diss}}{T_2} = \frac{q - q'}{T_2} = \frac{q}{T_2} - \frac{q}{T_1}$$

which is > 0 only if $T_2 < T_1$. This result confirms the well-known fact that heat will only flow spontaneously from a hotter to a colder body.

Alternatively, one could write ΔS_t as $\Delta S_1 + \Delta S_2 = \Delta(S_1 + S_2)$ where $\Delta S_1 = -q/T_1$ represents the entropy loss of reservoir T_1 and $\Delta S_2 = +q/T_2$ the entropy gain of reservoir T_2, which reconfirms the important fact that S is an extensive, that is, additive, quantity. Apparently, this remains true even if T is not uniform.

At this point, it may be instructive to mention an alternative approach to the entropy concept, which uses the fact that matter is actually composed of atoms and molecules (It should be stressed that throughout the preceding discussion there never was any need for this assumption!). This formulation is due to L. Boltzmann, who proposed that

$$S = k \ln W$$

where $k = R/L$ (L = Avogadro's constant) is called the Boltzmann constant, and W is the number of microstates ("complexions") that are compatible with a given macrostate.
This formula provides the basis for the development of Statistical Thermodynamics. The appearance of a logarithm can be justified by considering a combination of two systems, with numbers of complexions W_1 and W_2, say. The total number of microscopic realisations is then $W = W_1 W_2$, so that the total entropy equals

$$S = k \ln W = k \ln(W_1 W_2) = k \ln W_1 + k \ln W_2 = S_1 + S_2$$

Thus it is seen that the logarithm ensures the additivity property of S, and it is in fact the only way in which this can be realised. Increase of entropy in a spontaneous process is now interpreted in a statistical sense as the system striving to a state with maximum W, or, loosely speaking, maximum "disorder". It should be emphasized that this is a "global" property of entropy: Locally, entropy may actually decrease, but this decrease must always be offset by a (larger) increase in the entropy of the surroundings. This is exactly what happens in living organisms, which possess a high degree of order, or "self-organisation", which feeds on the entropy production in the environment via the intake of low-entropy nutrients and excretion of high-entropy waste products (including heat).

II.2 Further consequences of the Second Law. Free energy.

As stated in the previous section, a system and its surroundings ("atmosphere") combine to form an isolated system for which always $dS_t \geq 0$. Yet, it may be possible to reformulate the Second Law in terms of properties of the system alone in a manner that depends on how the system (which will be assumed *closed* throughout the following discussion) interacts with its surroundings. Several possibilities exist, and the two most important cases will be dealt with next.
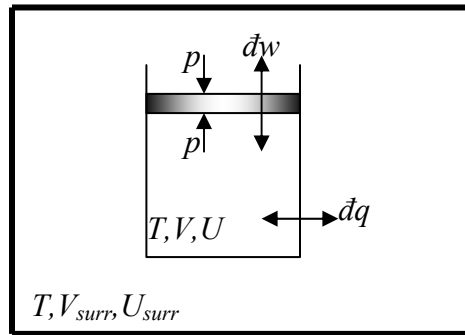
A very common situation is that in which the system is contained in a vessel equipped with a freely movable piston (or something to the same effect) and diathermal walls, allowing mechanical and thermal equilibrium to be established with its surroundings, i.e. p and T are uniform. System and surroundings can exchange heat and pV work only, subject to the constraints

$$dU_{surr} = -dU \quad \text{and} \quad dV_{surr} = -dV$$

If no irreversibility occurs in the surroundings we may write for an arbitrary small change of state

$$dU_{surr} = TdS_{surr} - pdV_{surr}$$

and

$$dS_t = dS + dS_{surr} \geq 0$$

which, after substitution for dS_{surr}, can also be written as

$$dS_t = dS - \frac{dU + pdV}{T} = -\frac{dU + pdV - TdS}{T} \geq 0$$

Since in the present case T and p are constants the inequality can be reorganised to

$$dS_t = -\frac{d(U + pV - TS)_{T,p}}{T} = -\frac{(dG)_{T,p}}{T} \geq 0$$

hence

$$(dG)_{T,p} \leq 0$$

where we have defined the *Gibbs (free) energy* of the *system* as

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

Thus, the Second Law implies that during a spontaneous isobaric/isothermal change in a closed system the Gibbs energy always *decreases*. This continues until G reaches a minimum as the system settles in its equilibrium state. This is represented schematically in the figure (α could be any parameter characterising the state of the system, for example a measure for the progress of a chemical reaction; see Ch. VI).
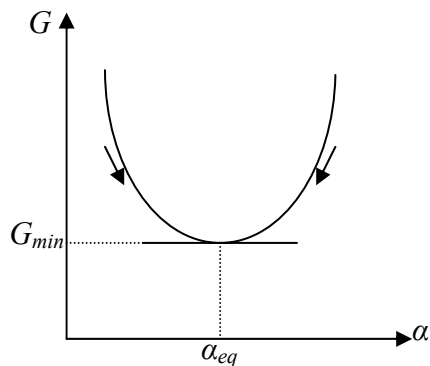
As a consequence,

$$(\delta G)_{T,p} = 0$$

for arbitrary infinitesimal excursions from the state of minimum G, as symbolised by δ (this symbol is used rather than d to indicate that these are *virtual*, as opposed to *actual* changes). Elaboration of this equation then leads to the *equilibrium conditions*. Examples will be given in subsequent chapters.

A second case of practical interest is that where the system is contained in a rigid vessel (constant V, e.g. a bomb calorimeter) and is only in thermal contact with the surroundings, so T is uniform. Following a similar argument as in the previous paragraph, we may now write

$$dU_{surr} = -dU \ , \quad dV = dV_{surr} = 0$$

hence $dU_{surr} = TdS_{surr}$ and

$$dS_t = dS + dS_{surr} = dS - \frac{dU}{T} = -\frac{dU - TdS}{T} \geq 0 \ \text{ if } \ T \text{ and } V \text{ are constant}$$

Equivalently,

$$d(U - TS)_{T,V} \leq 0$$

or

$$(dA)_{T,V} \leq 0$$

defining the *Helmholtz (free) energy* of the *system* as

$$A = U - TS$$

Under the present conditions, a system undergoing a spontaneous change strives to minimise its Helmholtz energy until, in equilibrium,

$$(\delta A)_{T,V} = 0$$

where δ has the same meaning as before. The equilibrium conditions that follow from this equation are identical to the ones that follow from $(\delta G)_{T,p} = 0$. Note that both G and A are extensive functions of state, i.e. the total G (or A) of a system equals the sum of the G's (or A's) of its parts if T and p (or just T in the case of A) are uniform.
In particular, for n moles of a homogeneous substance we can write $G = n\overline{G}(T, p)$ and $A = n\overline{A}(T, p)$, or $G = G(T, V)$, $A = A(T, V)$, etc.

N.B.: The above inequalities could also have been derived more directly via substitution of Clausius' inequality for the *system* into the First Law expression

$$dU = đq - pdV \leq TdS - pdV$$

This inequality immediately gives rise to $(dG)_{T,p} \leq 0$ if T and p are constant, and $(dA)_{T,V} \leq 0$ at constant T and V. Admittedly, this is a much more economical method than the somewhat circuitous argument presented above. However, the latter is more instructive as it brings out the role of the surroundings explicitly.

Because of their tendency to attain a minimum, functions like G and A are sometimes called *thermodynamic potentials*, by analogy with potentials in the theory of mechanics. The condition of minimum free energy bears out the fact that a thermodynamic equilibrium is always the result of a compromise between two opposing tendencies. Firstly, the system tends to settle in a state of lowest (potential) energy, while on the other hand the randomising effect of the thermal motion of the molecules at finite T leads to occupation of higher energy states and increased entropy. This is the reason why S appears with a "weight factor" T.

II.3 Miscellaneous results. Mathematical aspects of Thermodynamics.

For an arbitrary *reversible* change in the state of a *closed* system the accompanying change in Gibbs energy may be written as

$$dG = d(U - TS + pV) = dU - TdS - SdT + pdV + Vdp$$

Substituting $dU = TdS - pdV$ this simplifies to the following important differential relation

$$dG = -SdT + Vdp$$

Analogously, the corresponding change in A is

$$dA = d(U - TS) = dU - TdS - SdT$$

or

$$dA = -SdT - pdV$$

The expressions for dU, dG and dA share the same mathematical form which is that of the differential of a function $f(x,y)$ of two *independent* variables,

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

Each partial derivative is itself a function of x and y.

If U is regarded as a function of S and V, its partial derivatives can be identified from the above formula for dU as

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

Likewise we find

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \;,\; \left(\frac{\partial G}{\partial p}\right)_T = V \;,\; \left(\frac{\partial A}{\partial T}\right)_V = -S \;,\; \left(\frac{\partial A}{\partial V}\right)_T = -p$$

Of course, one can always construct higher order derivatives like $(\partial^2 f / \partial x^2)_y$, $(\partial^2 f / \partial y^2)_x$ or mixed derivatives like $\dfrac{\partial^2 f}{\partial y \partial x} \equiv \left(\dfrac{\partial}{\partial y}\right)_x \left(\dfrac{\partial f}{\partial x}\right)_y$ and $\dfrac{\partial^2 f}{\partial x \partial y} \equiv \left(\dfrac{\partial}{\partial x}\right)_y \left(\dfrac{\partial f}{\partial y}\right)_x$.

An important theorem of calculus states that the order of differentiation in mixed derivatives has no effect on the outcome, thus

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

When applied to the function $U(S,V)$, for example, this means that

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

or, using the results for $(\partial U / \partial V)_S$ and $(\partial U / \partial S)_V$ given above,

$$-\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

This procedure is called "cross-differentiation" and the type of thermodynamic relationship that is obtained in this manner is known as a *Maxwell relation*. The validity of such formulae ultimately rests on the fact that S is a state variable.

Similarly, application of this theorem to dG and dA produces two more Maxwell relations, *viz.*

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

respectively, where the right-hand sides can be evaluated from a knowledge of the equation of state.

For example, for one mol of an ideal gas $\overline{S}$ can be regarded as a function of p and T, with differential

$$d\overline{S} = \left(\frac{\partial \overline{S}}{\partial p}\right)_T dp + \left(\frac{\partial \overline{S}}{\partial T}\right)_p dT = -\left(\frac{\partial \overline{V}}{\partial T}\right)_p dp + \frac{\overline{C}_p}{T} dT = -Rd\ln p + \overline{C}_p d\ln T$$

where, in the second equality, we have used a Maxwell relation and the definition of $\overline{C}_p$.

In the last step, the fact was used that, for an ideal gas, $(\partial \overline{V} / \partial T)_p = R / p$.

Integrating this differential expression leads to the following functional form of the molar entropy of a perfect gas in terms of p and T:

$$\overline{S}(p,T) = \overline{S}_0 - R\ln p + \overline{C}_p \ln T$$

with $\overline{S}_0$ an integration constant.

An important corollary to the above equations for the partial derivatives of G is obtained by differentiating the function G/T with respect to T while keeping p constant:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2} = -\frac{G+TS}{T^2} = -\frac{H}{T^2}$$

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

which tells us that H can be obtained from a knowledge of the function $G = n\overline{G}(T,p)$ (dividing the equation on both sides by the constant n gives the molar enthalpy $\overline{H}$).

This expression is known as the *Gibbs-Helmholtz equation.*

It may be observed from the foregoing that G can be used, in principle, to "generate" all other state functions such as S, V, H, $U = H - pV$, $A = G - pV$, C_V and C_p by simple differentiation with respect to T or p.

III. PHASE EQUILIBRIA OF A PURE SUBSTANCE.

The system under consideration is a fixed amount (n moles) of a single chemical component (e.g. water), distributed between two phases in equilibrium: liquid (L) and vapour (V), say, and contained in a cylinder with freely movable piston. The cylinder plus contents are maintained at ambient pressure p and temperature T (the latter through a thermal contact with a heat reservoir).

The general principles of Thermodynamics will now be brought to bear on this two-phase equilibrium.

Two conditions for phase equilibrium are immediately obvious: *Thermal equilibrium* between L and V requires that $T_L = T_V = T$ (for otherwise heat would flow spontaneously between L and V, leading to a further increase in $S_t = S_L + S_V + S_{surr}$).

Likewise, *mechanical equilibrium* is ensured if $p_L = p_V = p$. If this were not the case, the pressure difference could be utilised to perform work which, when dissipated, would also generate entropy.
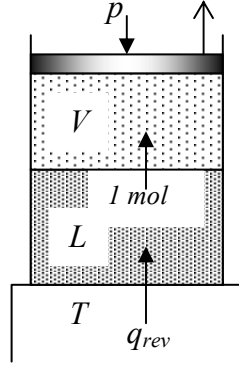
Still, this is not enough to ensure phase equilibrium. This is a *dynamic* equilibrium for which: rate of evaporation from L = rate of condensation from V.

To see how Thermodynamics deals with this, imagine a *reversible* process in which one mol of liquid is transferred to the vapour phase by slowly raising the piston while simultaneously absorbing heat q_{rev} from the reservoir. For this closed system the energy balance can be put in the form

$$\Delta \overline{U} = T\Delta \overline{S} - p\Delta \overline{V}$$

where $\Delta \overline{U} = \overline{U}_V - \overline{U}_L$, $\Delta \overline{S} = \overline{S}_V - \overline{S}_L$, $\Delta \overline{V} = \overline{V}_V - \overline{V}_L$ (since one mol of liquid is replaced by one mol of vapour at the same T and p).

$\overline{U}, \overline{S}, \overline{V}$ are molar quantities with a different functional dependence on T and p for L and V phases. Note that the energy balance may also be written as

$$(\Delta \overline{H}_{vap})_p = T\Delta \overline{S} (= q_{rev})$$

which defines the *latent heat* or *molar enthalpy of vaporisation*.

Substitution for $\Delta \overline{U}, \Delta \overline{S}, \Delta \overline{V}$ and subsequent rearrangement leads to the sought condition of *material equilibrium*

$$\overline{U}_V + p\overline{V}_V - T\overline{S}_V = \overline{U}_L + p\overline{V}_L - T\overline{S}_L$$

or

$$\overline{G}_V(T, p) = \overline{G}_L(T, p)$$

Henceforth, a different symbol for the molar Gibbs energy $\overline{G}$ will be used: μ, which is termed the *chemical potential*. Thus the above condition becomes

$$\mu_V(T, p) = \mu_L(T, p)$$

This is an equation in terms of T and p, which could be solved, in principle, to give p as a function of T, where p is the *saturation pressure*: $p_{sat}(T)$ at a given T.
In the *p-T* plane, or *phase diagram*, this relationship defines a *coexistence line* for L/V equilibrium.
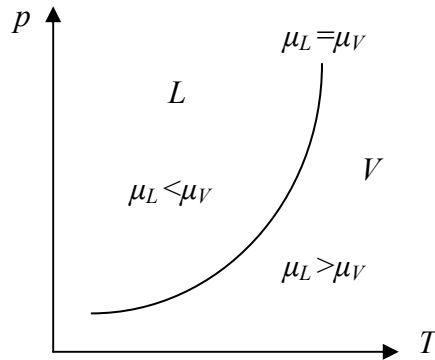
An alternative approach to the problem of material equilibrium is based on the fact that the G of a closed system is at a minimum if p and T are held fixed: $(\delta G)_{T,p} = 0$, and may serve to illustrate the use of this minimum principle.
G can be written alternatively as

$$G = G_L + G_V = n_L \mu_L + n_V \mu_V$$

where, in the first equation, use is made of the fact that G is an extensive function of state, and in the second the definition of μ has been used ($n_{L,V}$ = number of moles in L and V phases). The infinitesimal variation δ is conceived of as the transfer of a small amount δn_V moles from L to V, such that $\delta n_L = -\delta n_V$ (since in this closed system $n = n_L + n_V$ = constant). Noting that μ_L and μ_V are both constant during this change, because T and p are constant, the effect on G is given by

$$(\delta G)_{T,p} = (\mu_V - \mu_L)\delta n_V$$

and for this to be $= 0$ we obviously need $\mu_L = \mu_V$.
The formula for δG also contains some information about the fate of non-equilibrium states, like when T and p are uniform but $\mu_L \neq \mu_V$. If $\mu_L > \mu_V$ then $(dG)_{T,p} = (\mu_V - \mu_L)dn_V < 0$ if $dn_V > 0$, i.e. *G decreases* if liquid evaporates, which will therefore occur spontaneously and continues until all liquid has been converted to vapour.

This situation arises for (T, p) combinations below the saturation curve in the diagram; here, V is more stable than L. Conversely, above this curve, $\mu_L < \mu_V$ and so L is the more stable phase. Thus, the $p_{sat}(T)$ curve divides the p-T plane into stability regions. This example is illustrative of a more general principle which states that whenever μ is not uniform, matter will flow spontaneously from places with the higher to places with the lower μ (hence the name: chemical *potential*).
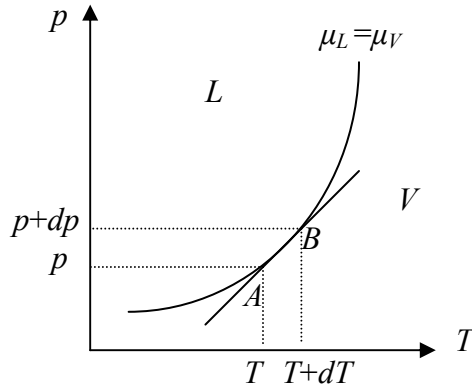
Now let us return to the coexistence curve and see what general conclusions may be drawn regarding its functional form. To this end, suppose that the system moves from point A with coordinates T and p to a nearby point B, also on the curve, at $T + dT$, $p + dp$. Since equilibrium is maintained it is obviously true that $d\mu_L = d\mu_V$ for this change of state. From earlier mathematical considerations it follows that a small change in $\mu_{L,V} = G_{L,V} / n_{L,V}$ consequent upon small variations of T and p is given as

$$d\mu_{L,V} = -\overline{S}_{L,V} dT + \overline{V}_{L,V} dp$$

Substituting this into the above equation yields the relationship

$$-\overline{S}_L dT + \overline{V}_L dp = -\overline{S}_V dT + \overline{V}_V dp$$

or, equivalently,

$$\left(\frac{dp}{dT} \right)_{sat} = \frac{\overline{S}_V - \overline{S}_L}{\overline{V}_V - \overline{V}_L} = \frac{\Delta\overline{S}}{\Delta\overline{V}}$$

which can also be written as

$$\left(\frac{dp}{dT} \right)_{sat} = \frac{\Delta\overline{H}_{vap}}{T\Delta\overline{V}}$$

This is the *Clausius-Clapeyron equation,* which relates the slope of the tangent to the p_{sat} vs. *T* curve at each point to the volume and latent heat of vaporisation at the same point. It applies generally to so-called *first-order phase transitions*, i.e. those with $\Delta \overline{S} \neq 0$ and $\Delta \overline{V} \neq 0$, which is the case for most phase equilibria of chemical interest.
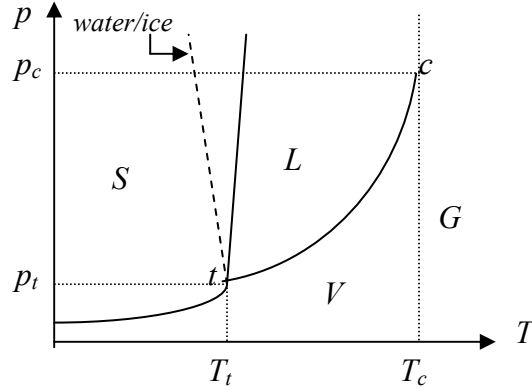
What has been said about the L/V equilibrium applies equally to solid/liquid (S/L) and solid/vapour (S/V) equilibria. For each case, a Clausius-Clapeyron equation can be formulated with $\Delta \overline{H}_{vap}$ replaced by the latent heat of *fusion* ($\Delta \overline{H}_{fus}$) and *sublimation* ($\Delta \overline{H}_{sub}$), respectively, and similarly for the molar volumes of transformation. These equilibria are also represented by coexistence lines in a *p-T* diagram. The three curves meet at one point, the *triple point, t(T_t, p_t)*, where all three phases coexist. Two equilibrium conditions,

$$\mu_L(T_t, p_t) = \mu_V(T_t, p_t) = \mu_S(T_t, p_t)$$

should be obeyed simultaneously at this point, which determine its position unambiguously (for water, $T_t \cong 298K$, $p_t = 6 \times 10^{-3} atm$).

Another important feature of a *p-T* diagram is the *critical point* (*c*), which marks the temperature T_c above which vapour can no longer be condensed, no matter how high the applied pressure. Only a homogeneous gas phase (G) can exist for $T > T_c$.

For most substances, the coexistence lines have positive slopes. A notable exception is water, where the melting line has a negative slope because $\Delta \overline{V}_{fus} < 0$ (ice has a lower density than water, that is why it floats), so that increasing the pressure on ice at constant *T* will eventually cause it to melt. This can be explained as being the result of the collapse of the diamond-like ice structure to form water, which is more compact. Explicit formulas for the vapour and sublimation lines can be obtained if the vapour is assumed to behave approximately as an ideal gas, so that $\overline{V}_V \cong RT / p_{sat}$ while furthermore the fact that $\overline{V}_V \gg \overline{V}_L, \overline{V}_S$ allows $\Delta \overline{V}$ to be approximated by $\overline{V}_V$. Substitution into the Clausius-Clapeyron equation gives

$$\frac{dp_{sat}}{dT} = \frac{p_{sat}\Delta\overline{H}}{RT^2}$$

Rearranging,

$$\frac{dp_{sat}}{p_{sat}} = \frac{\Delta\overline{H}}{R}\frac{dT}{T^2}$$

which is equivalent to

$$\frac{d\ln p_{sat}}{d(1/T)} = -\frac{\Delta\overline{H}}{R}$$

If $\Delta\overline{H}_{vap}$ or $\Delta\overline{H}_{sub}$ can be regarded as constant (this is often a good approximation within a broad range of temperatures), this result implies that a plot of $\ln p_{sat}$ vs. $1/T$ should produce a straight line with negative slope $-\Delta\overline{H}/R$.

If $\Delta\overline{H}_{vap}, \Delta\overline{H}_{sub}$ and $\Delta\overline{H}_{fus}$ are constant, knowledge of any two of them allows the third to be calculated based on the argument that, at the triple point, sublimation of 1 mol of solid can either take place directly or proceed in two steps, namely as melting followed by evaporation:

$$1\ mol\ S \rightarrow 1\ mol\ L \rightarrow 1\ mol\ V$$
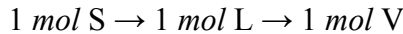
The net $\Delta\overline{H}$ is the same in each case (Hess' law), therefore

$$\Delta\overline{H}_{sub} = \Delta\overline{H}_{fus} + \Delta\overline{H}_{vap}$$

It should be pointed out that the phase diagram by itself does not contain sufficient information to help us understand the *process* of phase transformation. It often happens that a phase transition does not occur when one would expect it based on the phase diagram: A liquid may persist in a metastable *superheated* or *supercooled* state, or a vapour may be cooled below the boiling point without condensing (*supersaturated vapour*). These phenomena occur because a new phase never appears in bulk form all at once, but rather emerges from the "parent" phase in the form of small bubbles, crystals or droplets which initially have a high, energetically unfavourable, area-to-volume ratio. The result is that a relatively high surface (free) energy creates a *nucleation barrier* against the onset of phase transformation, an effect that we have hitherto neglected. This barrier may be overcome by agitation or by "seeding", i.e. providing a rough surface to kick-start the nucleation of the new phase (for instance, this is the reason for adding solid chips to a liquid prior to boiling, so as to prevent overheating and "bumping"). Otherwise, nucleation is a purely random ("stochastic") process.

IV. THERMODYNAMICS OF OPEN SYSTEMS.

IV.1 Homogeneous one-component system.

Next, the restriction n = constant will be dropped. The effect on G of an arbitrary reversible variation in the state of a homogeneous pure substance, that is, of a change in the parameters T, p and n, can be found most easily starting from the definition of μ,

$$G = n\mu(T, p)$$

from which we derive

$$dG = d(n\mu) = nd\mu + \mu dn = n(-\bar{S}dT + \bar{V}dp) + \mu dn$$

hence

$$dG = -SdT + Vdp + \mu dn$$

If n = constant (dn = 0), this expression simplifies to the familiar result for a closed system. If T, p constant, $dG = \mu dn$, which is a formula that we used earlier when discussing phase equilibria (remember that each phase by itself is to be regarded as an open system since it can exchange matter with the other phase!).

Corresponding formulas for dU and dA can be easily derived using their definitions:

$$dU = d(G + TS - pV) = dG + TdS + SdT - pdV - Vdp$$

from which follows, after substitution for dG,

$$dU = TdS - pdV + \mu dn$$

Similarly we find

$$dA = -SdT - pdV + \mu dn$$

In each case, an extra term μdn is added to the corresponding expression for a closed system.

From the above equations, three alternative (but equivalent) expressions for μ can be formulated:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = \left(\frac{\partial U}{\partial n}\right)_{S,V} = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

Of these, the third is the least useful and will not be considered further. Based on the form of dU, the new term μdn can be interpreted as a contribution involving the

reversible work of inserting *dn* moles into the phase at constant *V* and *S*. This raises a rather subtle issue of physical interpretation: How does one keep *S* constant while adding molecules? And what is the energy carried into the system by these molecules? The only way out of this problem is to define a reference state for the type of molecule under consideration, with $U \equiv 0$ and $S \equiv 0$. This point will not be pursued further, however, as it will be of little or no consequence to subsequent discussions and applications. This is especially so since, in practice, only chemical potential *differences* have physical significance. As an example, the condition for L/V phase equilibrium given in the previous chapter could be written as $\mu_V - \mu_L = 0$.

IV.2 Homogeneous mixtures.

The results of the preceding section can be readily extended to the case of a homogeneous mixture of *C* components for which the differentials *dU* and *dG*, corresponding to reversible changes, are now written as

$$dU = TdS - pdV + \sum_{i=1}^{C} \mu_i dn_i$$

and

$$dG = -SdT + Vdp + \sum_{i=1}^{C} \mu_i dn_i$$

respectively, defining the chemical potential for each constituent alternatively as

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_{j \neq i}}$$

or as

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} \equiv \overline{G}_i$$

The latter definition expresses μ_i as the so-called *partial molar Gibbs energy* of component i. Chemical potentials are *intensive* functions of state, depending on *T*, *p* and the composition of the mixture, expressed in terms of a suitable set of concentration variables. The natural choice for thermodynamic purposes is the set of *mol fractions*, $x_i = n_i / \sum_{j=1}^{C} n_j$, which obviously obey the condition $\sum_{i=1}^{C} x_i = 1$, i.e. only $C-1$ of them can be chosen independently. Together with *T* and *p* they constitute $C+1$ independent

intensive variables (provided that the mixture is non-reactive) or *degrees of freedom* (d.f.). We can therefore write formally

$$\mu_i = \mu_i(T, p, x_1, ..., x_{C-1}) \qquad (i = 1, 2, ..., C)$$

The reason why μ_i is sometimes referred to as a partial molar Gibbs energy will now be explained. We imagine the mixture to be formed by a process of successive addition of small amounts dn_i to an (initially empty) container in which constant T and p are maintained in the usual manner (thermostat T, external atmosphere p, movable piston). After each such addition, the increment of G equals

$$(dG)_{T,p} = \sum_i \mu_i dn_i$$

If these dn_i are added in ratios that reflect the mol ratio in the final mixture, i.e.

$$dn_1 : dn_2 : ... : dn_C = n_1 : n_2 : ... : n_C$$

then throughout this process not only T and p but also all the x_j, and hence the μ_i, remain constant. Thus, the total Gibbs energy can be evaluated by simple integration

$$G = \int_0^G dG = \int \sum_i \mu_i dn_i = \sum_i \mu_i \int_0^{n_i} dn_i = \sum_i n_i \mu_i$$

The reason for naming μ_i the "partial molar Gibbs energy of component i" should now be clear. Thus, we have two alternative expressions for G:

$$G = U - TS + pV = \sum_i n_i \mu_i$$

Correspondingly, for an arbitrary (reversible) change of state, dG can be expressed in two different ways:

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$

$$= d\left(\sum_i n_i \mu_i\right) = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$$

from which immediately follows one of the most important equations of chemical Thermodynamics,

$$-SdT + Vdp = \sum_i n_i d\mu_i$$

the so-called *Gibbs-Duhem relation* which tells us that, in a homogeneous mixture, the intensive variables T, p and the C μ_i's can not be varied independently but that any change in $C+1$ of them automatically fixes the last one. This is of course consistent with the previously established fact that the system possesses $C+1$ d.f.

It is important to realise that the argument which led to the new formula for G was very general and could have been applied to *any* extensive quantity $X = U, V, S, A, H, C_V$ or C_p, each one of these being a function of the variables $T, p, n_1, n_2,\ldots, n_C$. Thus,

$$(dX)_{T,p} = \sum_i \overline{X}_i dn_i$$

where

$$\overline{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

(an intensive quantity) is the partial molar energy, volume, entropy,…
Integration yields, as before,

$$X = \sum_i n_i \overline{X}_i$$

In the special case of a *binary* mixture of molecules A and B we get

$$(dX)_{T,p} = \overline{X}_A dn_A + \overline{X}_B dn_B$$

At the same time, since

$$X = n_A \overline{X}_A + n_B \overline{X}_B$$

we also have that

$$dX = \overline{X}_A dn_A + \overline{X}_B dn_B + n_A d\overline{X}_A + n_B d\overline{X}_B$$

and therefore

$$n_A d\overline{X}_A + n_B d\overline{X}_B = 0 \quad (T, p \text{ constant})$$

which is a generalised form of the Gibbs-Duhem relation with $dT = dp = 0$. At T, p constant, any change in $\overline{X}_{A,B}$ can only result from a change in composition $x_A \equiv x$ ($\therefore x_B = 1-x$). We now define $\overline{X} = X /(n_A + n_B)$, which is then also equal to
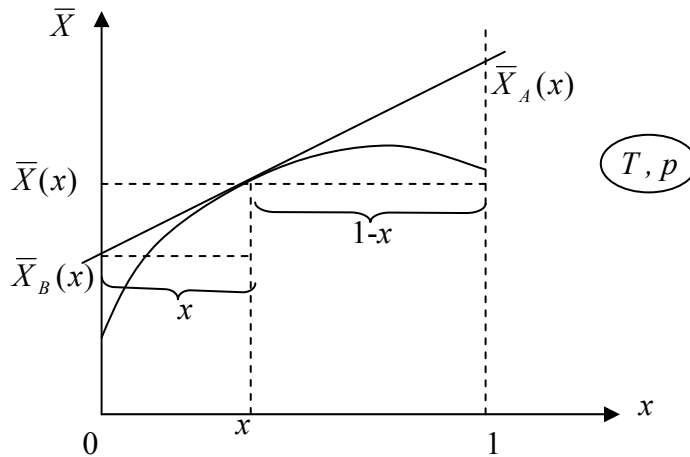
$$\overline{X} = x\overline{X}_A + (1-x)\overline{X}_B$$

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whence, $d\overline{X} = (\overline{X}_A - \overline{X}_B)dx + xd\overline{X}_A + (1-x)d\overline{X}_B$, where the last two terms add up to zero on account of the Gibbs-Duhem relation, so that

$$\frac{d\overline{X}}{dx} = \overline{X}_A - \overline{X}_B$$

From these last two equations, $\overline{X}_A$ and $\overline{X}_B$ can be solved formally in terms of $\overline{X}$ and $d\overline{X}/dx$:

$$\overline{X}_A = \overline{X} + (1-x)\frac{d\overline{X}}{dx}$$

$$\overline{X}_B = \overline{X} - x\frac{d\overline{X}}{dx}$$

If $\overline{X}$ is plotted as a function of x, $\overline{X}_A(x)$ and $\overline{X}_B(x)$ may be found from the graph by drawing the tangent to the curve at the point $(x, \overline{X}(x))$, which has a slope $d\overline{X}/dx$, and evaluating its intercept with the vertical lines $x = 1$ and $x = 0$, respectively. In this manner one could, for example, obtain partial molar volumes from the experimental $\overline{V}$ vs. x relationship, or if $X = G$, the intercepts would yield μ_A and μ_B as functions of x.
This graphical technique is appropriately called the *method of intercepts*.

IV.3 General properties of the μ_i.

Since we now have two alternative expressions for G, its partial derivative with respect to T at constant p and $\{n_j\}$ can be written in two forms:

$$\left(\frac{\partial G}{\partial T}\right)_{p,\{n_j\}} = -S = -\sum_i n_i \overline{S}_i$$

as well as

$$\left(\frac{\partial G}{\partial T}\right)_{p,\{n_j\}} = \sum_i n_i \left(\frac{\partial \mu_i}{\partial T}\right)_{p,\{x_j\}}$$

The n_j are arbitrary, so comparison of the right-hand sides of the above equations gives

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\{x_j\}} = -\overline{S}_i$$

Similarly, by taking the p-derivative of the two forms of G, we obtain

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{x_j\}} = \overline{V}_i$$

It is worthy of notice that these relationships could also have been derived from

$$dG = -SdT + Vdp + \sum_k \mu_k dn_k$$

by cross-differentiation between the $-SdT$ and $\mu_i dn_i$ terms and the Vdp and $\mu_i dn_i$ terms, respectively, so that the above formulae can in fact be regarded as examples of Maxwell relations (Section II.3).

A general variation of μ_i can now be expressed in terms of the variations of its arguments, as follows

$$d\mu_i = -\overline{S}_i dT + \overline{V}_i dp + \sum_{j=1}^{C-1} \left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,p,x_{k \neq j}} dx_j \qquad (i=1,...,C)$$

which is an obvious generalisation of the equation $d\mu = -\overline{S}dT + \overline{V}dp$ for a one-component system ($x = 1$).

Substitution of this formula for $d\mu_i$ in the Gibbs-Duhem relation, and division by $n = \sum_k n_k$, yields another perfectly general relationship

$$\sum_{i=1}^{C} x_i \sum_{j=1}^{C-1} \left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,p,x_{k \neq j}} dx_j = 0$$

This equation provides a strong criterion for the internal consistency with respect to the composition-dependence of any set of theoretical μ_i's.

V. HETEROGENEOUS MIXTURES: THE PHASE RULE.

We shall now generalise our treatment of mixtures to a consideration of a heterogeneous, but still non-reactive, system consisting of P phases. By a "phase" is meant a (part of a) system which is uniform in both composition and physical properties. For example, an aqueous solution that is saturated with two salts, like KCl and Na_2CO_3, both of which are present in excess, comprises a three-phase system with one liquid phase (the solution) and two solid phases (the excess KCl and Na_2CO_3) in equilibrium with each other.

In Chapter IV we have dealt exhaustively with the Thermodynamics of individual phases. The question is now under what conditions the P phases containing C chemical components can coexist.

As before, thermal and mechanical equilibria require that T and p be the same in all of the P phases. Since the system as a whole is closed, the general criterion for equilibrium $(\delta G)_{T,p} = 0$ applies here. If components are indicated by subscripts i $(i = 1,...,C)$ and phases by bracketed superscripts (j) $(j = 1,...,P)$, the fact that the system is closed means that

$$\sum_{j=1}^{P} n_i^{(j)} \equiv n_i = \text{constant for } i = 1,...,C$$

The total Gibbs energy is

$$G = \sum_{j=1}^{P} G^{(j)}$$
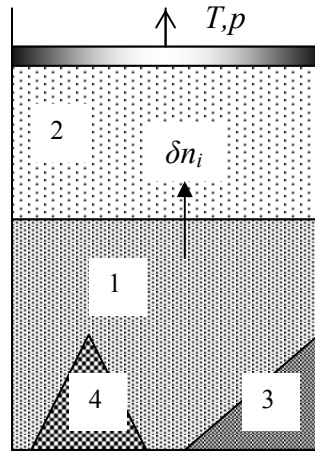
Imagine that the small virtual departure from equilibrium, δ, consists of a small amount δn_i of component i being transferred from phase (1) to phase (2), all other $n_k^{(j)}$ remaining constant (see figure, where $P = 4$ with phase (1) a liquid, (2) a vapour and two solid phases, (3) and (4)). The variation only affects $G^{(1)}$ and $G^{(2)}$, with $\delta G^{(1)} = -\mu_i^{(1)} \delta n_i$ and $\delta G^{(2)} = \mu_i^{(2)} \delta n_i$, hence

$$(\delta G)_{T,p} = \delta G^{(1)} + \delta G^{(2)} = (\mu_i^{(2)} - \mu_i^{(1)})\delta n_i$$

which $= 0$ only if $\mu_i^{(1)} = \mu_i^{(2)}$. The same argument can be repeated for any pair of phases, leading to the following conditions for material equilibrium,

$$\mu_i^{(j)} = \mu_i, \text{ independent of } j \ (i = 1,...,C)$$

Written out in full, the equilibrium conditions are

T, p uniform
$$\mu_1^{(1)} = \mu_1^{(2)} = ... = \mu_1^{(P)}$$
$$\mu_2^{(1)} = \mu_2^{(2)} = ... = \mu_2^{(P)}$$
$$\vdots \qquad\qquad \vdots$$
$$\mu_C^{(1)} = \mu_C^{(2)} = ... = \mu_C^{(P)}$$

Here, it has been tacitly assumed that each one of the C components is present in every phase, a situation that usually does not prevail in practice.

Now recall that $\mu_i^{(j)}$ is a function of the set of intensive variables $(T, p, x_1^{(j)},..., x_{C-1}^{(j)})$. The above conditions are therefore a set of equations relating a total of $2 + P(C-1)$ variables. For each component i there are $P-1$ independent equations (the number of $=$ signs in each line), so in all we have $C(P-1)$ equations. These are used to successively eliminate $C(P-1)$ of the $2 + P(C-1)$ variables (by expressing any one of them in terms of the remaining variables), thus leaving $2 + P(C-1) - C(P-1) = 2 + C - P$ *independent* intensive variables,

$$\therefore \quad F = 2 + C - P$$

F is called the *variance* (that is, the d.f.) of the system, i.e. the number of intensive variables that can be chosen arbitrarily while preserving the P-phase equilibrium.

This simple formula expresses the celebrated *phase rule* (J. Willard Gibbs, 1875).

If one component, i, is absent from one phase, (j), there is obviously one variable less to be considered, namely $x_i^{(j)}$. At the same time, we have to remove $\mu_i^{(j)}$ from the equations, so that their number is also less by one. Clearly, F is left unaffected by this and so the phase rule still applies even if not every component occurs in each phase.

Some examples:

(1) A homogeneous mixture has $P = 1$ and $F = C + 1$, as we saw before.

(2) One-component, two-phase system: $P = 2$, $C = 1$, and hence $F = 1$ (see Ch.III, where T was chosen as independent variable, which uniquely determines p_{sat}).

(3) One-component, three-phase equilibrium (L/V/S): $C = 1$, $P = 3$, $F = 0$ (triple point).

(4) Two-component, two-phase system (e.g. chloroform (x)/acetone $(1-x)$ mixture in equilibrium with its vapour): $C = 2$, $P = 2$, $F = 2$ (e.g. p and x_L determine T and x_V).

VI. CHEMICAL REACTIONS AND EQUILIBRIUM.

The final constraint left to be removed is that on the reactivity of homogeneous and heterogeneous mixtures. Formally, a reactive mixture is an *open* system in the thermodynamic sense, where certain components "appear" or "disappear" in fixed stoichiometric ratios.

Consider a chemical equilibrium of the form

$$v_A A + v_B B \rightleftharpoons v_C C$$
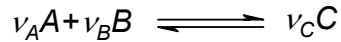
Suppose that the equilibrium is perturbed slightly by allowing $-\delta n_A = v_A \delta\alpha$ moles of A and $-\delta n_B = v_B \delta\alpha$ moles of B to react, producing $\delta n_C = v_C \delta\alpha$ moles of C. $\delta\alpha$ is a small change in a parameter α, which measures the advance of a reaction, away from its equilibrium value, α_{eq}. As T and p are held fixed, $(\delta G)_{T,p}$ should vanish for this virtual change. In this case, we have that

$$(\delta G)_{T,p} = \mu_A \delta n_A + \mu_B \delta n_B + \mu_C \delta n_C = (v_C \mu_C - v_A \mu_A - v_B \mu_B)\delta\alpha = 0$$

and therefore

$$\Delta G_{rxn} \equiv v_C \mu_C - v_A \mu_A - v_B \mu_B = 0$$

where we have defined the *Gibbs energy of reaction*, $\Delta G_{rxn} (\equiv$ minus the *chemical affinity*).

Note that the μ's no longer carry the phase superscripts since these are superfluous for a system in equilibrium. Consequently, the above equilibrium condition applies to homogeneous and heterogeneous chemical equilibria alike.

This equilibrium condition can be immediately generalised to any type of reaction and written as

$$\Delta G_{rxn} = \sum_r v_r \mu_r = 0$$

where r labels the participants in the reaction and the stoichiometric coefficients v_r are understood to be > 0 for "products" and < 0 for "reactants". Of course, in equilibrium it is entirely immaterial whether a set of reagents on one side of the arrows is designated as reactants or as products. The above equation is essentially the thermodynamic expression for the *law of mass action*.

If there are a number, say R, of *independent* chemical equilibria present simultaneously in a heterogeneous system of P phases and C components, the corresponding equilibrium conditions add a further R, algebraically independent, constraints to the $C(P-1)$ conditions for material equilibrium between phases. This reduces the variance F by R so that we finally get

$$F = 2 + C - R - P$$

which is the most general form of the phase rule.
As an example, consider the heterogeneous equilibrium

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

with $C = 3$, $P = 3$, $R = 1$, hence $F = 1$. The system is therefore *monovariant*, which means that p_{CO_2} is a unique function of T.

In a *non-equilibrium* reactive system, a reaction will only occur spontaneously in a given direction at the prevailing T and p if $(\Delta G_{rxn})_{T,p} < 0$ (for example, in a temporarily short-circuited galvanic cell). The accompanying changes in other thermodynamic properties can be readily obtained from the corresponding ΔG_{rxn} by means of the general relationships derived earlier, e.g. the entropy change of the reaction mixture is

$$\Delta S_{rxn} = -\left(\frac{\partial \Delta G_{rxn}}{\partial T}\right)_p = \sum_r \nu_r \overline{S}_r$$

while the enthalpy of reaction can be evaluated using the Gibbs-Helmholtz equation

$$\Delta H_{rxn} = -T^2 \left(\frac{\partial(\Delta G_{rxn}/T)}{\partial T}\right)_p = \sum_r \nu_r \overline{H}_r$$

In writing these formulae, it has been assumed that the extent of the conversion is such as to leave the mixture's composition $\{x_j\}$ practically unchanged.

N.B.: $T\Delta S_{rxn}$ is to be interpreted as the *reversible heat of reaction*, i.e. the heat absorbed by the mixture if the reaction were to proceed reversibly in some controlled manner while converting the free energy change $-\Delta G_{rxn}$ into useful (non-pV) work. This is what actually takes place in a reversibly operating galvanic cell, where electrical work is extracted from the reactants that are kept in separate compartments (half-cells).
Without this intervention, $-\Delta G_{rxn}$ is simply dissipated as heat, generating an amount of (universal) entropy equal to

$$\Delta S_t = \frac{w_{diss}}{T} = \frac{-\Delta G_{rxn}}{T} > 0$$

In that case, $\Delta H_{rxn} = \Delta G_{rxn} + T\Delta S_{rxn}$ represents the total amount of heat *absorbed* by the mixture during the spontaneous reaction. If $\Delta H_{rxn} > 0$ the reaction is *endothermic*, and *exothermic* if $\Delta H_{rxn} < 0$. If $\Delta H_{rxn} = 0$, the reaction is said to be *athermal*.

VII. MIXTURES OF PERFECT GASES.

VII.1 Thermodynamics of mixing. Chemical potentials.

The general results obtained in the previous chapters will now be applied to ideal gas mixtures. It should by now be clear that the most useful concept in Chemical Thermodynamics is the chemical potential, μ_i. Once the explicit dependence of the μ_i on T, p and the composition variables is known, all equilibrium thermodynamic properties of a mixture can be derived from its Gibbs energy $G = \sum_i n_i \mu_i$.

First, consider an ideal gas composed of molecules of a single chemical species, for which the p-dependence of $\mu(T, p)$ can be easily found from the relation

$$\left(\frac{\partial \mu}{\partial p} \right)_T = \overline{V} = RT / p$$

via integration between $p^\theta = 1$ *atm* and p *atm*:

$$\mu(T, p) - \mu^\theta (T) = RT \int_1^p \frac{dp}{p} = RT \ln p$$

or

$$\mu(T, p) = \mu^\theta (T) + RT \ln p$$

where $\mu^\theta (T)$ is the chemical potential at temperature T and at a "standard" pressure, arbitrarily chosen as 1 *atm*.
 Next, we shall investigate the effect of composition upon the μ_i in a binary gas mixture of molecular species A and B. To this end, the thermodynamics of the process of mixing will be dealt with in some detail.
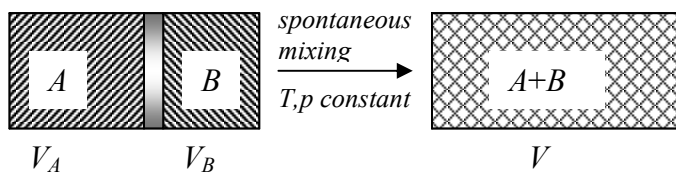
Suppose that n_A moles of A and n_B moles of B are initially kept separated in two compartments with volumes V_A and V_B by a freely movable diathermal partition, so that T and p are the same on both sides. The Gibbs energy in this initial state is then given by

$$G^* = n_A \mu_A * + n_B \mu_B *$$

where the asterisks refer to the gases in their pure form. When the partition is removed, the gases spontaneously interdiffuse until they form a uniform mixture with the same T and p as initially (because A and B are perfect gases), filling the volume $V = V_A + V_B$. Since neither the total energy U nor the total volume V change during the mixing process, we can write $\Delta U_{mix} = 0$ and $\Delta V_{mix} = 0$, and hence

$$\Delta G_{mix} = -T\Delta S_{mix}$$

The Gibbs energy in the final state is thus

$$G = G * + \Delta G_{mix} = G * - T\Delta S_{mix}$$

It is now left to evaluate the entropy of mixing, ΔS_{mix}. This is most easily accomplished by considering mixing as the result of two free expansions, one of gas A from V_A to V, and a second of gas B from V_B to V. The corresponding entropy changes have been calculated before, at the end of section II.1. This yields

$$\Delta S_{mix} = -n_A R \ln\left(\frac{V_A}{V}\right) - n_B R \ln\left(\frac{V_B}{V}\right)$$

Using the equation of state, the volume ratios can be rewritten as

$$\frac{V_A}{V} = \frac{n_A RT / p}{nRT / p} = \frac{n_A}{n} = x_A$$

where $n = n_A + n_B$, and similarly $V_B / V = x_B$. This gives

$$\Delta S_{mix} = -R(n_A \ln x_A + n_B \ln x_B) > 0$$

as well as

$$\Delta G_{mix} = RT(n_A \ln x_A + n_B \ln x_B) < 0 \qquad (T, p \text{ constant})$$

so that mixing is indeed spontaneous. This is always true for gases, for which $\Delta H_{mix} \cong 0$, but not necessarily for liquids. For example, water and oil do not mix at ordinary T because $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} > 0$ due mainly to the fact that $\Delta S_{mix} < 0$, as a result of increased ordering of the water molecules in the presence of hydrocarbons.

Of course, ΔS_{mix} is only $\neq 0$ if A and B are different, say if $A = N_2$ and $B = O_2$. If both compartments contain the same gas, O_2 say, it would not be reasonable to speak of mixing, even though individual O_2 molecules now have a larger volume, V, to move around in. From a macroscopic viewpoint, however, the initial and final states are indistinguishable and we should therefore set $\Delta S_{mix} = 0$ if $A = B$. This apparent failure of

the above formula is commonly referred to as the *Gibbs paradox*. Now, of course molecules are either identical or they are not, so there is no real problem in practice.

The formula for ΔS_{mix} may be readily generalised to mixtures of more than two components, as follows

$$\Delta S_{mix} = -R \sum_i n_i \ln x_i$$

while the Gibbs energy of the mixture can be written as

$$G = G^* - T\Delta S_{mix} = \sum_i n_i \mu_i^*(T, p) + RT \sum_i n_i \ln x_i$$
$$= \sum_i n_i \{\mu_i^*(T, p) + RT \ln x_i\}$$

According to the general theory of mixtures this is also equal to $G = \sum_i n_i \mu_i$. Comparison of these two expressions for G leads us to conclude that

$$\mu_i = \mu_i^*(T, p) + RT \ln x_i$$

It is important to note that the x-dependence of μ_i complies with the Gibbs-Duhem relation, as it should, for T, p constant. After division by $n = \sum_i n_i$ this equation becomes

$$\sum_i x_i d\mu_i = RT \sum_i x_i d \ln x_i = RT \sum_i \cancel{x_i} \frac{dx_i}{\cancel{x_i}} = 0$$

since $\sum_i dx_i = d\sum_i x_i = d(1) = 0$.

An alternative expression for μ_i is obtained after substitution of the explicit form $\mu_i^*(T, p) = \mu_i^\theta(T) + RT \ln p$ given at the beginning of this section, leading to

$$\mu_i = \mu_i^\theta(T) + RT \ln(x_i p)$$

Now, according to *Dalton's law* for a mixture of perfect gases,

$$p = \sum_i p_i = \sum_i n_i RT / V = nRT / V$$

from which it follows that the partial pressure exerted by component i equals

$$p_i = \frac{n_i RT}{V} = \frac{n_i}{n} \frac{nRT}{V} = x_i p$$

so that μ_i can be written simply as

$$\mu_i = \mu_i^\theta (T) + RT \ln p_i$$

(with p_i expressed in *atm*), a direct generalisation of the formula for $\mu_i * (x_i = 1)$.

VII.2 Chemical equilibrium in gas mixtures.

For the sake of argument, let us consider a gas-phase equilibrium of the form

$$v_A A + v_B B \rightleftharpoons v_C C$$
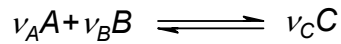
The general equilibrium condition ($\Delta G_{rxn} = 0$) reads as

$$v_A \mu_A + v_B \mu_B = v_C \mu_C$$

where we can now substitute the explicit expressions for the μ_r

$$v_A (\mu_A^\theta (T) + RT \ln p_A) + v_B (\mu_B^\theta (T) + RT \ln p_B) = v_C (\mu_C^\theta (T) + RT \ln p_C)$$

This is equivalent to

$$\ln \left(\frac{p_C^{v_C}}{p_A^{v_A} p_B^{v_B}} \right)_{eq} = -(v_C \mu_C^\theta - v_A \mu_A^\theta - v_B \mu_B^\theta) / RT$$

Defining the *standard Gibbs energy of reaction* as

$$\Delta G_{rxn}^\theta (T) = v_C \mu_C^\theta - v_A \mu_A^\theta - v_B \mu_B^\theta$$

and the *equilibrium constant K_p* as

$$K_p = \left(\frac{p_C^{v_C}}{p_A^{v_A} p_B^{v_B}} \right)_{eq}$$

which is a function of T only according to the above equation, the *law of mass action* thus takes the more concise form

$$\ln K_p (T) = -\Delta G_{rxn}^\theta (T) / RT$$

One arrives at another useful form of this equation after substituting $p_i = x_i p$,

$$K_p = \left(\frac{x_C^{\nu_C}}{x_A^{\nu_A} x_B^{\nu_B}} \right)_{eq} p^{\nu_C - \nu_A - \nu_B}$$

If we define $\Delta \nu = \nu_C - \nu_A - \nu_B$ (the change in the number of molecules if the reaction proceeds from left to right), and a new equilibrium constant K_x as

$$K_x = \left(\frac{x_C^{\nu_C}}{x_A^{\nu_A} x_B^{\nu_B}} \right)_{eq}$$

then the equilibrium constants are related as follows

$$K_x(T, p) = K_p(T) p^{-\Delta \nu}$$

or

$$\ln K_x(T, p) = \ln K_p(T) - \Delta \nu \ln p$$

The effect of temperature on the position of the equilibrium is established by taking the partial derivative $(\partial / \partial T)_p$ of $\ln K_x$:

$$\left(\frac{\partial \ln K_x}{\partial T} \right)_p = \frac{d \ln K_p}{dT} = -\frac{1}{R} \frac{d(\Delta G_{rxn}^\theta / T)}{dT} = \frac{\Delta H_{rxn}^\theta}{RT^2}$$

where, in the last step, use has been made of the Gibbs-Helmholtz equation, introducing the *standard enthalpy of reaction* ΔH_{rxn}^θ (pertaining to a mixture in which all reactants exert partial pressures $= 1$ *atm*). It is not hard to show, however, that ΔH_{rxn} only depends on T and not on the p_r. This is so, because at constant T, p: $\Delta H_{rxn} = \Delta U_{rxn} + p\Delta V_{rxn} = \Delta U_{rxn}(T) + \Delta \nu RT$, which is obviously independent of the p_r's. Therefore, $\Delta H_{rxn}^\theta(T) = \Delta H_{rxn}(T)$ where all $p_r = p_{r,eq}$, for example. Thus,

$$\left(\frac{\partial \ln K_x}{\partial T} \right)_p = \frac{\Delta H_{rxn}(T)}{RT^2}$$

which is the celebrated *Van't Hoff isobar*. In particular, it implies that if the reaction is endothermic going from left to right, i.e. $\Delta H_{rxn} > 0$, then K_x increases with increasing T, and *vice versa*. Hence, upon increasing temperature, a chemical equilibrium always shifts in the direction in which the reaction is endothermic. This result is consistent with a

general statement, known as *Le Châtelier's principle,* concerning the effect of an externally applied stress upon chemical equilibria.
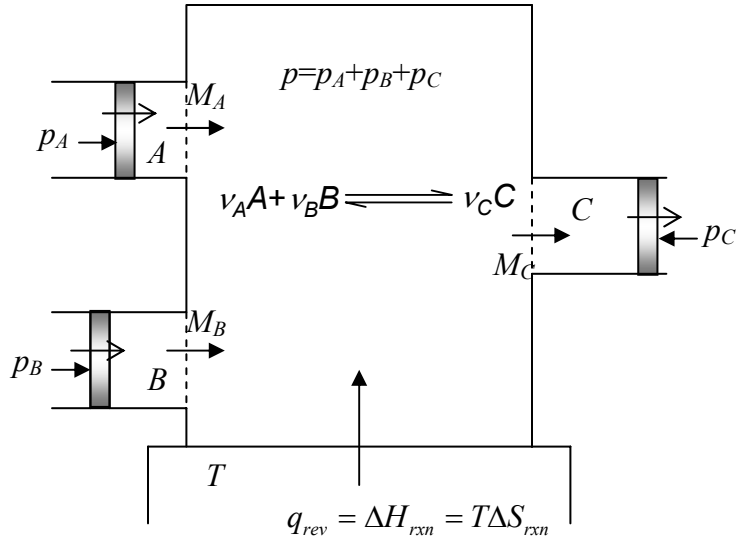
The heat of reaction ΔH_{rxn} for an equilibrium mixture may be measured using a *flow reactor,* which is basically a rigid vessel fitted with semi-permeable membranes M, one for each reactant (r), and cylinders containing the reactants/products as shown in the diagram. Note that ΔH_{rxn} is measured as *reversible heat*: $\Delta H_{rxn} = T\Delta S_{rxn} = q_{rev,rxn}$ because $\Delta G_{rxn} = 0$. The gases in the cylinders and in the reaction chamber will only be in equilibrium if μ_r is the same on both sides of membrane M$_r$, i.e. if $\mu_r = \mu_r^{\theta}(T) + RT\ln p_r$ is uniform, which means that each p_r should be uniform.

$\Delta H_{rxn}(T)$ is equal to the heat absorbed from the surroundings if the pistons are slowly pushed/pulled toward the right such as to supply v_A moles of A and v_B moles of B which (reversibly) react to produce v_C moles of C, which are subsequently drained off through membrane M$_C$.

The effect of pressure on the equilibrium is similarly found by taking the partial derivative $(\partial/\partial p)_T$ of $\ln K_x(T,p)$, which equals

$$\left(\frac{\partial \ln K_x}{\partial p}\right)_T = -\frac{\Delta v}{p} \quad (= -\frac{\Delta V_{rxn}}{RT})$$

This means that if $\Delta v < 0$, K_x will increase with increasing p, and the equilibrium shifts to the right, and *vice versa*. In other words, an increase in pressure will cause a shift towards the side with the smallest number of molecules. This is again in agreement with Le Châtelier's principle, which therefore turns out to be a logical consequence of the laws of Thermodynamics. If $\Delta v = 0$, the equilibrium is *indifferent* with respect to pressure changes.

VIII. LIQUID MIXTURES.

VIII.1 Ideal solutions.

VIII.1.1 Raoult's law. *p-x* and *T-x* diagrams.

A suitable starting point for a general discussion of solutions is a hypothetical mixture called an *ideal solution*, where the interaction forces between any pair of molecules (attractive Van der Waals-London forces) is taken to be independent of the chemical nature of the molecules. This situation is approximated in a benzene/bromobenzene mixture, for example, and holds nearly exactly for isotopic mixtures such as $^{12}CCl_4/^{13}CCl_4$.

Consider an ideal binary liquid mixture of compounds *A* and *B*, in equilibrium with its vapour. Both *A* and *B* are assumed to be volatile, and the vapour is approximately an ideal gas mixture with total pressure $p = p_A + p_B$.

As we saw before, this is a bivariant system ($F = 2$), so for specified *T* and *p* the compositions of liquid ($x_A^L, x_B^L = 1 - x_A^L$) and vapour ($x_A^V, x_B^V = 1 - x_A^V$) are uniquely determined. According to Dalton's law,

$$p_A = x_A^V p \quad , \quad p_B = x_B^V p$$

The equilibrium vapour pressures of *pure A* and *B* at the same *T* as the mixture will be denoted by $p_A *$ and $p_B *$, respectively. $p*$ can be considered as a measure of the tendency of molecules to escape from the liquid, i.e. of the *volatility*, at a given *T*.

Because in an ideal mixture the *A-A*, *B-B* and *A-B* interactions are identical, an *A* molecule has the same tendency to escape from an *A/B* mixture as from the pure *A* liquid. The rate at which molecules *A* leave a unit of surface area at temperature *T* is therefore x_A^L times the rate at which molecules *A* evaporate from the surface of pure *A* liquid at the same *T* (*p* has hardly any effect on this rate). To maintain equilibrium with the vapour phase, the partial pressure p_A (which is a measure of the rate of condensation of *A*) should then be equal to the same fraction x_A^L of the vapour pressure of pure *A*, $p_A *$. Similar considerations apply to component *B*, and we thus arrive at *Raoult's law*,

$$p_A = x_A^L p_A * \quad , \quad p_B = x_B^L p_B *$$

Although the above discussion provides no more than a plausibility argument, Raoult's law has been confirmed experimentally in a large number of cases.

Raoult's law can be expressed graphically in a *p* vs. x_A^L diagram, corresponding to the prevailing temperature *T*, as shown (*A* is assumed to be more volatile than *B*).
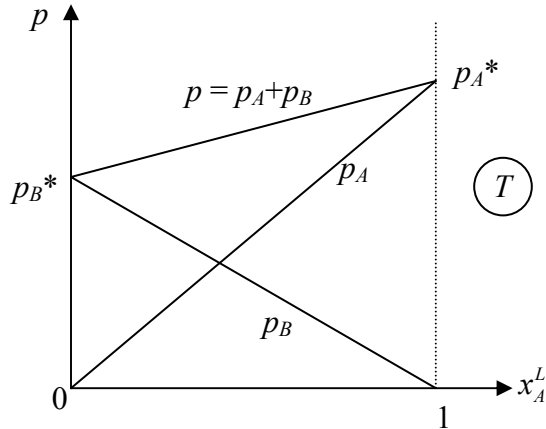
Remember that we now have two alternative expressions for the partial vapour pressures,

$$p_A = x_A^V p = x_A^L p_A *$$
$$p_B = x_B^V p = x_B^L p_B *$$

where the first equality expresses Dalton's law, the second Raoult's law.

The information contained in these equations can be summarised conveniently in a diagram, where we plot pressure against compositions $x_A^L \equiv x^L$ and $x_A^V \equiv x^V$ of *both* liquid (L) and vapour (V) (for a given T!), using the p vs. x_A^L plot as a basis.
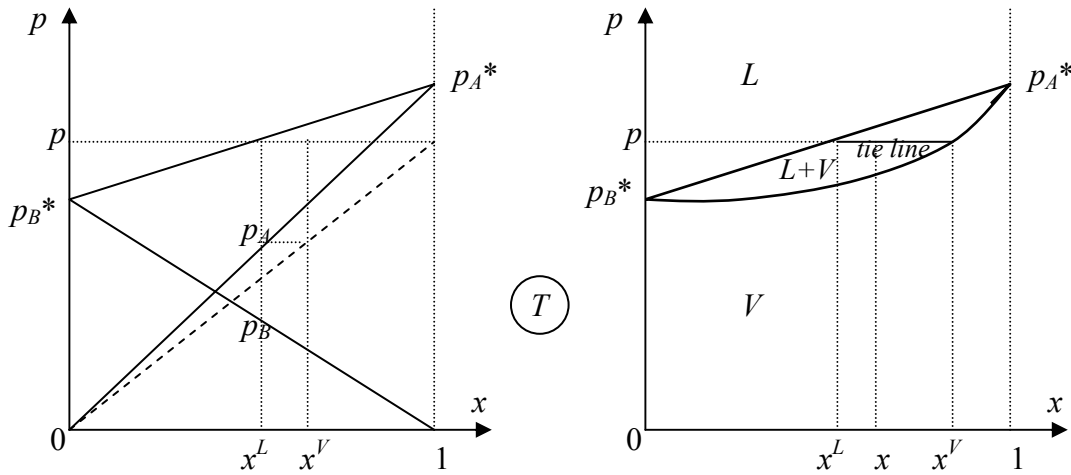
The abscissa is now simply labelled x, and could denote either x^L or x^V, depending on which line or curve is considered. The p vs. x^V curve is constructed by first choosing a pressure p, and reading off the corresponding x^L and p_A. To find x^V, draw an auxiliary line from (0,0) to (1,p). The horizontal projection of the point (x^L,p_A) onto this line leads to x^V on the x-axis, as shown. One easily checks that this construction is in agreement with Dalton's law. Repeating this procedure for all p between $p_B *$ and $p_A *$, the p vs. x^V

curve is obtained. Thus, for a given T and p, the compositions of liquid and vapour can be readily found from this p-x phase diagram.

Next, consider a L/V equilibrium at T, p with compositions x^L, x^V as shown in the diagram. We imagine a hypothetical state of this system, where A and B are thoroughly mixed, forming a uniform mixture of composition x. If the total number of moles of liquid and vapour are n_L and n_V, respectively, the total number of moles of A can be written alternatively as

$$\# \text{ moles } A = n_V x^V + n_L x^L = (n_L + n_V)x$$

This can be rearranged into

$$n_L(x - x^L) = n_V(x^V - x)$$

or

$$\frac{n_L}{n_V} = \frac{x^V - x}{x - x^L}$$

Since $n_{L,V} \geq 0$, we must have that $x^L \leq x \leq x^V$. In other words, an L/V equilibrium will only form spontaneously from a homogeneous mixture of composition x at a certain p and T if the point (x,p) lies somewhere in the region bounded by the liquid and vapour lines in the p-x diagram. The relative amounts of the two phases are then given by the above formula, which is an example of a *lever rule*. This is also the ratio of the segments into which the point (x,p) divides the horizontal *tie line* joining the boundaries of the L and V stability regions across the L/V coexistence region.

For practical purposes, however, the p-x diagrams are rarely useful since most experimental studies are performed at constant p and varying T, rather than the other way around. The same information can be represented more conveniently, therefore, in terms of T-x, or *boiling point*, diagrams (one for each p). A typical example of this type of phase diagram is shown in the figure below (note that if A is more volatile than B, then $T_A{}^* < T_B{}^*$).

The general layout is similar to that of the *p-x* diagram, only now the L-region occupies the lower part and the V-region the upper part of the *T-x* plane. In particular, all considerations about tie lines apply equally to this case.

These *T-x* diagrams are particularly useful to describe what happens during the process of *fractional distillation*.

Suppose we want to extract a specimen of nearly pure *A* from a liquid *A/B* mixture in a state characterised by the point X. The liquid is first heated (1) until the vapour forms. Heating continues until enough vapour has formed (assuming that x^L is not noticeably affected by the evaporation), which is then drawn off (2) and subsequently condensed (3) to a liquid enriched in *A*. From the diagram it can be inferred how many times this sequence should be repeated to obtain a sample of the desired purity. Conversely, one could distill off *B* from the mixture by going in the opposite direction, i.e. evaporate most of the sample, retain the liquid (which is now enriched in *B*), and continue in this manner.

VIII.1.2 Thermodynamic properties of ideal solutions.

Again, consider an L/V equilibrium of the ideal binary *A/B* mixture at *T, p*. Material equilibrium with respect to *A* requires that

$$\mu_A^L = \mu_A^V$$

Using the explicit form of μ_A^V as well as Raoult's law, this can be written alternatively as

$$\mu_A^L = \mu_A^\theta(T) + RT \ln p_A(T, p)$$

$$= \mu_A^\theta(T) + RT \ln p_A*(T) + RT \ln x_A^L(T, p)$$

The sum of the first two terms in the last expression is equal to the chemical potential of pure *A* liquid in equilibrium with its vapour, which allows us to write

$$\mu_A^L = \mu_A^L*(T, p_A*) + RT \ln x_A^L$$

It can be shown that the error that is introduced by replacing p_A* by p in the argument of μ_A^L* is negligible in comparison to the logarithmic term so that, to a very good approximation, for a component of an ideal mixture,

$$\mu_i^{id} = \mu_i*(T, p) + RT \ln x_i$$

where the superscripts ^{L} have been dropped (Note the similarity with the corresponding formula for perfect gas mixtures; in particular, this means that these μ_i^{id} are also consistent with the Gibbs-Duhem relation). This result is simply extrapolated to arbitrary combinations of *T, p* and x_j's.

Changes in thermodynamic quantities that occur as a result of mixing can now be evaluated by using the standard methods.

First, the Gibbs energy of mixing (T, p constant) equals

$$\Delta G^{id}_{mix} = G^{id} - G^* = \sum_i n_i (\mu^{id}_i - \mu_i *) = RT \sum_i n_i \ln x_i < 0$$

so mixing occurs spontaneously under conditions of constant T and p.
The ideal entropy of mixing is

$$\Delta S^{id}_{mix} = -\left(\frac{\partial \Delta G^{id}_{mix}}{\partial T} \right)_{p,\{n_j\}} = -R \sum_i n_i \ln x_i > 0$$

The volume change consequent upon mixing is

$$\Delta V^{id}_{mix} = \left(\frac{\partial \Delta G^{id}_{mix}}{\partial p} \right)_{T,\{n_j\}} = 0$$

while for the enthalpy (heat) of mixing we find

$$\Delta H^{id}_{mix} = \Delta G^{id}_{mix} + T \Delta S^{id}_{mix} = 0$$

i.e., an ideal mixture is athermal.
The mathematical form of each thermodynamic function of mixing is obviously identical to that of the corresponding function pertaining to the mixing of ideal gases.

VIII.2 Non-ideal solutions.

VIII.2.1 Phase diagrams. Activity.

Deviations from Raoult's law in binary mixtures may be classified as belonging to either one of two categories, according to whether the *A-B* interaction is weaker than both *A-A* and *B-B* interactions (1), or stronger than both of them (2).

(1) (*A-B*) < (*A-A*), (*B-B*). In this case we say that the mixture shows *positive* deviation from Raoult's law, with $\Delta H_{mix} > 0$ in general (mixing is *endothermic*).

The weaker interactions in solution lead to increased volatility of both *A* and *B* as compared with the ideal case. This is shown schematically in the *p-x* diagram on the next page. Note that the curves for p_A and p_B asymptotically approach Raoult-type behaviour as $x^L \to 1$ and 0, respectively. This is not surprising as in these limits the mixture is essentially a dilute solution consisting almost entirely of *A* or *B* , respectively, which then plays the role of *solvent,* while the other component should be regarded as the *solute.* Clearly, the tangent of the slope to the p_A curve at $x^L_A = 0$ will differ from $p_A *$ and will depend on temperature as well as on the nature of *B*. The same is true for *B* as $x^L_B \to 0$.
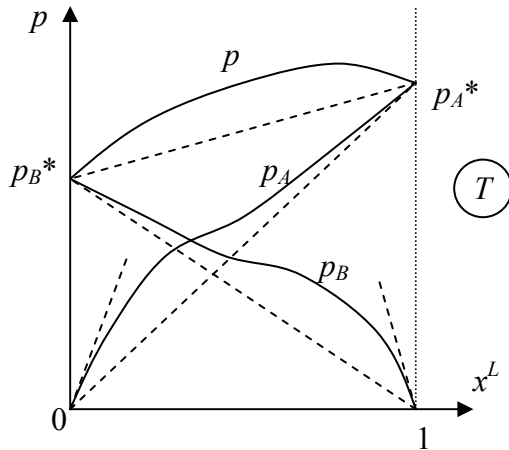
This limiting behaviour of dilute solutions is expressed by the linear relation

$$p_{A,B} = K_{A,B}(T)x^L_{A,B} \quad \text{if } x^L_{A,B} \ll 1$$

This relation is called *Henry's law*.

(2) $(A\text{-}B) > (A\text{-}A), (B\text{-}B)$. Similar considerations apply to this case, which is characterised by $\Delta H_{mix} < 0$, i.e. *exothermic* mixing. Here, of course, evaporation of both A and B is suppressed by the stronger A-B interaction, and we now observe *negative* deviation from Raoult's law (see figure).
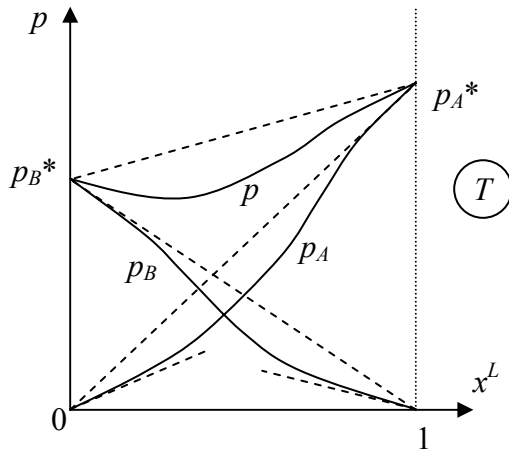
For non-ideal solutions we can again construct *p-x* and *T-x* diagrams in the usual manner, which contain all the information on the variation of liquid and vapour composition, x^L and x^V, with p or T, at some constant T or p, respectively.

For example, in the case of strong *positive* deviation from Raoult's law, these diagrams typically look like the ones shown on the next page, where the boundaries of the L and V regions touch at the *maximum* in the *p-x* diagram or at the *minimum* in the *T-x* diagram. This is a pictorial representation of the so-called *Gibbs-Konovalov theorem*. Clearly, the

point of contact has to be an extremum, for otherwise tie lines could be drawn that connect two liquid states, which would be meaningless. This point corresponds to an *azeotrope*, with $x^L = x^V$. An azeotrope behaves like a pure compound ($C = 1$) with well-defined boiling point. An azeotropic equilibrium is therefore monovariant ($F = 1$).
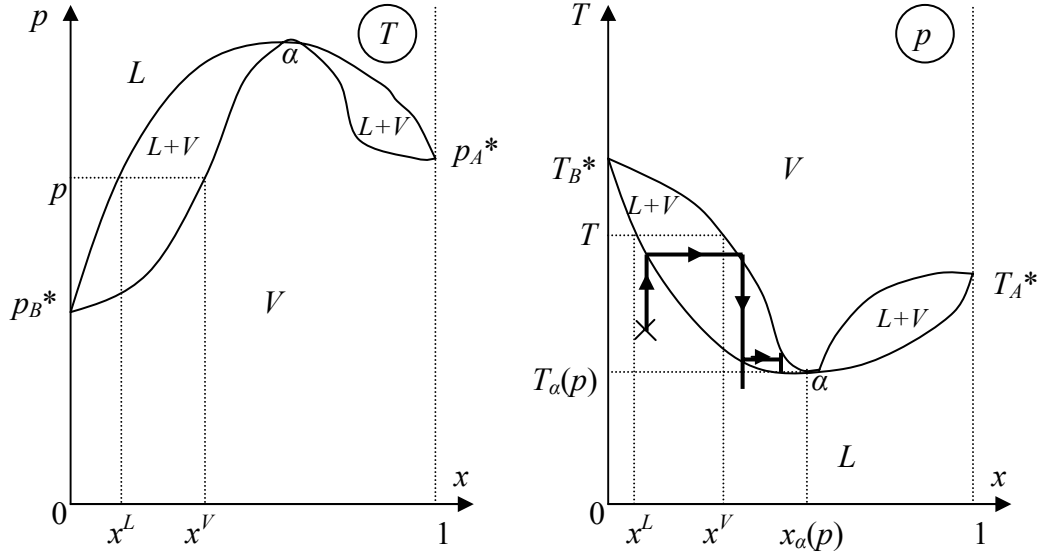
It is obvious that a mixture that shows strong (positive or negative) deviation from Raoult's law can not be separated by means of fractional distillation when the azeotropic point is approached, unless we vary p, for example, or add a third component.

The treatment of mixtures that exhibit (strong) *negative* deviations from ideal behaviour is entirely analogous, the difference being that now the L curve seems to "press down" against the V curve in the *p-x* diagram and "pushes up" against it from below in the *T-x* diagram.

The effect of non-ideality on the chemical potentials and other quantities can be treated empirically or on the basis of some microscopic model, such as the *regular mixture* model, which takes into account the interactions between molecules in direct contact (nearest-neighbour interactions). A generic form of μ_i has been defined which formally includes these effects, as follows

$$\mu_i = \mu_i *(T, p) + RT \ln a_i$$

where we have introduced the *activity* a_i (a function of T, p and the x_j), and which itself is often written as the product of x_i and a so-called *activity coefficient* γ_i:

$$a_i \equiv \gamma_i x_i$$

where γ_i tends to 1 if x_i approaches 1, in accordance with Raoult's law.

We may now write

$$\mu_i = \mu_i*(T, p) + RT \ln x_i + RT \ln \gamma_i \equiv \mu_i^{id} + \mu_i^E$$

where $\mu_i^E = RT \ln \gamma_i$ describes the departure from ideality and is called the *excess chemical potential* of i. At constant T and p these μ_i^E must satisfy the Gibbs-Duhem relation

$$\sum_i x_i d\mu_i^E = 0$$

since the μ_i^{id} do so already.

In particular, the Gibbs energy of mixing is now written as the sum of an ideal and an excess contribution,

$$\Delta G_{mix} = \Delta G_{mix}^{id} + \Delta G_{mix}^E$$

with $\Delta G_{mix}^E = \sum_i n_i \mu_i^E$, the excess Gibbs energy of mixing. This ΔG_{mix}^E can subsequently be used to calculate the other excess functions of mixing, ΔS_{mix}^E, ΔV_{mix}^E ($= \Delta V_{mix}$) and ΔH_{mix}^E ($= \Delta H_{mix}$), in the usual way.

VIII.2.2 Incomplete miscibility.

In binary mixtures that exhibit a *positive* deviation from Raoult's law one typically observes the phenomenon of *phase separation*. Here, for any T below a certain *critical* (or *consolute*) *temperature* T_c there is a range of x values for which the mixture spontaneously splits into two liquid phases, L_1 and L_2, of different composition.
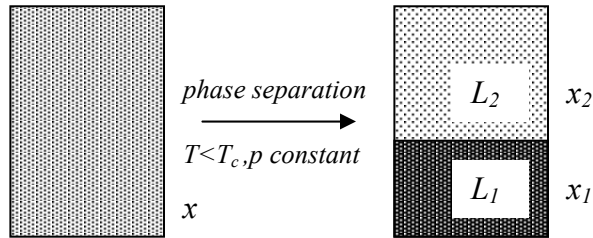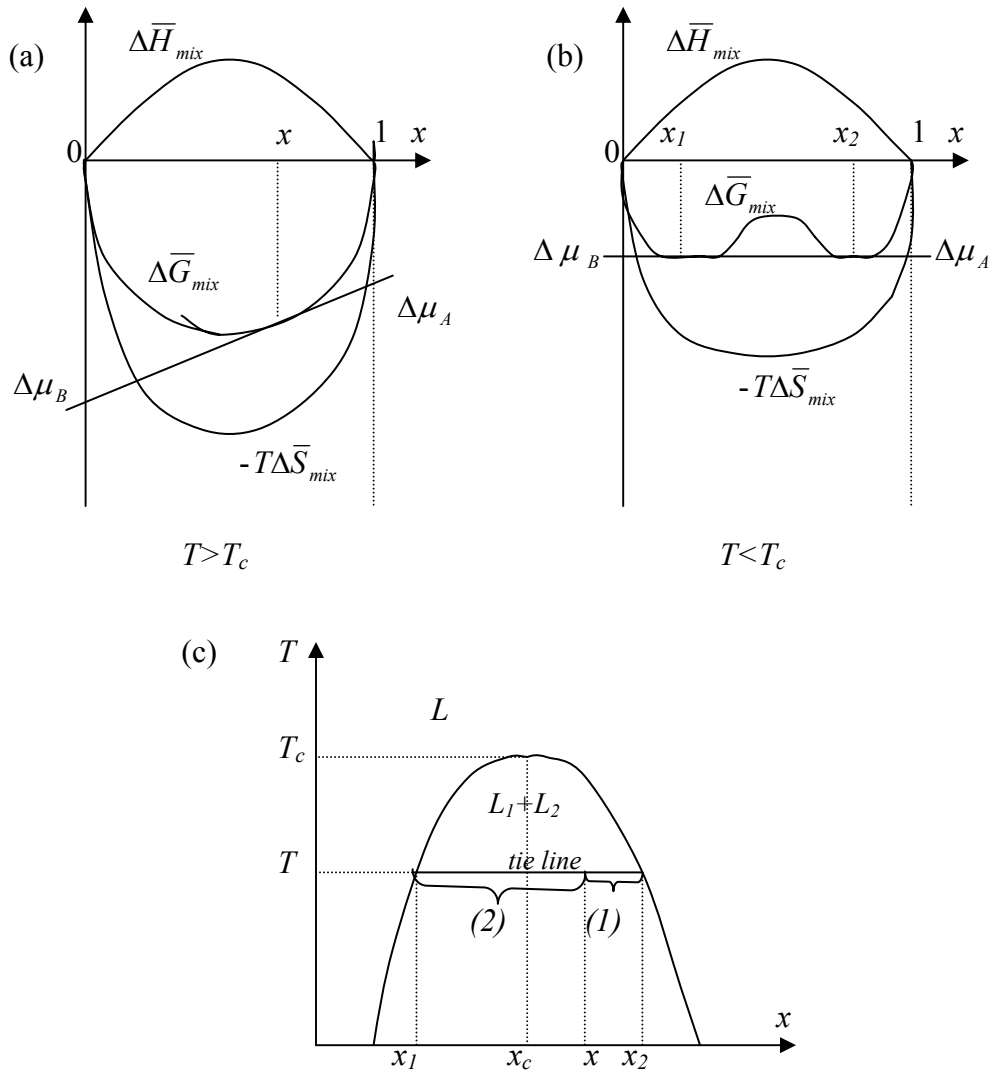

This partial de-mixing can be understood by analysing the molar Gibbs energy of mixing,

$$\Delta \overline{G}_{mix}(T, x) = \Delta \overline{H}_{mix}(x) - T\Delta \overline{S}_{mix}(x)$$

where $\Delta \overline{S}_{mix}, \Delta \overline{H}_{mix} > 0$ for $0 \leq x \leq 1$, and presumably independent of T.
If $T > T_c$, the mixture is stable for all $0 \leq x \leq 1$ (figure (a)).

(a)

$\Delta \overline{H}_{mix}$

x 1 x

0

$\Delta \overline{G}_{mix}$

$\Delta\mu_A$

$\Delta\mu_B$

$-T\Delta\overline{S}_{mix}$

$T>T_c$

(b)

$\Delta \overline{H}_{mix}$

x_1 x_2 1 x

0

$\Delta \overline{G}_{mix}$

$\Delta\mu_B$ $\Delta\mu_A$

$-T\Delta\overline{S}_{mix}$

$T<T_c$

(c) T

L

T_c

L_1+L_2

T tie line

(2)   (1)

x_1 x_c x x_2

For any x, the chemical potential of A or B can be obtained from $G = G^* + \Delta G_{mix}$ via differentiation with respect to n_A or n_B, respectively, so that we can formally write

$$\mu_i(x) = \mu_i^* + \Delta\mu_i(x) \qquad (i = A, B)$$

where $\Delta\mu_i = RT \ln a_i$ represents the "mixing part" of μ_i. The latter can be found by applying the method of intercepts (section IV.2) to the $\Delta\overline{G}_{mix}$ vs. x plot, as shown.

If $T < T_c$, a "hump" appears on the $\Delta\overline{G}_{mix}(x)$ curve (b). This means that there are *two* points, at x_1 and at x_2, which share the same *bitangent*. Therefore, $\Delta\mu_A(x_1) = \Delta\mu_A(x_2)$ and $\Delta\mu_B(x_1) = \Delta\mu_B(x_2)$, hence $\mu_A^{(1)} = \mu_A^{(2)}$ and $\mu_B^{(1)} = \mu_B^{(2)}$. The phases L_1 and L_2 with compositions x_1 and x_2, can therefore coexist, provided that the Gibbs energy of mixing

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for the two-phase system, $\Delta G_{mix}^{(1)} + \Delta G_{mix}^{(2)}$, is less than that of the uniform mixture with composition x, $\Delta G_{mix}(x)$, from which it emerges. Following the same argument that led to the formulation of the lever rule (section VIII.1.1) one can easily show that this situation can only arise if $x_1 \leq x \leq x_2$. It can also be shown that, within this range, $(\Delta G_{mix}^{(1)} + \Delta G_{mix}^{(2)})/n$ is represented geometrically by the bitangent, which obviously lies below the $\Delta \overline{G}_{mix}(x)$ curve so that the two-phase system is indeed more stable than the homogeneous mixture. The interval $x_1 \leq x \leq x_2$ is called the *miscibility gap* corresponding to the given temperature $T < T_c$.

In a *T-x* phase diagram (c) the coexistence region is demarcated by a curve (called the *binodial curve*) in the shape of an inverted parabola with a maximum at the point (x_c, T_c), where x_c is the *critical composition*. The binodial curve is virtually independent of p.

Relative amounts of phases L_1 and L_2 corresponding to some x between x_1 and x_2 can again be determined by drawing a horizontal tie line at the appropriate T and applying the lever rule.

For binary mixtures that display a positive deviation from Raoult's law, the complete (L/V part of the) *T-x* phase diagram will look similar to the one depicted below, for those cases where the consolute temperature lies below the azeotropic boiling point.
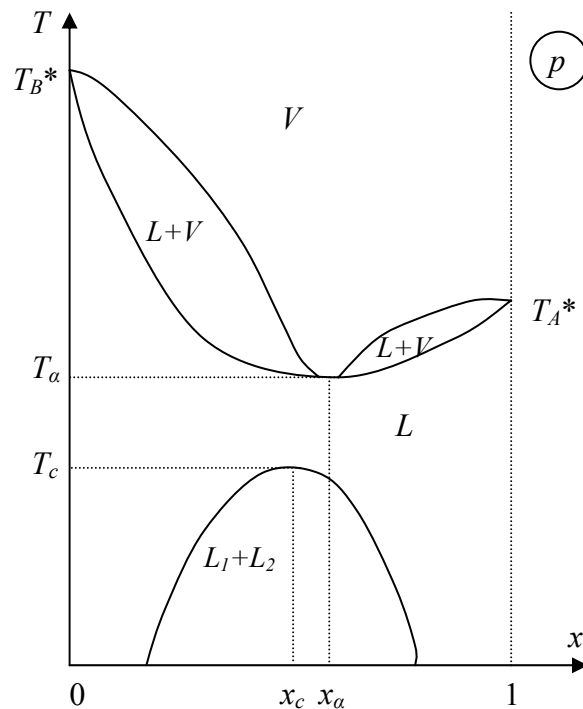
IX. DILUTE SOLUTIONS.

IX.1 Chemical potentials.

A dilute solution consists of one major component, the *solvent* (*s*), with $x_s \cong 1$ and one or more *solutes* (labelled by subscripts i) with $x_i << 1$. Volatile solutes obey *Henry's law* (see section VIII.2.1)

$$p_i = K_i(T)x_i$$

where p_i is the partial pressure of solute i in the equilibrium vapour and x_i is its mol fraction in solution. The factor $K_i(T)$ also depends on the nature of the solvent.

To calculate the chemical potential of i in solution, we again utilise the L/V equilibrium condition

$$\mu_i^L = \mu_i^V = \mu_i^\theta(T) + RT \ln p_i$$
$$= \mu_i^\theta(T) + RT \ln K_i(T) + RT \ln x_i$$
$$= \mu_i^0(T, p^*) + RT \ln x_i, \text{ with } p^* \text{ the vapour pressure at } T \text{ for the solvent}$$

In general, for arbitrary p,

$$\mu_i = \mu_i^0(T, p) + RT \ln x_i$$

if $x_i << 1$ (*N.B.*: $\mu_i^0 \neq \mu_i^*$!).

It is customary to replace x_i with a different measure of concentration, the *molarity* (expressed in mol dm^{-3})

$$c_i = \frac{n_i}{V} = \frac{n_i}{n}\frac{n}{V} = x_i / \overline{V}$$

or, to a good approximation $x_i \cong c_i \overline{V}_s *$.

Substitution for x_i in the formula for μ_i gives

$$\mu_i = \mu_i^\oplus(T, p) + RT \ln c_i$$

where $\mu_i^\oplus(T, p)$ is the *standard chemical potential*, that is, the value of μ_i in a hypothetical *standard state* with $c_i = 1$ mol dm^{-3} and no interactions among solutes, as in the case of extreme dilution (the interactions are "switched off", so to speak).

The solvent, on the other hand, obeys Raoult's law

$$\mu_s = \mu_s*(T, p) + RT \ln x_s$$

which, using $\ln x_s = \ln(1 - \sum_i x_i) \cong -\sum_i x_i$, equals, to a good approximation,

$$\mu_s \cong \mu_s*(T, p) - RT \sum_i x_i$$

Thus, adding solutes to the solvent reduces the chemical potential of the latter, thereby increasing its thermodynamic stability.

IX.2 Colligative properties.

The effects of *non-volatile* solutes on various equilibria involving the solvent are collectively referred to as *colligative phenomena*. Here, four of these will be discussed: (1) Osmosis, (2) elevation of boiling point, (3) depression of freezing point and (4) lowering of vapour pressure.

(1) *Osmosis*.

Consider a two-compartment osmotic cell where the partition contains a selective membrane M that only lets through solvent molecules. Initially, pure solvent is present in both compartments (1) and (2). Assume that (2) is much larger than (1).
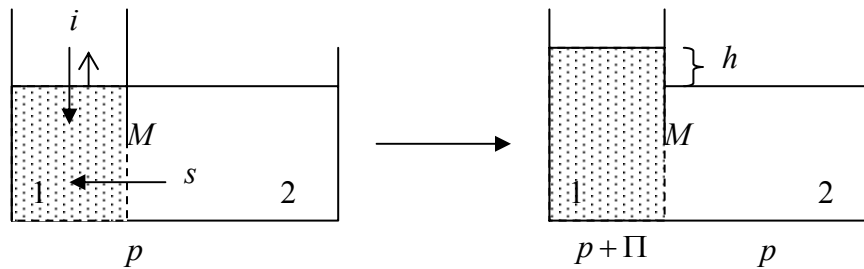
Addition of solute i to compartment (1) lowers μ_s and causes an influx of s (osmosis) from (2). This in turn leads to a rise in the fluid level in (1) and a concomitant increase in pressure to the left of M, restoring μ_s to the constant value imposed by the solvent in (2). The result is an *osmotic (membrane) equilibrium*.
The Gibbs-Duhem relation will now be applied to the solution in (1) to calculate the pressure increase consequent upon the addition of a small amount of solute. The equation is simplified by the conditions $T = $ constant and $\mu_s = $ constant, i.e. $dT = d\mu_s = 0$:

$$Vdp = \sum_i n_i d\mu_i$$

or

$$dp = \sum_i c_i d\mu_i$$

Integrating between the initial pressure p and the final pressure $p + \Pi$, where Π denotes the *osmotic pressure* across the membrane, we find

$$\Pi = \int_p^{p+\Pi} dp = \sum_i \int c_i d\mu_i$$

If we assume that $\overline{V}_s *$ is independent of p (the solvent is *incompressible*), $d\mu_i$ equals

$$d\mu_i = \overline{V}_i dp + RT dc_i / c_i$$

from which

$$\Pi = \sum_i \int_p^{p+\Pi} c_i \overline{V}_i dp + RT \sum_i \int_0^{c_i} \phi_i \frac{dc_i}{\phi_i}$$

The first term on the right-hand side is of second order in the c_i and can be neglected. This leaves

$$\Pi = RT \sum_i c_i$$

a result known as *Van't Hoff's law* for the osmotic pressure of a dilute solution.

It is possible to derive Van't Hoff's law in yet another way. In this case, we make direct use of the equilibrium condition $d\mu_s = 0$, which can be written more explicitly, using the approximate form of μ_s given previously, as

$$d\mu_s = d\mu_s *(T, p) - RT \sum_i dx_i = \overline{V}_s * dp - RT \sum_i dx_i = 0$$

The last equality, after rearrangement and integration, yields

$$\Pi = \int_p^{p+\Pi} dp = \frac{RT}{\overline{V}_s *} \sum_i \int_0^{x_i} dx_i = \frac{RT}{\overline{V}_s *} \sum_i x_i$$

This is indeed identical to the above formula for osmotic pressure.

Van't Hoff's law looks very similar to the formula for the pressure of a mixture of ideal gases. However, this resemblance is deceptive: The pressure is exerted by the solution as

a whole, that is, almost entirely by the *solvent*. With a fluid head h the osmotic pressure can be identified with the hydrostatic pressure

$$\Pi = \rho g h$$

where ρ = density of the solution (practically equal to ρ_s) and g = acceleration of gravity.

It is important to note that if a solute dissociates in solution, its dissociation products contribute separately to the sum $\sum_i$, so for example, if NaCl is dissolved in water to a concentration c, then the resulting osmotic pressure is $\Pi = 2RTc$.

(2) *Elevation of boiling point.*

Suppose that the pure solvent (indicated by *) is heated to its boiling point T_b* at the constant ambient pressure p. Equilibrium is attained if

$$\mu_s^V* = \mu_s^L*$$
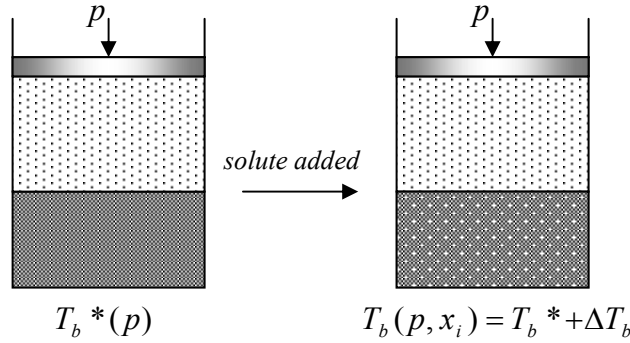
$$T_b*(p) \qquad\qquad T_b(p, x_i) = T_b* + \Delta T_b$$

Adding a small quantity of non-volatile solutes to the liquid phase (to mol fractions x_i) lowers μ_s and causes the vapour to condense. To restore the L/V equilibrium (make the solution boil), the temperature needs to be raised to $T_b(p, x_i) = T_b* + \Delta T_b$, at which point $\mu_s^L = \mu_s^V$. Writing $\mu_s^L = \mu_s^L* + \Delta\mu_s^L$ and $\mu_s^V = \mu_s^V* + \Delta\mu_s^V$, the equilibrium condition is equivalent to

$$\Delta\mu_s^L = \Delta\mu_s^V$$

Now

$$\Delta\mu_s^V = \left(\frac{\partial\mu_s^V}{\partial T}\right)_p \Delta T_b = -\overline{S}_s^V * \Delta T_b$$

and

$$\Delta \mu_s^L \cong \left(\frac{\partial \mu_s^{L*}}{\partial T} \right)_p \Delta T_b - RT_b * \sum_i x_i = -\overline{S}_s^L * \Delta T_b - RT_b * \sum_i x_i$$

where a second order term $-R\Delta T_b \sum_i x_i$ has been neglected.

From these equations it follows that

$$\Delta T_b = \frac{RT_b *}{\overline{S}_s^V * - \overline{S}_s^L *} \sum_i x_i$$

or, substituting $\overline{S}_s^V * - \overline{S}_s^L * = \Delta \overline{H}_{vap} / T_b *$,

$$\Delta T_b = \frac{RT_b *^2}{\Delta \overline{H}_{vap}} \sum_i x_i$$

In this formula, x_i is usually approximated by n_i / n_s.

(3) *Depression of freezing point.*

Adding solute to the pure solvent at the freezing point $T_f *$ lowers μ_s^L and results in melting of the solid ("antifreeze"). The S/L equilibrium can be restored if we lower the temperature by ΔT_f. It can be shown by an argument entirely analogous to that used in deriving ΔT_b that

$$\Delta T_f = -\frac{RT_f *^2}{\Delta \overline{H}_{fus}} \sum_i x_i$$

where it has been assumed that no solutes are incorporated into the solid.
The effects of solute on T_b and T_f can be represented in a *p-T* phase diagram as a shift of the L/V and S/L coexistence lines, as shown on the next page. The increased stability of *s* is evidenced by the expansion of the L region. Evidently, the sublimation line is left unaffected by the presence of solute. The triple point has shifted along it to the left, and has thus acquired one degree of freedom.

(4) *Lowering of vapour pressure.*

From the phase diagram it is obvious that a third colligative effect occurs if $T = T_b *$ is held fixed, rather than *p*, while solute is added to a solvent in equilibrium with its vapour.
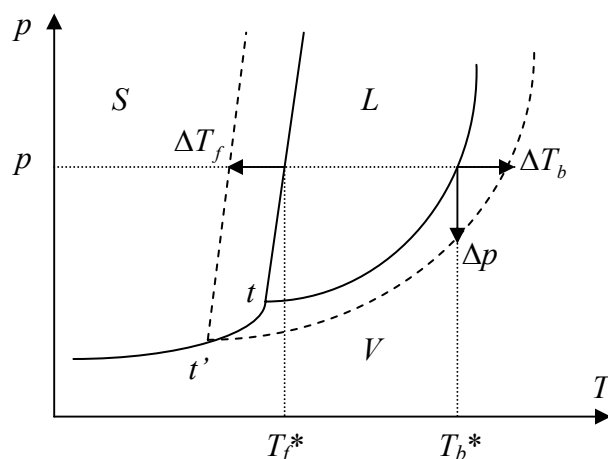
The L/V equilibrium is now recovered by lowering the pressure by Δp, which can be calculated most easily by noting that the solvent follows Raoult's law,

$$p_{vap} = x_s p^* = (1 - \sum_i x_i) p^* = p^* + \Delta p$$

$$\therefore \quad \Delta p = -p^* \sum_i x_i$$

It is seen that all colligative effects follow a similar pattern, as they are all proportional to $\sum_i x_i \ll 1$ and independent of the chemical identity of the solutes, whereas the proportionality factors depend exclusively upon properties of the solvent component, s.

An obvious application of colligative effects is the determination of molecular weights of unknown compounds. If a small purified sample of the (non-dissociating) compound is dissolved in a known quantity of a suitable solvent, the magnitude of the effect is measured and used to find the mol equivalent. The preferred technique is *osmometry*, in view of its relative accuracy and practical convenience.

IX.3 Chemical equilibrium in dilute solutions. Solubility. Activity.

For a chemical equilibrium, the general condition

$$\sum_r \nu_r \mu_r = 0$$

applies, where

$$\mu_r = \mu_r^\oplus (T, p) + RT \ln c_r$$

if r is a solute, and

$$\mu_s \cong \mu_s^*(T, p) \qquad \text{(ideal dilute solution)}$$

if the solvent takes part in the reaction (e.g. hydrolysis, if water is the solvent).
Of course, strictly speaking the solvent is always a participant in any reaction that takes place in solution, which in any case involves (de)solvation steps.
Substitution into the equilibrium condition yields the well-known form of the law of mass action

$$\ln K_c = -\Delta G_{rxn}^{\ominus} / RT$$

with equilibrium constant

$$K_c = \left(\prod_r c_r^{\nu_r} \right)_{eq}$$

Here, r only labels the *solutes* participating in the process. If a term $\nu_s \mu_s^*$ occurs in the equilibrium condition, it should be included in $\Delta G_{rxn}^{\ominus}$:

$$\Delta G_{rxn}^{\ominus} = \sum_r \nu_r \mu_r^{\ominus} + \nu_s \mu_s^*$$

The effect of temperature on the position of the equilibrium is expressed in terms of the T-derivative, at constant p, of $\ln K_c$:

$$\left(\frac{\partial \ln K_c}{\partial T} \right)_p = \frac{\Delta H_{rxn}}{RT^2}$$

where the Gibbs-Helmholtz equation has been employed, as usual, and also the fact that in an ideal solution ΔH_{rxn} does not depend on concentration, so that the superscript $^{\ominus}$ can be deleted. This formula is called the *Van't Hoff equation*, and is analogous to the Van't Hoff isobar for gas-phase equilibria. Evidently, this result is again in accordance with Le Châtelier's principle. It is to be noted that pressure usually has negligible effect on equilibria in solution, so that the subscript $_p$ in the above formula is actually redundant.

The theory outlined above also applies to *heterogeneous* equilibria, involving both solid and solution phases. The simplest example is the dissolution equilibrium of a sparingly soluble salt, such as AgCl:

$$AgCl(s) \;\rightleftharpoons\; Ag^+(aq) + Cl^-(aq)$$
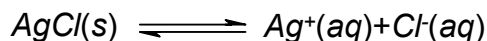
The law of mass action now assumes the form

$$\mu_+^\oplus(T,p) + \mu_-^\oplus(T,p) + 2RT \ln s = \mu_{salt}*(T,p)$$

where s is the *solubility* of AgCl at the given T, which can be solved from this equation,

$$s = \exp\{(\mu_{salt}* - \mu_+^\oplus - \mu_-^\oplus)/2RT\}$$

At elevated concentrations, the formulae for the μ_r obviously are no longer valid as interactions between solutes become more important. To account for departures from ideality, once again the notions of *activity* and *activity coefficient* are invoked:

$$\mu_i = \mu_i^\oplus + RT \ln a_i$$

where $a_i \equiv y_i c_i$, such that $y_i \to 1$ if $\sum_j c_j \to 0$.

For the solvent,

$$\mu_s = \mu_s* + RT \ln a_s$$

where $a_s \to 1$ if $\sum_j c_j \to 0$.

a_s depends on the y_i via the Gibbs-Duhem relation which, for constant T and p, reads as

$$x_s d \ln a_s + \sum_i x_i d \ln(y_i c_i) = 0$$

When dealing with chemical equilibria in concentrated solutions, one obviously needs to replace the equilibrium constant K_c by the *activity product*, $K = \left(\prod_r a_r^{v_r}\right)_{eq}$, where the r should now include s.

The effects of solute-solute interactions are particularly strong in electrolyte solutions, due to the long range of electrostatic forces. As a result, signs of non-ideality already show up at low concentrations. The *Debye-Hückel theory* accounts for these effects in dilute electrolyte solutions. Essentially, this theory provides us with an approximate analytical expression for the y_i. This will be discussed in more detail in the C33J course on Electrochemistry.

Another type of non-ideality arises as a result of a vast difference in size between solute and solvent molecules, as is the case with polymer solutions. Here, the change in conformational entropy of polymer coils that occurs upon mixing is largely responsible for the departure from ideal behaviour (see also the C33K course on Polymer Chemistry).