SENIOR FRESHMAN CHEMISTRY

Chemical Thermodynamics   Prof J. Corish

(Course of ten lectures)   jcorish@tcd.ie

COURSE SYNOPSIS

This course will follow from your Junior Freshman treatment of this subject with the three laws of thermodynamics being formally introduced. The course will extend the range of state functions that are considered and in terms of the First Law develop the relationship between C_p and C_v (heat capacities at constant pressure and constant volume, respectively) and introduce the variation of enthalpy changes with temperature (Kirchoff's Law).

The concept of entropy, used in the second law to assist in the derivation of a criterion for direction of chemical change, will be introduced by means of the Carnot cycle. The methods used to evaluate Third Law entropies will be explained, as will the existence and nature of residual entropy in some substances.

The course will then move on to consider the thermodynamics of open systems and the concept of the chemical potential. After its introduction, the chemical potential will be utilised to describe and to derive relationships for both physical and chemical equilibria. The thermodynamic basis for the Gibbs Phase Rule will be illustrated and the Clausius-Clapeyron and Van't Hoff equations derived. Finally, relationships between the chemical potentials of a component present at equilibrium in different phases will be used to develop the thermodynamic treatment of ideal mixtures. Equations will be derived for the ideal solubilities of gases and solids and the thermodynamic basis for Henry's and Raoult's Laws and for the colligative properties of solutions will be illustrated. In this way a firm thermodynamic foundation will be provided for a number of the concepts and equations introduced empirically in Junior Fresh Physical Chemistry.

Reading:

The chapters on thermodynamics in modern Physical Chemistry (such as those authored or co-authored by P. W. Atkins) will probably be most easily readable and useful.
Other books are:
'The Principles of Chemical Equilibrium', K. Denbigh (Cambridge)
'Chemical Thermodynamics' D. J. G. Ives (McDonald)
'An introduction to the study of Chemical Thermodynamics' D.H.Everett (Longmans)
'Basic Chemical Thermodynamics' E. Brian Smith (Clarendon, Oxford)
'The Second Law' P. W. Atkins (Scientific American Books)
Relevant Chapters in 'Physical Chemistry' Thomas Engel and Philip Reid (Pearson)

Some Definitions – and a review

Thermodynamics: Science of heat and temperature and of the laws governing their inter-conversion i.e., heat into mechanical, electrical, chemical, or biological forms of energy.

Phenomenological theory concerning **macroscopic** properties such as pressure, temperature volume etc… It is **independent of microscopic explanations** e.g., the atomic theory.
      strengths: not dependent on these explanations.
      weaknesses: does not give any insight into atomic phenomena.

Classical Thermodynamics:
self-contained, constructed as a set of postulates – the **laws** of thermodynamics – **completely general** and is used by physicists, chemists, engineers and biologists. Can be handled **completely mathematically** and then adapted for specific cases – this is not how we will handle it.

It is an exact science – similar to geometry - and based on a number of theorems or laws – the laws of thermodynamics

_____

As a matter of interest – we are not in a position to and will not study this aspect of the subject – classical thermodynamics can be shown to be bridged to atomic theory and behaviour by statistical thermodynamics (statistical mechanics). So it is, in fact, in complete harmony with our current understanding of chemistry and other subjects. This bridge would **not** be necessary in order for classical thermodynamics to stand.

_____

 Deals with **EQUILIBRIUM STATES** only

not with paths by which such different states are connected.

not with the rates at which such paths may be traversed.

EQUILIBRUIM STATES particularly as the term relates to chemical systems:

temperature uniform throughout and at equilibrium with its surroundings;
mechanical properties balanced i.e. **pressure** uniform; and
No net **chemical change -** this allows for dynamic equilibrium.

<u>SYSTEM</u>:   A thermodynamic **system** is that part of the physical universe the properties of which are under observation. The system is confined to a definite place in space by boundaries that separate it from the rest of the universe – the **surroundings.**

A system is **isolated** when its boundary prevents any interaction with the surroundings. Clearly a completely isolated system would not be observable and so the concept is ideal.

Closed system: possibility of energy exchange with the surroundings but no transfer of matter
Open System: can exchange both energy and matter with its surroundings
Adiabatic System: no heat transfer across the boundary is possible.

PROPERTIES OF A SYSTEM

Extensive Properties: the value of the property for the whole body is the sum of the values for all of its constituent parts e.g., mass, volume….

Intensive Properties: can be specified at each point in a system and may vary from point to point when equilibrium has not been attained e.g., pressure, density….

The **STATE** of a system is specified by giving the values of all pertinent macroscopic properties so that the system can be precisely duplicated elsewhere.

A **change in state** is completely defined when the initial and final states are specified.

The **path** of the change is defined by giving the initial state, the sequence of intermediate states arranged in order traversed and the final state.

A **cycle** is traversed when a system that has undergone a change in state returns to its initial state.

STATE FUNCTIONS (thermodynamic properties)

Quantities that depend on the state of the system only and not, for example, on its history are called state functions e.g., volume, temperature and pressure are state variables for a homogeneous system.

$$\Delta X \qquad = \qquad X_f \qquad - \qquad X_i$$

| change in | Final | Initial |
| state function | Value | Value |

ΔX is independent of the path followed to effect the change. The change in the value of a **state function** taken through a **cycle** must therefore be equal to zero.
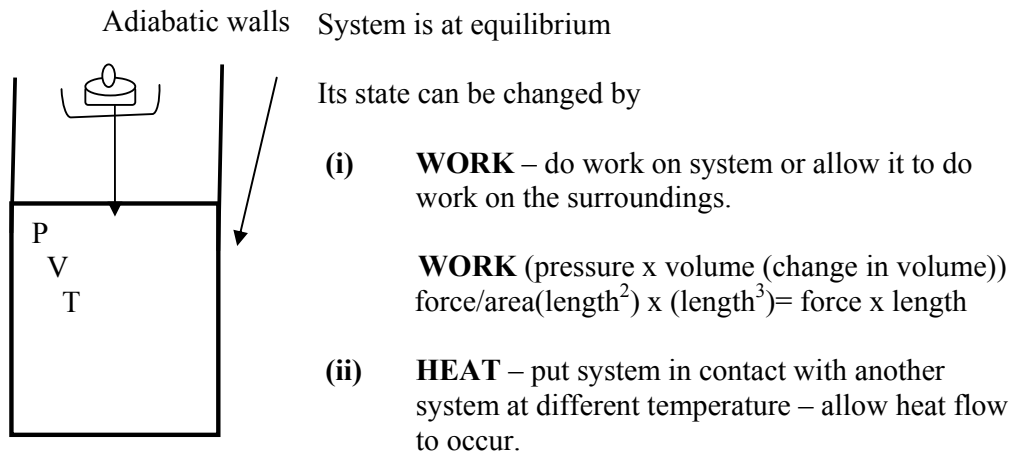
State functions may be related by an **equation of state** e.g., that for an ideal gas

$$PV = nRT$$

FIRST LAW OF THERMODYNAMICS

"Die Energie der Welt ist konstant" (Clausius)

This law is an extension of the principle of the conservation of energy and can be introduced by looking at a number of different ways in which energy can be put into a system.

Adiabatic walls   System is at equilibrium

Its state can be changed by

(i) **WORK** – do work on system or allow it to do work on the surroundings.

WORK (pressure x volume (change in volume)) force/area(length^2) x (length^3)= force x length

(ii) **HEAT** – put system in contact with another system at different temperature – allow heat flow to occur.

P
V
T

These do not take account of other possible changes which could be brought about by external fields (magnetic, electrical etc.) or by addition or removal of gas from the system.

Results: the **work** required to bring a thermally insulated system from one state to another is independent of the source of the work and of the path followed.

Suggestion: for a thermally isolated system there is certain property that changes by the amount of work done on or by the system.

Called INTERNAL ENERGY   Symbol U

$\Delta U(\text{adiabatic}) = - w(\text{adiabatic})$

$\mathbf{\Delta U}$ = change in the internal energy   **w** = **work** done by the system

U is a state function (thermodynamic property)

$\mathbf{\Delta U = U_f - U_i}$ independent of source of the work and of the path followed from state i to state f.

(i $\equiv$ initial and f $\equiv$ final)

Results: Second method: it turns out that when no work is done on or by the system that the changes in the internal energy of the system ΔU are equal to the energy transferred to or from the system by thermal contact, i.e., the **heat** transferred.

$\boxed{\Delta U(\text{zero work}) = q(\text{zero work})}$

ΔU = change in the internal q = **heat** absorbed
energy of the system   by the system

The First Law can then be formulated as follows:

$\boxed{\Delta U = \ q - w}$

Change in internal energy = heat absorbed by the system - work done by the system
_____

U **is** a state function

q and w are **not,** in general**,** state functions

_____

Q. How is the internal energy stored?

A. As the translational, vibrational, rotational, electronic intermolecular energies of the atoms, molecules in the system. These molecules possess electronic energy and are constantly moving about and rotating and vibrating – if heated they can move, vibrate etc. more quickly.

         NO ABSOLUTE VALUES of U -   we can speak only of changes in U, or ΔU.
_____

WORK: exists only at the time at which it is done – form of energy transfer.

Units - the fundamental unit is the Joule – a force of 1 Newton along a path of 1 meter – remember force x distance

Electrically -   1 coulomb through 1 volt.

(the thermodynamical calorie is defined as 4.1840 Joules).

DIFFERENCE BETWEEN HEAT AND WORK

HEAT: transfer that causes or utilizes chaotic "motion" in the surroundings

WORK: transfer of energy that utilizes or causes uniform motion of atoms in the surroundings.

(Fire came before machines!)

Having established the principal idea regarding the internal energy we will now see that it is better to use another type of energy which takes pressure-volume work into account automatically – called the **heat content** or **enthalpy**. It is especially suitable because we live in a constant pressure (1 atmosphere) world. For this reason you have already been introduced to enthalpy.

Expansion/Contraction work is very common and important. System expands against or is compressed by an outside pressure P – typically 1 atmosphere.

$$
\begin{aligned}
dw = \text{work done} \quad &= \quad \text{force x displacement} \\
&= \quad P \text{ x } A \text{ x } dx \\
&= \quad p \, dV
\end{aligned}
$$

Here P is the pressure, A the area over which it acts and dx the displacement so that A x dx is the volume change dV. Integrating from the final to the initial volume then gives the work done, w as being equal to

$$
w = \int_{V_i}^{V_f} PdV
$$

From the First law $q = \Delta U + w$

We can measure heat changes (calorimetrically) fairly readily. So that if no work other than pressure volume work is done and if the increase in volume during a reaction is ΔV then

$\Delta U = q - w = q - PdV = q - P(V_f - V_i)$

$\therefore U_f - U_i = \Delta U = q - PV_f + PV_i$ so that

$(U_f + PV_f) - (U_i + PV_i) = q$

6

Here it is obvious that the **heat absorbed** during the reaction is a quantity that depends only on the initial and final states because U, P and V are all state functions.

So this more useful state function is defined as the enthalpy (or heat content.
The symbol is **H**

ENTHALPY $\boxed{H = U + PV}$

U is part of this function – again we do not attempt to give absolute values – only changes, i.e., ΔH values, are measured.

ENTHALPY is the basis for thermochemistry (Leaving Certificate course and JF).

Reminder about the Law of Hess (see also below):

Although this law was originally derived from empirical observation and formulated by Hess, it is clear that it follows automatically from the fact that enthalpy is a state function.

ΔH, the enthalpy change, is the heat absorbed or given out in a reaction occurring at constant pressure. We shall see later that ΔH always influences, and sometimes dominates, the size of the equilibrium constant, K, for a reaction.

heat absorbed (taken in)	ENDOTHERMIC	ΔH positive
heat evolved (given out)	EXOTHERMIC	ΔH negative

RELATIONSHIP BETWEEN C_p AND C_v

- GENERAL CASE AND IDEAL GAS CASE

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \qquad\qquad C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_P \qquad\qquad (1)$$

$$H = U + PV$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad\qquad \Delta P = O$$

at constant P   (2)

$$U = f(T,V)$$

$$dU = \left(\frac{\partial V}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{(total differential)}$$

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_V \qquad\qquad (3)$$

Substitute (2) into (1)

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_T \qquad\qquad (4)$$

Substitute (3) into (4)

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_P$$

$$\text{Cp-Cv} \quad = P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P$$

External – Contribution to Cp
Through change in volume with
Temperature by external pressure P

Internal – change in internal
energy with volume with volume
with P

$$C_p - C_v \quad = \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}\left(\frac{\partial V}{\partial T}\right)_P$$

For a perfect gas $\left(\frac{\partial U}{\partial V}\right)_T = O$ Joules Experiment $U = f(T)$

only for ideal gas

$$C_p - C_v = p\left(\frac{VU}{\partial T}\right)_P$$

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

$$= p\left(\frac{nR}{P}\right) = nR$$

1 mole $\qquad C_p - C_v = R$ for ideal gas

(i)   In general $C_p > C_v$ because extra work is done in expansion against external pressure and "internal" pressure $\left(\frac{\partial U}{\partial V}\right)_T$.

(ii)   Internal contribution is zero for ideal gas – large for liquids and solids.

ISOTHERMAL REVERSIBLE COMPRESSION OF AN IDEAL GAS

A very common type of work is EXPANSION work which is done when a system expands against an outside pressure or is compressed by such an external pressure.

$$dw = \text{work done} = \text{force x displacement}$$
$$= \text{pressure x area x displacement}$$
$$= pdV$$

so that
$$w = \int_{V_i}^{V_f} pdV$$

p is the pressure and V_i and V_f are the initial and final volumes, respectively.

In the limit a reversible reaction proceeds infinitely slowly through a sequence of equilibrium states: therefore the equation of state for an ideal gas can be used

$$pV = nRT$$

so that
$$p = \frac{nRT}{V} \quad \text{and}$$

hence
$$w = \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

and since the process is isothermal

$$w = nRT \int_{V_i}^{V_f} \frac{dV}{V} \quad \text{so that}$$

$$= nRT \ln \frac{V_f}{V_i}$$

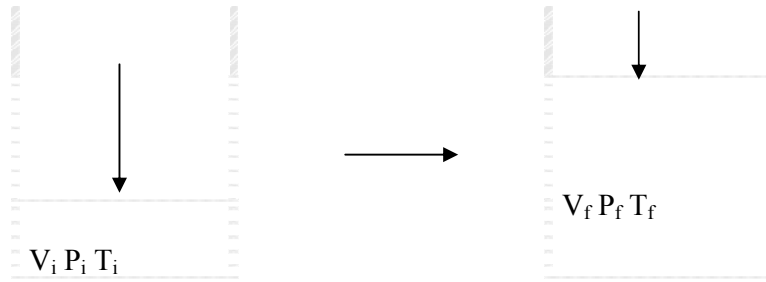also since $p_i V_i = p_f V_f$ for an ideal gas the work is also equal

to
$$nRT\ln \frac{p_i}{p_f} =$$

Questions:

(i) What would the value of w be if the expansion took place against a constant pressure?

(ii) What is the maximum work obtainable from the expansion of a gas?

REVERSIBLE ADIABATIC EXPANSION OF AN IDEAL GAS

$V_i\, P_i\, T_i$

$V_f\, P_f\, T_f$

Because the change is adiabatic $T_i \neq T_f$

$$dU \quad = \delta q - \delta w \qquad (\delta q = 0)$$

$$= - \delta w = -PdV$$

$$\text{also } c_v = \frac{dU}{dT}_v$$

U for an ideal gas is independent of V and p and depends only on T

$$dU = c_v dT \qquad dU = -pdV$$

$$c_v dT + pdV = 0 \quad \text{also for ideal gas } pV = nRT$$

$$c_v dT + \frac{nRT}{V} dV = 0$$

$$c_v \frac{dT}{T} + nR \frac{dV}{V} = 0$$

Integrate initial to final state and assume and assume c_v independent of T.

now $\qquad c_p - c_v = nR$ and we define $\left(\dfrac{c_p}{c_v}\right) = \gamma$

Therefore $\qquad \gamma - 1 = \dfrac{c_p}{c_v} - 1 = \dfrac{c_p - c_v}{c_v} = \dfrac{nR}{c_v}$

11

$$\ln\left(\frac{T_f}{T_i}\right) + (\gamma - 1) \ln\left(\frac{V_f}{V_i}\right) = 0$$

Therefore
$$\frac{T_i}{T_f} = \left(\frac{V_f}{V_i}\right)^{\gamma - 1}$$

also
$$\frac{T_i}{T_f} = \frac{P_i V_i}{P_f V_f}$$

Therefore
$$\frac{P_i V_i}{P_f V_f} = \left(\frac{V_f}{V_i}\right)^{\gamma - 1}$$
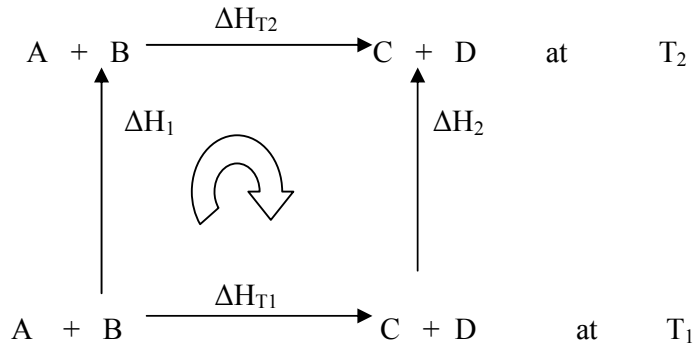
or
$$\boxed{P_i V_i^{\gamma} = P_f V_f^{\gamma}}$$

Problem: 100g of nitrogen at 298K are held by a piston under 30 atm pressure. The pressure is suddenly released to 10 atm and the gas adiabatically expands. If c_v for nitrogen is 20.71 J mol^{-1} K^{-1} calculate the final temperature of the gas.

What are ΔU and ΔH for the change?

Assume that the gas is ideal.

12

VARIATION OF ENTHALPY WTH TEMPERATURE

(Kirchoff, 1858)

$$A + B \xrightarrow{\Delta H_{T2}} C + D \qquad at \qquad T_2$$

$\Delta H_1 \quad\quad\quad \Delta H_2$

$$A + B \xrightarrow{\Delta H_{T1}} C + D \qquad at \qquad T_1$$

Same reaction at two temperatures, T_1 and T_2

Are the enthalpies of reaction, ΔH_{T2} and ΔH_{T1} the same?

Complete the cyclic pathway: $\oint \Delta H = O$

$\Delta H_1 + \Delta H_{T2} - \Delta H_2 - \Delta H_{T1} = O$ so that

$\Delta H_{T2} = \Delta H_{T1} - \Delta H_1 + \Delta H_2$

$$\Delta H_2 = \int_{T_1}^{T_2} C_p (\text{reactants}) \, dT$$

$$\Delta H_2 = \int_{T_1}^{T_2} C_p (\text{products}) \, dT$$

So that if we define $C_p(\text{products}) - C_p(\text{reactants}) = \Delta C_p$ we have

$$\Delta H_{T2} = \Delta H_{T1} + \int_{T_1}^{T_2} \Delta C_p \, dT$$

_____

The difference between ΔH_{T2} and ΔH_{T1} depends on

(i)   the difference between T_2 and T_1
          - if $T_2 \approx T_1$, then $\Delta H_{T2} \approx \Delta H_{T1}$

(ii)   the value of ΔC_p - would you expect this be large?

13

Problem 1

The value of ΔH at 298 K is -92.422 kJ for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Given the heat capacity at constant pressure values (JK^{-1} mol^{-1}) below calculate the value of the enthalpy change for this reaction at 932 K.

C_p (H_2)= $28.772 + 0.276 \times 10^{-3}T + 1.167 \times 10^{-6}T^2$
C_p (N_2)= $26.347 + 7.607 \times 10^{-3}T - 14.428 \times 10^{-6}T^2$
C_p (NH_3)   = $24.757 + 37.483 \times 10^{-3}T + 7.377 \times 10^{-6}T^2$

Problem 2   **Supplemental 1996 Question 1(b)**

The value of the enthalpy change, ΔH, for the reaction

$$2A(g) + B(g) \Rightarrow C(g)$$
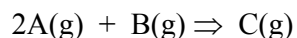
at 300 K is 24.2 kJ mol^{-1}. Calculate the value of ΔH at 500 K given the following heat capacity data.

Substance	Heat Capacity (C_p $JK^{-1}mol^{-1}$)
A	$12.6 + 0.50 \times 10^{-3}T$
B	$29.4 + 0.75 \times 10^{-3}T$
C	$31.7 + 0.68 \times 10^{-3}T$

What would be the effect of increasing the pressure on this reaction?

14

SENIOR FRESHMAN CHEMISTRY

FUNCTIONS OF TWO VARIABLES
– EXACT DIFFERENTIALS

A linear differential expression containing two variables of the form

$$dZ(x,y) \quad = M(x,y)\, dx \; + N(x,y)\, dy$$

is an exact differential if there exists a function f(x,y) such that df(x,y) = dZ(x,y)

If dZ is an exact differential the line integral (i.e., the integral over some path), $\int dz(x,y)$ depends only on the initial and final states i.e.

State Function.

The integral over a cycle $\oint dZ(x,y) = O$ (initial and final states the same) and

$$\frac{\partial^z Z}{\partial x \partial y} \quad = \quad \frac{\partial^2 Z}{\partial y \partial x} \qquad \textbf{CROSS DIFFENTITIATION}$$
$$\textbf{IDENTITY}$$

Example 1 $\qquad Z \; = \; f(x,y) \; = \; 2x^3 + 3x^2y^2 + 4x + 3y^2 + 1$

$$\left(\frac{\partial Z}{\partial x}\right)_y = 6x + 6xy^2 + 4 \quad \text{and} \quad \left(\frac{\partial Z}{\partial y}\right)_x = 6x^2y + 6y$$

also

$$\left(\frac{\partial^2 Z}{\partial x \delta y}\right) = 12\, xy \qquad \text{and} \qquad \left(\frac{\partial^2 Z}{\partial y \partial x}\right) = 12\, xy$$

$$\text{i.e. } \left(\frac{\partial^2 Z}{\partial x \delta y}\right) \qquad = \qquad \left(\frac{\partial^2 Z}{\partial y \, \delta x}\right)$$

Example 2   Ideal Gas $PV = nRT$ or $P = \dfrac{nRT}{V}$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2} \qquad\qquad \textbf{and} \qquad \left(\frac{\partial^2 P}{\partial V \partial T}\right) = -\frac{nR}{V^2}$$

while

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \qquad \text{and} \qquad \left(\frac{\partial^z P}{\partial T \delta V}\right) = -\frac{nR}{V^2}$$

<div align="center">

CROSS DIFFERENTIATION IDENTITY

</div>

EULER OR MAXWELL RELATIONS

1. $\underline{du = \quad TdS - pdV}$

$$\left(\frac{\partial u}{\partial V}\right)_S - p; \quad \left(\frac{\partial u}{\partial s}\right)_V = T \qquad\qquad \left(\frac{\partial P}{\partial s}\right)_V - \left(\frac{\partial T}{\partial V}\right)_V$$

2. $\underline{dH = TdS + VdP}$

$$\left(\frac{\partial H}{\partial P}\right)_S = V; \quad \left(\frac{\partial H}{\partial s}\right)_P = T \qquad\qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial v}{\partial s}\right) P$$

3. $\underline{dF = -SdT - PdV}$

$$\left(\frac{\partial F}{\partial V}\right)_T = -p; \quad \left(\frac{\partial F}{\partial T}\right)_V = -S \qquad\qquad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

4. $\underline{dG = -SdT + VdP}$

$$\left(\frac{\partial G}{\partial P}\right)_T = V; \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \qquad\qquad \underline{\left(\frac{\partial V}{\partial T}\right)_P} = -\underline{\left(\frac{\partial S}{\partial P}\right)_T}$$

<div align="center">

2nd Differentials

</div>

16

THE SECOND LAW OF THERMODYNAMICS

The First Law 'balances the books' – energy may be transformed from one form to another – never created or destroyed. This is intuitively easy to understand but does not give any indication of the direction of change. The Second Law sums up our experiences with equilibria just as the First Law sums up our experiences with energy and so it allows us to predict the direction of physical and chemical changes.

The purpose here is to establish a criterion for the feasibility of a given physical or chemical transformation under specified conditions. What is needed to do this is a **state function** (thermodynamic property) that changes in a characteristic manner when the reaction proceeds spontaneously. The objective is attained indirectly by considering a function called **entropy** (symbol **S**) which is the criterion for change in an isolated system and then combining it with the tendency for energy change to get the criterion for change in a real system. This combination, which is the criterion for spontaneous change, turns out to be the change in the **Gibbs Free Energy** function, **ΔG,** given by the equation

$$\Delta G \; = \; \Delta H \; - \; T\Delta S$$

ΔG is less than zero for all spontaneous changes: when ΔG is equal to zero the system is at equilibrium and a change for which ΔG is greater than zero is not thermodynamically feasible in the direction specified.

ENTROPY

The entropy, S, of a system is an extensive state function which is defined for an infinitesimal isothermal process by:

$$dS \; = \; \delta q_{rev} / T$$

Here δq_{rev} is the heat absorbed by the system if the process is carried out reversibly. This equation clearly shows the importance of reversible processes in thermodynamics even though they cannot occur in nature and even if they could they would be so slow as to take an infinite time to progress through a series of equilibrium states. The value of the entropy can only be found if we can invent a means to determine the value of δq_{rev} – i.e., devise a way in which the change can be carried out reversibly and the heat change calculated.

We will use the Carnot cycle to show that entropy so defined is a State function.

In a physical interpretation entropy is a measure of molecular disorder and may also be defined as

$$S = k \, ln \, \Omega$$

Here Ω is the number of microscopic realisations of specified macrostate of fixed energy. The tendency is for Ω to maximise under the randomising influence of temperature.

The concept of entropy in an isolated system will be demonstrated by examining in detail the isothermal intermixing of two gases. To do this it is convenient to consider that an infinitesimal change in entropy (dS) for a system can be divided into an external part due to its interaction with its surroundings (d_eS) and an internal part due to changes occurring within the system itself (d_iS) so that:

$$dS = d_eS + d_iS$$

In all cases $d_eS = \delta q / T$ and this can be easily measured but we can say only that $d_iS \geq 0$. For reversible changes $d_iS = 0$ and for irreversible (natural, spontaneous) changes $d_iS > 0$. So for a change carried out reversibly we have $dS = \delta q_{rev} / T$.

In an isolated system where $d_eS = 0$, $dS = d_iS$. Because for a spontaneous change $d_iS > 0$ in an isolated system $dS > 0$.

This is the basis of the well-known statement of the Second Law:

In an isolated system only those changes are possible that result in an increase in the entropy of the system

We will begin by considering something that we know to be a spontaneous process – the intermixing of two perfect gases. To calculate the entropy change we need to invent a reversible path. In this case the direction is opposite to that of the mixing – but because entropy is a state function we will simply need at the end to change the sign of the value calculated.

Next we will go through the Carnot cycle with a view to showing that entropy is a State function. Note that we will be making use of parts of what we discussed earlier, namely isothermal and adiabatic expansions/compressions of perfect gases, in considering this hypothetical heat engine.

We will then introduce the Free Energy Functions and show why the names 'Free' or 'Available' energy are appropriate. The most important of these for chemistry is the **Gibbs Free Energy**, G.

TO CALCULATE THE CHANGE IN ENTROPY FOR THE INTERMIXING

OF TWO PERFECT GASES

V/2	V/2
T n_{H_2}	T n_{N_2}
P	P

Remove
$\rightarrow$
Partition

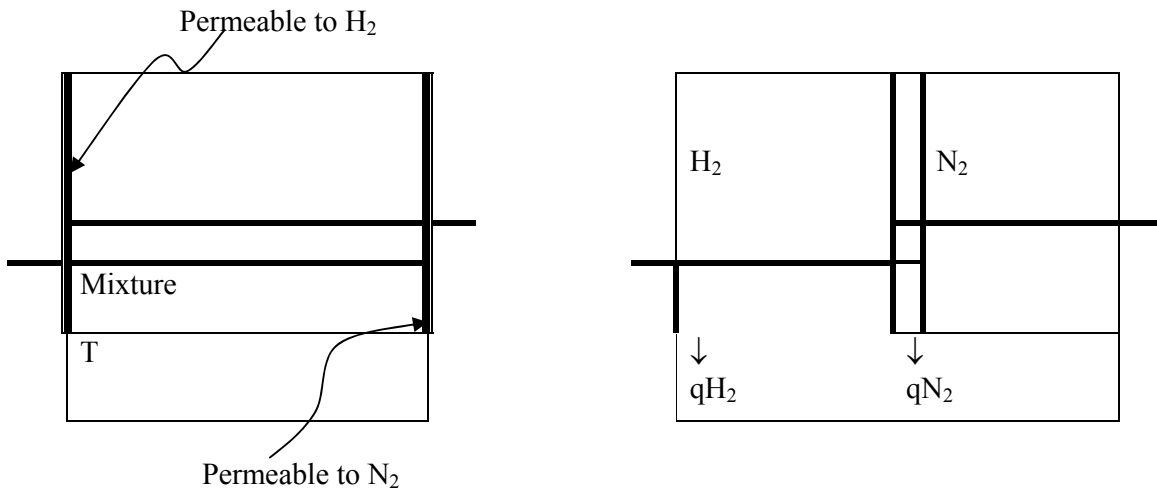| V |
|---|
| T n_{H2} + n_{N_2} |
| P |
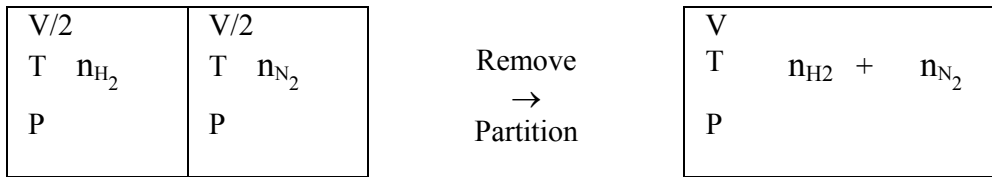
$$\Delta S = S_{f-} Si$$

$$\Delta S = \Delta_e S + \Delta_i S$$
$$\Delta_e S = O$$

so that $\Delta S = \Delta_i S$

which is $> O$ for a
spontaneous change

_____-

To calculate ΔS we will unmix the gases reversibly – because S is a state function
$\Delta S_{rev} = \Delta S_{irrev}$ but we can only evaluate ΔS in a reversible process.

Permeable to H_2

Mixture

T

Permeable to N_2

H_2 N_2

$\downarrow$ $\downarrow$
qH_2 qN_2

T, the initial temperature of the gases is unchanged.

$$S = \Delta_e S + \Delta_i S, \quad \text{Reversible process } \Delta_i S = O$$

Therefore $\Delta S = {}^{q_{rev}}/T$; $q = qH_2 + qN_2$

First Law: $\Delta U = q - w$
$$= qH_2 + qN_2 - wH_2 - wN_2$$
But $\Delta U = O$ for isothermal reversible expansion/contraction ideal gas

so that $qH_2 + qN_2 = wH_2 + wN_2$

19

And we can calculate these two work quantities immediately

$$W_{H2} = n_{H2}RT\ln(V/2)/V = -n_{H2} \, RT\ln 2$$
$$W_{N2} = n_{N2}RT\ln(V/2)/V = -n_{N2} \, RT\ln 2$$

so that $W_{H2} + W_{N2} = -(n_{H2} + n_{N2}) \, RT\ln 2$

Therefore $\Delta S_{rev} = q^{rev}/T = -(n_{H2} + n_{N2}) \, R\ln 2$

Note that this is clearly negative

But this is for the "unmixing" so that for the initial mixing (irreversible, spontaneous) reaction

$$\Delta S_{irrev} = -\Delta S_{rev} = (n_{H2} + n_{N2}) \, RT\ln 2$$

And this is clearly positive i. e., mixing would therefore be spontaneous with $\Delta S > 0$

The entropy change associated with a phase change, e.g., melting, evaporation, is

$$\Delta S_{transformation} = \frac{\Delta H_{transformation}}{T_{transformation}}$$

ΔH is the enthalpy and T the temperature of the transformation.

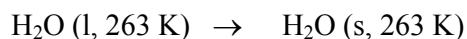The entropy change associated with heating is

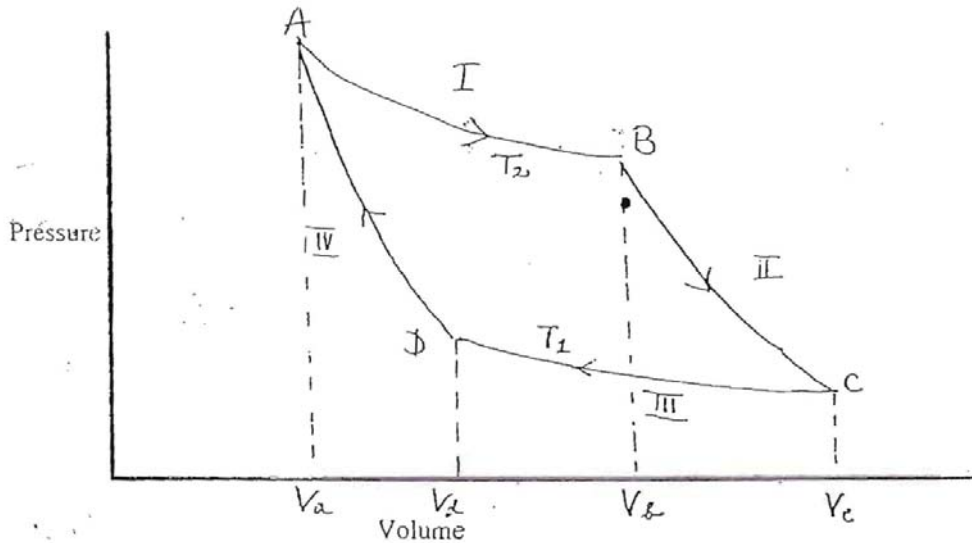$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} \, dT$$

Problem

$$H_2O \, (l, 263 \text{ K}) \rightarrow H_2O \, (s, 263 \text{ K})$$

Will this change occur spontaneously in an isolated system?

$$\underline{C}_p \, (H_2O, s) = 34.57 \;\; J\,K^{-1}mol^{-1}$$
$$\underline{C}_p \, (H_2O, l) = 71.48 \;\; J\,K^{-1}mol^{-1}$$
Therefore $\Delta H_f \, (H_2O) = 5998.3 \text{ J mol}^{-1}$

$$(\Delta H_f \equiv \text{Enthalpy of fusion})$$

THE CARNOT CYCLE

		WORK DONE	HEAT ABSORBED
Isothermal curve AB and reversible in reservoir T_2	Step I	$RT_2 \ln V_b/V_a$	$RT_2 \ln V_b/V_a$
Reversible, adiabatic expansion -temperature falls to that of lower reservoir	Step II	$C_v (T_2-T_1)$	0
At reservoir at T_1-isothermal reversible compression	Step III	$RT_1 \ln V_d/V_c$	$RT_2 \ln V_d/V_c$
Reversible, adiabatic compression –temperature rises $T_1 \rightarrow T_2$ back to original state	Step IV	$C_v(T_1-T_2)$	0

Total work done is sum of four terms but $W_{II} = - W_{IV}$ so that

$W_{total} = W_I + W_{III} = RT_2 \ln V_b/V_a + RT_1 \ln V_d/V_c.$

But now A and D lie on an adiabatic curve as do B and C.

$$\text{Therefore} \quad \left(\frac{V_d}{V_a}\right)^{\gamma-1} = \frac{T_2}{T_1} \quad \text{and} \quad \left(\frac{V_c}{V_b}\right)^{\gamma-1} = \frac{T_2}{T_1}$$

$$\text{So that} \quad \frac{V_d}{V_a} = \frac{V_c}{V_b} \quad \text{or} \quad \frac{V_b}{V_a} = \frac{V_c}{V_d}$$

$$\text{Therefore} \quad W_{total} = RT_2 \ln \frac{V_b}{V_a} - RT_1 \ln \frac{V_b}{V_a} = R(T_2 - T_1)\ln \frac{V_b}{V_a}$$

21

Now by definition the efficiency of a heat engine is equal to the ratio of the total work done, W_{total}, in the cycle to the heat, Q_2, taken in the higher temperature so that the efficiency of the hypothetical CARNOT ENGINE $\dfrac{W_{total}}{Q_2} = \dfrac{T_2 - T_1}{T_2}$.

Note that the lower the temperature of the sink, the greater will be the efficiency – absolute zero impossible at which the efficiency would be unity. Similarly for a given temperature of the sink the efficiency will be increased by using a higher temperature source.

Entropy Change   From the first law $\Delta U = 0$ for the cycle
$$Q_{total} - W_{total} = 0$$

W_{total} has been evaluated: Steps II and IV are adiabatic so that Q_{total} is given by the sum of Q_2 and Q_1 absorbed at T_2 and T_1.

$$W_{total} = Q_{total} = Q_2 + Q_1 \equiv W$$

$$\frac{W}{Q_2} = \frac{Q_2 + Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}$$

therefore $Q_2 + Q_1 = Q_2 - \dfrac{T_1}{T_2} (Q_2)$

therefore $\dfrac{Q_1}{T_1} = - \dfrac{Q_2}{T_2}$ or $\dfrac{Q_1}{T_1} + \dfrac{Q_2}{T_2} = 0$ or $\Sigma \dfrac{Q}{T} = 0$

for an infinitely small change the steps may be replaced by the integral

$$\int \frac{\delta Q}{T} = 0 \quad \text{so that} \oint ds = 0$$

THIS SHOWS THAT ENTROPY IS A STATE FUNCTION

FREE ENERGY FUNCTIONS

Available Energy	Free Energy
(Helmholtz Free Energy)	(Gibbs Free Energy)
$F = U - TS$	$G = H - TS$
Also known as the Work Function, F, but not so useful in chemical systems	We will deal almost exclusively with G because it suits conditions of constant T and P

Both are obviously state functions but apart from the definitions what are these functions?

THE HELMHOLTZ FREE ENERGY FUNCTION, F

$F = U - TS$ so that for an infinitesimal change

$dF = dU - TdS - SdT$ If we assume constant temperature, then $dT = 0$ and

$dF = dU - TdS$

also $dU = \delta q - \delta w$ so that $dF = \delta q - \delta w - TdS$

and $dS = d_eS + d_iS = \delta q/T + d_iS$ so that

$\delta q = TdS - Td_iS$

Substitution gives

$dF = TdS - Td_iS - \delta W - TdS$

so that $\boxed{dF = -\delta W - Td_iS}$

for a reversible change $d_iS = O$ therefore $Td_iS = O$ and $dF_{rev} = -\delta W_{rev}$

for an irreversible change $d_iS > O$ therefore $Td_iS > O$

$d F_{irrev} < -\delta W_{irrev}$

Reminder: **F is a state function so that $dF_{rev} = dF_{irrev}$**

_____

So that $\quad - \delta W_{rev} < - \delta W_{irrev}$

_____

Reminder: **W is the work done by the system; - W is work done on the system**

So for a given change of state the maximum obtainable work (work that can be done on the surroundings) is the reversible work. This is the same for all reversible paths and is – dF.

This is the origin of terms "available" or "free energies"

THE GIBBS FREE ENERGY FUNCTION, G

Follow a similar sequence to show

$$dG_{rev} = - \delta W^{/} \qquad \text{at constant T and P with}$$
$$dG_{irrev} = - \delta W^{/} \qquad \delta W^{/} \equiv \text{work other than PdV work}$$

if $W^{/}$ be taken as zero i.e., no work other than "pressure volume" work then

$dG \quad = 0 \quad$ System at equilibrium

$dG \quad < 0 \quad$ process has a tendency to proceed spontaneously

$dG \quad > 0 \quad$ process will tend to be spontaneous in the opposite direction.

_____

THE THIRD LAW OF THERMODYNAMICS

The interest here lies in the determination of values of $\Delta\mathbf{G}$ from purely calorimetric (that is the determination of heat changes) measurements. Enthalpy changes can be determined in this way using a calorimeter as you have done in the laboratory (thermochemistry) and it turns out that the entropy values for a substance can also be determined calorimetrically if we can say something about the value of that entropy when the substance is at the absolute zero of temperature. Historically this objective (to obtain Gibbs Free Energy values from calorimetric measurements) was approached incrementally over a period of years as our knowledge of thermodynamics increased and some of these efforts will be described in the lecture.

The following statement of the Third Law made by Lewis and Randall in 1923 is the one that we will use because it is of most relevance in chemistry:

If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero and does so become in the case of perfectly crystalline substances.

THIRD LAW ENTROPIES

This provides the basis for what are called 'third law', 'calorimetric', 'practical', 'conventional' and even 'absolute' entropies. The statement will also be very helpful for our understanding of something called **residual entropy**, which occurs in a number of substances that retain some entropy (i.e., disorder) even when they approach the absolute zero of temperature.

The value of the third law entropy of a substance at any temperature is therefore determined by measuring the heat changes as the substance is heated up from or cooled down to the absolute zero of temperature to the temperature in question. These processes can be carried out, at least in our minds, reversibly and so

$$\Delta S \ = \ q_{rev} / T$$

can be evaluated for each step in the process. The series of steps traversed may entail changes in phase and the heating of each of the phases as we progress from absolute zero, where all substances are solids, to the gas phase. Because we cannot attain the absolute zero of temperature an extrapolation procedure must be used at the lowest temperatures. Such a determination of Third Law entropy will be illustrated by considering the data for chlorine gas. We will also use calorimetric data measured on the allotropes of sulphur, monoclinic and rhombohedral, to verify the Third Law.

RESIDUAL ENTROPY

Finally we will consider the phenomenon of **residual entropy** more closely using two quite different examples. The first of these is carbon monoxide in which the molecules are not packed into a perfect crystal as absolute zero is approached. The second is hydrogen in which the phenomenon is due to the existence of two forms, *ortho-* and *para-*, which without a catalyst fail to attain their equilibrium mixture proportions as the substance is cooled.

ENTROPIES AT TEMPERATURES OTHER THAN ABSOLUTE ZERO

The Third Law opens the way for the determination, using calorimetric measurements, of entropies at temperatures other than zero Kelvin. By combining these with enthalpy data we can therefore determine values of ΔG – and hence predict the position of equilibrium – from purely calorimetric measurements. The value of the entropy of a substance at a temperature T Kelvin, denoted by S_{TK}, is related to its value at zero Kelvin, S_{0K}, by

$$S_{TK} = S_{OK} + \int_{O}^{T} \frac{Cp}{T} dT + \sum \Delta S_{\text{phase transformations}}$$

There will be at least one term

for each phase: solid, liquid and gas

Each of these is equal to

$$\frac{\Delta H_{transformation}}{T_{transformation}}$$ for each transformation

See later the example for Chlorine gas where each of theses terms is dealt with and evaluated in detail. There is a low temperature extrapolation term, a term for heating the solid, a term for the fusion, a term for heating the liquid, a term for the vaporisation and finally a term for heating the gas. There is also a correction term for the ideal gas,

ENTROPIES AT TEMPERATURES OTHER THAN ABSOLUTE ZERO (II)

CALCULATIONS FOR CHLORINE GAS
W.F. Giauque and F.M. Powell, J.A.C.S., **61**, (1939), 1970

Temp. Range orTransition Temperature (K)	Type of calculation/measurement	Entropy mole^{-1} (cal K^{-1})*
0-15	From Debye function (0 = 115)	0.331
15 – 172.12	Graphical from C_p for solid	16.573
172.12	Fusion: $\Delta H_{fus} = 1531$ cal mole^{-1}	8.895
172.12 – 239.05	Graphical from C_p for liquid	5.231
239.05	Vaporisation: $\Delta H_{vap} = 4878$ cal mole^{-1}	20.406
	Entropy of actual gas at boiling point	51.44
	Correction for gas imperfection	0.12
	Entropy ideal gas at boiling point	51.56
	(*1 cal = 4.184 Joule)	

This is experimentally measured third law entropy.

EXPERIMENTAL VERIFICATION OF THE THIRD LAW

This is a relatively simple verification involving the forms of sulphur – monoclinic and rhombic. Here the transition temperature from one form to the other is 368.5 K with $\Delta H = -96.0$ cal mol^{-1}. At this temperature the two forms are in equilibrium but it is possible to obtain monoclinic sulphur stable below its transition temperature. This can then be taken down as near as possible to absolute zero – the necessary calorimetric data can be taken on both forms.

Experimentally

$$S^{rhombic}_{368.5K} = S^{R}_{OK} + \int_{O}^{368.5} \frac{C_p^R}{T} dT = S^{R}_{OK} + 8.81$$

$$S^{monoclinic}_{368.5K} = S^{M}_{OK} + \int_{O}^{368.5} \frac{C_p^M}{T} dT = S^{M}_{OK} + 9.04$$

so that $\quad S^{R}_{368.5K} - S^{M}_{368.5K} = S^{R}_{OK} - S^{M}_{OK} - 0.23$

ΔH for the transition $= -96.0$ cal mol^{-1}

therefore $\quad S^{R}_{368.5} - S^{M}_{368.5} = -96.0/368.5 - 0.261$ cal mol^{-1} K^{-1}

so that $\quad S^{R}_{OK} - S^{M}_{OK} = -0.031$ cal mol^{-1} K^{-1}

This may be taken as zero within the limits of the experimental errors involved.

More accurate data are available for the system white-tin grey tin.

RESIDUAL ENTROPY

For gases standard entropies can be calculated from statistical theories and spectroscopic data which give the energies in the various quantum states. To do this use the SAKUR TETRODE equation:

For a monatomic gas $S_T = \frac{3}{2} R\ln M + \frac{5}{2} R\ln T - R\ln P - 2.314$

$$S^O_{T=298.15} = \frac{3}{2} R\ln M + 108.7\, JK^{-1}\, mol^{-1}$$

Polyatomic gases would have the above terms plus terms for vibrational and rotational entropies.

The table below compares the values determined as above (labelled Spectroscopic) with experimental Third Law values determined using the method illustrated previously for Chlorine gas.

Substance	^{S}**Spectroscopic**	^{S}**Third Law**
N_2	191.45	191.95
O_2	205.04	205.33
H_2S	205.34	205.54
CO_2	213.57	213.74
C_2N_4	219.43	219.47
H_2	130.60	124.37
CO	197.85	193.21

The values in the table are for ideal gas state at 298.15 K in $J\,K^{-1}\,mol^{-1}$

The experimental Third Law values in the final column for H_2 and CO are lower because the assumption that the entropy is zero at 0.0 K is **not** correct for these substances – the crystals contain residual entropy. Incidentally the agreement between the values determined by the two methods for the other substances shows the correctness of the Third Law.

29

Carbon Monoxide CO

$S = Rln\Omega$ which in a completely random arrangement in the crystal is

$$Rln2 = 8.3144 \times 0.6931$$
$$= 5.763 \text{ JK}^{-1} \text{ mol}^{-1} \quad \text{or } 1.378 \text{ cal K}^{-1} \text{ mol}^{-1}$$

From the table $\Delta = 4.64$ which implies that the orientation is not fully random. Good discussion of this in Chemical Thermodynamics by D.J.G.Ives. Note also the residual entropy of ice due to hydrogen bonding.

Ortho- and para-hydrogen

Rotational lines in far UV spectrum show 3:1 ratio in intensity which is consistent with the restriction of transitions to those between rotational states of even $J = 0, 2, 4...$ (Symmetrical wave functions) or between odd states $J = 1, 3, 5...$ (antisymmetrical wave functions). Latter have three times the statistical weight of the former – two kinds of H_2 molecules present – proton spin $i = \frac{1}{2}$ (in units of $h/2\pi$).

Symmetrical parallel spins – resultant spin of 1 so we have -1, 0, +1 with $(2i + 1) = 3$
This is ORTHO

Antisymmetrical (opposed) have a resultant of 0 so that $(2i + 1) = 1$ i.e., single weight
This is **PARA**

Normal hydrogen gas at room temperature is composed of 3 parts of ortho and 1 part of para hydrogen. These components separately give rise to rotational spectrum lines.

As the temperature falls the equilibrium ortho to para ratio decreases so that as absolute zero is approached all of the ortho hydrogen present would be converted to para. The pure para hydrogen can go to $J = 0$ and so get rid of its rotational energy – ortho hydrogen, in contrast, cannot do this. See the diagram on the following page which illustrates this and shows how the residual entropy arises in hydrogen cooled in the absence of a catalyst that would convert ortho to para form. Under these circumstances the room temperature ratio (3:1 of ortho:para) forms is retained through the cooling process. Compare the areas under the curves in the diagram to see the residual entropy.
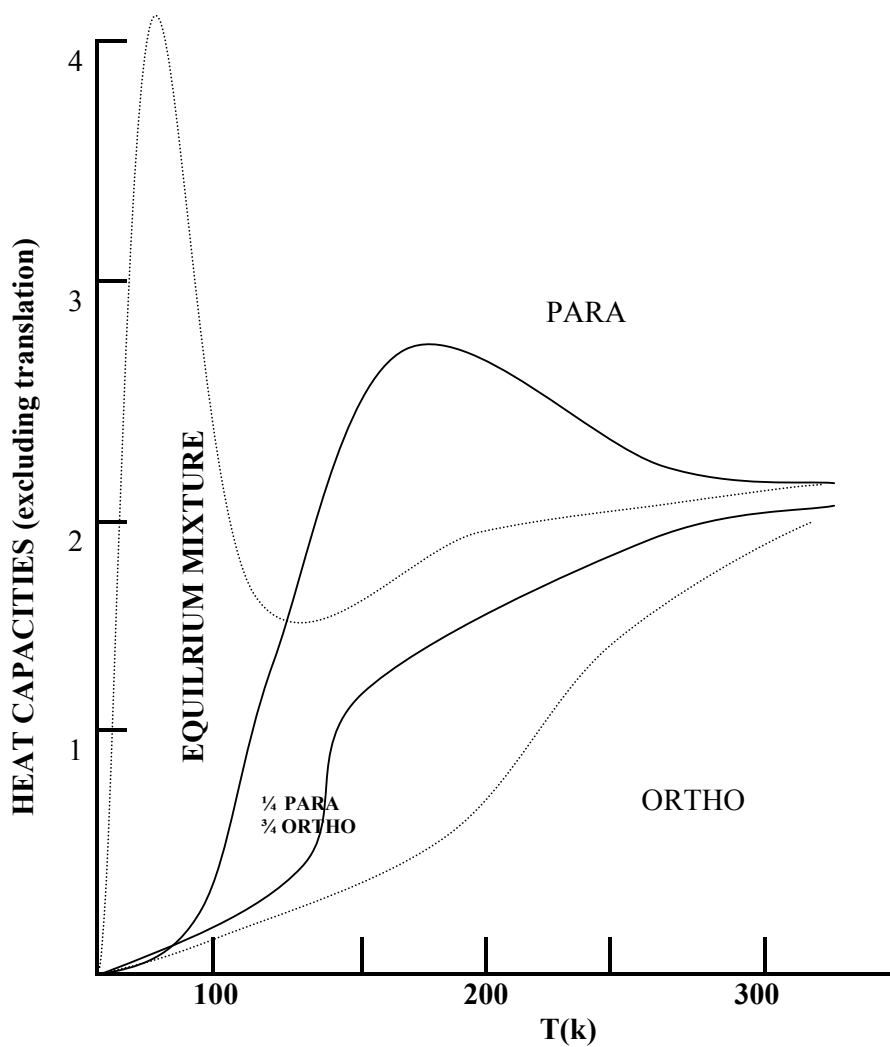
This diagram illustrates the heat capacities excluding translations for *ortho, para*, the equilibrium mixture and a mixture containing *ortho* to *para* in a 3:1 ratio taken from W.F. Giauque, **JACS, 52** (1930) 4816.

FOUR FUNDAMENTAL EQUATIONS FOR A CLOSED SYSTEM

Derived by combining: $dU = \delta q - \delta w$; $\delta w = -PdV$;

$H = U + PV$; $\delta q_{rev} = TdS$;

$F = U - TS$; $G = H - TS$

―――――――――――――――――――――――

1. dU = $\delta q - \delta w$
    dU = $TdS - PdV$

2. H = $U + PV$
    dH = $dU + PdV + VdP$
    dH = $TdS + VdP$
    dH = $TdS + VdP$

3. F = $U - TS$
    dH = $dU - TdS - SdT$
    dF = $\cancel{TdS} - PdV - \cancel{TdS} - SdT$
    dF = $-SdT - PdV$

4. G = $H - TS$
    G = $U + PV - TS$
    dG = $dU + PdV + VdP - TdS - SdT$
    dG = $\cancel{TdS} - \cancel{PdV} + \cancel{PdV} + VdP - \cancel{TdS} - SdT$
    dG = $-SdT + VdP$

THE CHEMICAL POTENTIAL (μ_i)

We will now move on to consider open systems to which chemical species can be added or removed. This immediately creates the need to be able to express the effects of these changes in composition on the thermodynamic properties of the system. This is done using the concept of the **chemical potential**, which for a species i is given the symbol μ_i. In its most usual usage the **chemical potential** is considered to be the partial derivative of the Gibbs free energy function, G, with respect to the number of moles of the species i, n_i, with the temperature, T, pressure, P, and the numbers of moles of all other substances $n_{j \neq i}$ being held constant. So it is the rate of change of G with the number of moles of the component i that are added to or taken from the system.

$$\mu_i \quad = \quad (\partial g / \partial n_i)_{T,P, nj \neq i}$$

We identify the **intensity factors** Temperature and Pressure with the driving forces for transfers of energy via heat and mechanical work, respectively. The chemical potential, μ_i, is also an **intensity factor** and is identified in an analogous way with the driving force for changes in chemical composition.

Thus the term 'potential' has the same meaning as we place on an electrical potential. This implies that if the chemical of a species in two adjacent phases has the same value then there will be no tendency for that species to move across the interface. On the other hand if the chemical potential of a species in one of the phases has a higher value than in the other then this will cause that species to move from the phase in which its chemical potential has the higher value. So just as temperature differences drive heat transfers and pressure differences give rise to mechanical changes, differences in chemical potentials drive changes in chemical composition. On reflection this is hardly surprising since we have identified the Gibbs free energy, G, as the criterion for the direction of chemical change with the tendency for ΔG to become zero so that equilibrium can be achieved.

THE CHEMICAL POTENTIAL AND EQUILIBRIA

We will in the following lectures first examine a number of heterogeneous equilibria between phases using the principle that the values of the chemical potentials of each species must be equal in these phases if no transfer of that chemical species is to occur between them i.e., if they are at equilibrium. In this way a formal derivation of the Gibbs Phase Rule

$$F = C - P + 2$$

will be possible. The Clapeyron and Clausius-Clapeyron equations will also be derived. The latter

$$dlnP/dT = \Delta H_{trans} /RT^2$$

makes it possible to determine the heats of transformations from condensed to gaseous phases through a series of measurements of the vapour pressure of the condensed phase as the temperature is changed.

We will then consider homogeneous chemical equilibria to determine the well-known relationship between the standard free energy for a chemical reaction and its equilibrium constant, K. This leads naturally on to the Van't Hoff equation, which is a quantitative relationship between temperature and the value of the equilibrium constant for a chemical reaction

$$\mathbf{dlnK/dT \ = \ \Delta H_{rxn} \ /RT^2}$$

The integrated form of the Van't Hoff equation is very much used because it can be utilised derive the enthalpy of reaction from two measurements of the equilibrium constant for the reaction made at temperatures that are reasonably close to each other.

The integrated form of this equation is:

$$\mathbf{ln \ (K_1/K_2) \ = \ - \ (\Delta H_{rxn}/R) \ (1/T_1 - 1/T_2)}$$

where K_1 and K_2 are the equilibrium constants measured at the Kelvin temperatures T_1 and T_2, respectively, R is the gas constant and ΔH_{rxn} is the enthalpy change in the reaction assumed to be constant over the temperature range examined. There are five potential unknowns (ΔH_{rxn}, T_1, T_2, K_1 and K_2) in this equation so that if any four of them are known the fifth can be calculated. Note that the measurements of K should be made at temperatures that are reasonably close to each other to allow the assumption to be made that ΔH_{rxn} is not a function of temperature (cf. the Kirchoff equation as derived earlier).

THE CHEMICAL POTENTIAL OF A SPECIES i   -   (μ_i)

The chemical potential describes the contribution of a particular species in a many-component system. It is defined via the properties of single valued functions of many variables.

$$U = f\,(V,S,n_1,n_2n_3, \ldots) \qquad\qquad n_i = \text{number of moles of species i}$$

for small changes in V,S, n_i

$$dU = \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial S}\right)_{V,n} ds + \sum^{i} \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_{j\neq i}}$$

In a one component system all $dn = O$

$$dU = q - w = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,n} = -P \; and \left(\frac{\partial U}{\partial S}\right)_{V,n} = T \qquad\qquad \begin{array}{c}\text{Intensity}\\\text{Factors}\end{array}$$

for a open system we identify $\left(\dfrac{\partial U}{\partial n_i}\right)$ with a chemical intensity factor μ_i – CHEMICAL POTENTIAL

$$dU = TdS - PdV + \mu_i dn_i$$

_____

or more generally

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,v,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$
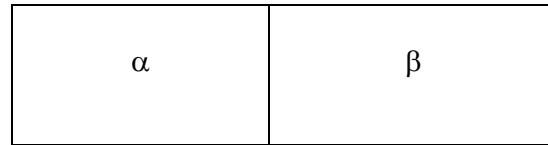
most usual usage is partial molar Gibbs Free Energy

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

HETEROGENEOUS EQUILIBRIA - BETWEEN TWO PHASES

Thermal Equilibrium

no net transfer of heat
any small transfers reversible
condition $dS = O$

α	β

i.e., for any small flow dq from $\alpha \rightarrow \beta$

$dS^\alpha + dS^\beta$ must equal zero

$$-\frac{dq}{T^\alpha} + \frac{dq}{T^\beta} = O \qquad\qquad \therefore T^\alpha = T^\beta$$

(if $T^\alpha > T^\beta$ then heat flows irreversibly $\alpha \rightarrow \beta$)

_____

Mechanical (Volume) Equilibrium   at constant T and V; $dF = 0$

i.e. for any small expansion dV in α, corresponding $-dV$ in β

$dF^\alpha + dF^\beta = O$

$-P^\alpha dV + P^\beta dV = O \qquad\qquad \therefore P^\alpha = P^\beta$

_____

Chemical Equilibrium   at given T and P; $dG = O$

i.e. for any small transfer dn_i moles of species i

$dG^\alpha + dG^\beta = O$

$\mu_i^\alpha (-dn_i) + \mu_i^\beta (dn_i) = O \qquad\qquad \mu_i^\alpha = \mu_i^\beta$

_____

Saturated Solution	μ_i (solution)	=	μ_i (crystal)
Boiling Point	μ_i (liquid)	=	μ_i (vapour)
Distribution	μ_I (H_2O)	=	μ_I (CCl_4) etc…

GIBBS PHASE RULE (1876)   **EQUILIBRIUM**

P Number of Phases:

A phase is homogeneous, physically distinct and mechanically separable part of the system. Each phase must therefore be separated from other phases by a physical boundary e.g.

(i)   any number of gases-mix to give
      1 phase

(ii) saturated solution; solution,
      undissolved solid and vapour
      3 phases

(iii) $CaCO_3 \rightleftharpoons CaO + CO_2$ two
        different solids and gas 3 phases

C Number of components:

Number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed either directly or in the form of a chemical equation. – Approach assumes a prior knowledge is available in form of description or chemical equation e.g.

(i) ice/water/water vapour
     1 component

(ii) $CaCO_3$ (solid) $\rightleftharpoons$ CaO (solid) + CO_2
     (gas). All phases can be made from
     CaO, CO_2
     2 components

F variance or number of Degrees of Freedom

The state of a system is completely defined when every intensive variable has been assigned some fixed value. The pressure, the temperature, the compositions of all the phases and all other properties are known. In order that such a state may be defined some minimum number of variables must be specified – number of degrees of freedom (variance).

General Case:

Equilibrium with C distinct components in each of P phases

To specify the state of each phase requires P,T and (C-1)

i.e. $2 + (C -1) = (C + 1)$ variables

∴ Total number of variables $P(C + 1)$

Equations:

$T^{\alpha} = T^b = T^{\gamma}$………. $\quad$ (P-1) equations

$P^{\alpha} = P^b = P^{\gamma}$………. $\quad$ (P-1) equations

$\mu_1^{\alpha} = \mu_1^b = \mu_1^{\gamma}$…… $\quad$ (P-1) equations

$\mu_2^{\alpha} = \mu_2^b = \mu_2^{\gamma}$…… $\quad$ (P-1) equations

-

-

-

-

$\mu_c^{\alpha} = \mu_c^b = \mu_c^{\gamma}$………. $\quad$ (P-1) equations

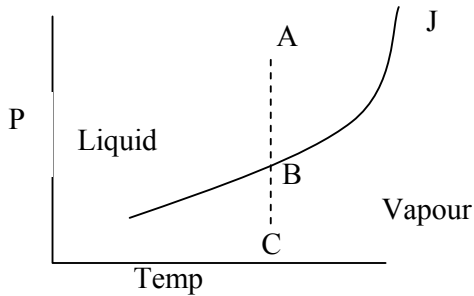∴ Total number of equations $(C +2)(P - 1)$

F = the number of variables not fixed is therefore

$$= P(C + 1) - (C + 2)(P - 1)$$

Which gives $\quad$ **F = C – P + 2 Gibbs Phase Rule**

38

ONE COMPONENT – TWO PHASES

(CLAPEYRON AND CLAUSIUS-CLAPEYRON EQUATIONS)

Heterogeneous equilibrium with one component in two phases. Along the line OBJ

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

At fixed temperature the vapour pressure is fixed.

As the temperature varies, the vapour pressure also varies i.e., the vapour pressure. is f(T)

Apply equilibrium condition – μ must have same value in both phases $\mu^\alpha = \mu^\beta$

If T is altered by dT, P shifts by dP and μ by dμ so that

$$d\,\mu^\alpha = d\,\mu^\beta\text{ - so that equilibrium is maintained.}$$

For a one-component system $\mu = \overline{G}$ i.e., it is the partial molar Gibbs Free energy.
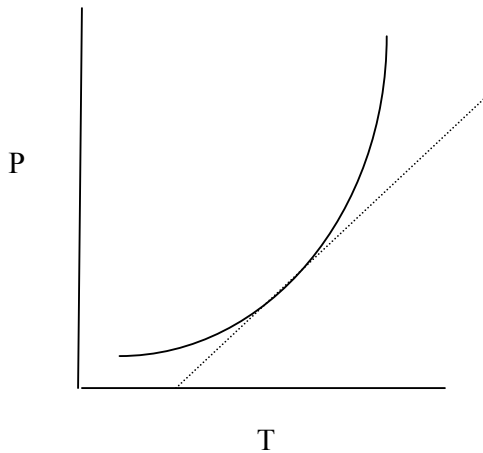
For changes in dP and dT

$$dG = \quad VdP - SdT \qquad \begin{array}{l} V \equiv \text{molar volume} \\ S \equiv \text{molar entropy} \end{array}$$

so that

$$d\,\mu^\alpha = V^\alpha\,dP - S^\alpha dT = d\,\mu^\beta = V^\beta dP - S^\beta dT$$

this gives

$$\frac{dP}{dT} = \frac{S^\alpha - S^\beta}{V^\alpha - V^\beta} = \frac{\Delta S}{\Delta V}$$

which is the difference in molar entropy of the phases divided by the difference in their molar volumes.

39

Interest lies in the value of this derivative, dP/dT, at a specified temperature and pressure.

For isothermal reversible (i.e., equilibrium) condition at constant pressure

$$S^{\alpha} - S^{\beta} = \Delta S = \int \frac{dq_p}{T}$$

$$= \frac{1}{T} \int dq_p = \frac{\Delta H}{T}$$

So that $\qquad \dfrac{dP}{dT} = \dfrac{\Delta H}{T\Delta V}$ $\qquad$ *CLAPEYRON EQTN.*
{ ANY TWO PHASES OF
ONE COMPONENT }

_____

A particularly convenient case arises when we deal with a gas and a condensed (solid or liquid) phase.

Here $\quad (V^{\alpha} - V^{\beta}) = (V_{gas} - V \text{ condensed phase}) \cong V_{gas}$

because $V_{gas} \gg V$ condensed phase

If we now assume that the gas is ideal then

$V_{gas} = RT/P$ so that

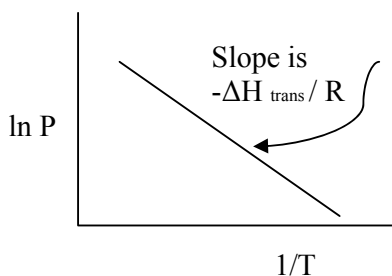$$\frac{dP}{dT} = \frac{\Delta H}{T(RT/P)} \quad = \quad \frac{P\Delta H}{RT^2}$$

or $\qquad \dfrac{1}{P}\dfrac{dP}{dT} = \dfrac{d \ln P}{dT} \quad = \quad \dfrac{\Delta H}{RT^2}$

CLAUSIUS-CLAPEYRON EQUATION

_____

For many substances over not too long a temperature range $\Delta H_{transformation}$ is essentially constant so that we can integrate the equation as follows

$$\ln \frac{P_1}{P_2} = -\frac{\Delta H}{R} \left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}$$

Slope is
$-\Delta H_{trans} / R$

ln P

1/T

A series of vapour pressure measurements made at known temperatures can yield the enthalpy of the phase transformation.

_____

What assumptions have been made in this derivation?

_____

HOMOGENEOUS CHEMICAL EQUILIBRIUM

General Chemical Equation

$$aA + bB \rightleftharpoons cC + dD \qquad K_p = \frac{p_C^c \; p_D^d}{p_A^a \; p_B^b}$$

At constant temperature and pressure the condition for equilibrium is that G is constant so that for any small change, $dG = O$.

_____

So far a small displacement of equilibrium – x moles left to right.

the mol of A that disappear	$dn_A = -xa$
the mol of B that disappear	$dn_B = -xb$
the mol of C that form	$dn_C = xc$
the mol of D that form	$dn_D = xd$

41

the free energy change associated with each is

$$dG_i = \mu_i dn_i$$

So that at equilibrium the values must satisfy

$$- xa\mu_A - xb\mu_B + xc\mu_C + xd\mu_D = 0$$

$$a\mu_A + b\mu_B = c\mu_C + d\mu_D$$

At equilibrium μ_i of the components have values related by the same formal equation as the stiochiometric chemical equation.

This means that if we can express the chemical potentials of substances in terms of their pressure or concentration and T, we can find the condition for equilibrium. The way to do this in a variety of cases is set out below.

CHEMICAL POTENTIAL OF A PERFECT GAS

This is expressed relative to its standard chemical potential in a standard or reference state. We need to formulate the free energy change involved (remember this is reversible work done) in moving from the reference to the state in question.

State at the given temperature but difficult pressure:

$$\text{Work} = \int_{V'}^{V''} PdV \quad = \quad \int_{V'}^{V''} \frac{nRT}{V} dV \quad = \quad nRT \, In \, \frac{V''}{V'}$$

$$\text{Free Energy } \Delta G = -w = -nRT\ln \frac{V''}{V'} = nRT\ln \frac{P''}{P'}$$

$$\Delta\mu = \frac{\partial \Delta G}{\partial n} = RT\ln \frac{P''}{P'}$$

For expansion from a standard state P' = 1.0 where $\mu = \mu^o$ to another at pressure P

$$\mu(P) = \mu^0 + RT\ln P$$

Chemical Potential of a Perfect Gas

HOMOGENEOUS REACTION OF PERFECT GASES

Substitute $\mu = \mu^o + RT\ln P$ for each gas into the equation for equilibrium

$$a\,\mu_A + b\,\mu_B = c\,\mu_c + d\,\mu_D$$

$$a\,\mu_A{}^o + b\,\mu_B{}^o - (c\,\mu_C{}^o + d\,\mu_D{}^o) = RT\ln \frac{p_c^{\,c}\; p_D^{\,d}}{p_A^{\,a}\; p_B^{\,b}} = RT\ln K_p$$

or $\mu^o{}_{products} - \mu^o{}_{reactants} = - RT\ln K_p$

which is constant at a given T

_____

$\therefore$ Equilibrium pressure function K_p must be constant at given temperature i.e., independent of pressure

_____

We have also established its relationship to the standard free energy change

$$\Delta G^o = \Delta\mu^o$$

so that $\ln K_p = -\Delta G^o/RT$

per mol or reaction

_____

VARIATION OF K_p WITH TEMPERATURE

(VAN'T HOFF ISOCHORE)

$$\frac{d\ln K_p}{dT} = -\frac{1}{R}\frac{d(\Delta G/T)}{dT}$$

$$= \frac{\Delta H^o}{RT^2}$$

$$\frac{d(\Delta G/T)}{dT}$$

$$= \left\{T\frac{d(\Delta G)}{dT} - \Delta G\frac{dT}{dT}\right\}/T^2$$

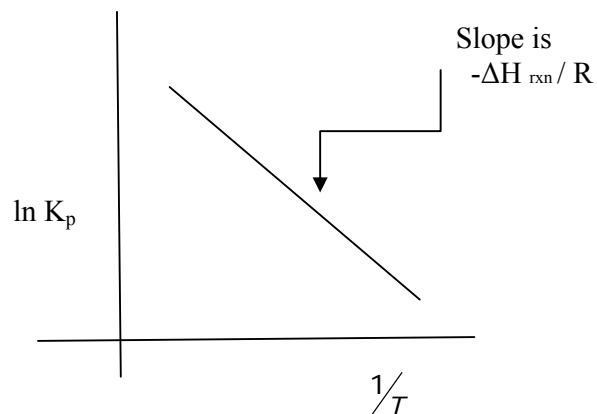$$= \{T(-\Delta S) - \Delta G\}/T^2$$

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

(VAN'T HOFF ISOCHORE)

Integrated form if we assume ΔH not to be a function of temperature over a short temperature range (cf. Kirchoff equation!).

$$\mathrm{Ln}\frac{K_{P_1}}{K_{P_2}} = -\frac{\Delta H^o}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}$$

Kp_1 measured at T_1

Kp_2 measured at T_2

the standard enthalpy change for the reaction can be determined from these data

$\ln K_p$

Slope is $-\Delta H_{rxn}/R$

$1/T$

Any assumptions?

FURTHER USES OF THE CHEMICAL POTENTIAL OF A SPECIES (μ_i)

We will now make further use of the same general approach and format as before i.e., the chemical potential of the component is expressed relative to a value in a chosen standard state to make it possible to develop equations governing ideal solubilities and their temperature dependences. We will also derive the thermodynamic basis for the colligative properties of solutions such as the depression of the freezing point, the elevation of the boiling point and osmotic pressure.

In each case the chemical potential of the component in the solution written with reference to its value in a standard state is made equal to the value of the chemical potential of the pure component with which it is at equilibrium and this equation is then manipulated to extract the value of the quantity of interest e.g., the solubility of a solute in a saturated solution or the vapour pressure of a solvent over a solution containing an non-volatile solute or whatever is being considered, and the required relationship can be derived.

CHEMICAL POTENTIALS IN IDEAL SOLUTION

For liquid mixtures – solutions of non-electrolyes

For each species: solvent is 1 and solutes 2,3.......i

$\mu_i = \mu_i^{\phi} + RT \ln N_i$	Standard State is the pure component N is the mole fraction

For solutions of electrolytes and for solute species

$\mu_i = \mu_i^{\Theta} + RT \ln C_i$	Standard State is the Infinite dilution C is the molar concentration

The difference between these standard chemical potentials μ_i^{ϕ} and μ_i^{Θ} and the behaviour of non-ideal solutions is illustrated below:

NON-IDEAL RANGE

$\mu_i = \mu_i^{o} + RT\ln N_i$

μ^{o}

$\mu = \mu^{\phi} + RT\ln N$

lnC

N=1
lnN=0
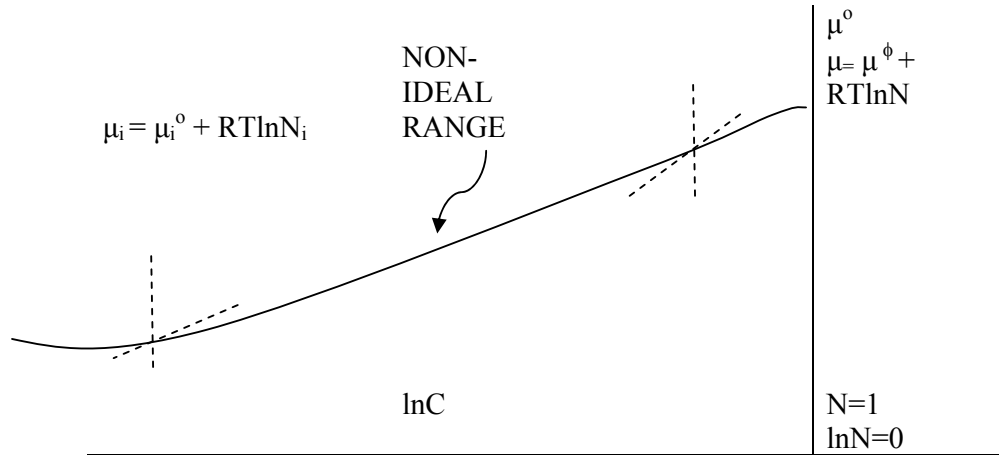
If we substitute for μ into the general equation for chemical equilibrium – as we did earlier for gases – we get.

$$RT\ln K_N \quad = \quad -\Delta\mu^{\phi} \text{ and } RT\ln K_C = -\Delta\mu^{\Theta}$$

$$\text{Where} \quad K_N = \frac{N_C^c N_D^c}{N_A^a N_B^b} \quad \text{and} \quad K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

K_N and K_C are the mole fraction and concentration equilibrium constants for the reactions, varying with temperature, but not with composition, provided that all components behave ideally i.e., that their chemical potentials obey the ideal equations given.

EQUILIBRIUM BETWEEN IDEAL SOLUTION AND VAPOUR

(Henry's Law and Raoult's Law)

Vapour Phase: single species i at pressure p_i - the ideal chemical potential is therefore

$$\mu_i = \mu_i^o + RT\ln p_i$$

Solution: Two species at mole fractions

N_1 (solvent)	$\mu_1 = \mu_1^\phi + RT\ln N_1$
N_2 (solute) $= 1 - N_1$	$\mu_2 = \mu_2^\phi + RT\ln N_2$

_____

These are **two** possibilities: either the solvent or the solute can be the vapour species.

(a)   **FIRST CASE - Vapour is solute species**   **HENRY'S LAW**

$$\mu_2^{vapour} = \mu_2^{solution} \qquad \text{at equilibrium}$$

$$\mu_2^o + RT\ln p_2 = \mu_2^\phi + RT\ln N_2$$

If we are interested in the mole fraction that is dissolved at equilibrium, N_2, then this is therefore given by

$$\ln N_2 = (\mu_2^o - \mu_2^\phi)/RT + \ln p_2$$

At a given value of T this is obviously constant so that we can write $N_2 = k_2 p_2$

This of course corresponds to HENRY'S LAW which was originally derived from empirical derivations.

_____

The solubility of a gas is therefore seen to be proportional to its pressure. From the derivation of the equation we can also extract the meaning of the solubility coefficient k_2.

$$k_2 = \exp\{(\mu_2^o - \mu_2^\phi)/RT\} = \exp(\Delta\mu_v/RT)$$

We can identify $\Delta\mu_v$ as ΔG_v i.e., the free energy change per mole for the transfer of 1 mole from the standard state in solution $N_2 = 1$ to standard state in gas i.e., 1 atm.

	$\mu_2{}^{\phi}$ $N_2 = 1$	(in solution at at temp. T liquefied gas)	$\Delta\mu_v$ is large and negative
$-\Delta H_{trans} / R$			So that exp $(\Delta\mu_v/RT)$ will be small and decreases at an increase in T
Free energy $\Delta\mu_v$ of vaporization			
	$\mu_2{}^{o}$	(in gas at $p = 1$ atm)	IDEAL SOLUBILITY OF GASES IS SMALL AND FALLS AS TEMPERATURE IS INCREASED

_____

(b)   **SECOND CASE: <u>Vapour is the solvent species</u>**   **RAOULT'S LAW**

$$\mu_1^{vapour} \quad = \quad \mu_1^{solution}$$

$$\mu_1^o + RT\ln p_1 = \mu_1^\phi + RT\ln N_1$$

and now the vapour pressure of the solution at equilibrium is the property of interest and is given by

$$\ln p_1 = (\mu_1^\phi - \mu_1^o)/RT + \ln N_1$$

which is seen to be constant at a given temperature so that we can write

$$p_1 = k_1 N_1$$ **RAOULT'S LAW** – once again first derived
from empirical observations

_____

But what is the value of this constant k_1?

Firstly it is the reciprocal of the Henry's Law constant for the species (the standard chemical potential terms are reversed). k_1 is also the value of the vapour pressure of the pure solvent ($N_1 = 1$) at this temperature, p_1^o so that we have:

$$p_1 \quad = \quad p_1^o N_1$$
$$= \quad p_1^o (1-N_2)$$

Whence we have $(p_1^o - p_1)/p_1^o = N_2$

i.e.,   The fractional lowering of the vapour pressure of the solvent is equal to the mole fraction of the solute. This is an alternative statement of Raoult's law.

_____

IDEAL SOLUBILITY OF GASES

k_2 is the mole fraction dissolved at unit pressure (atmospheric) and is the Henry's Law solubility coefficient – it is ideally equal to the reciprocal of the extrapolated saturation pressure of the liquefied gas at the same temperature, since the equilibrium equation, $N_2 = k_2 \, p_2$, can equally well be expressed in Raoult's Law form.

$$N_2 = p_2/p_2^o$$

p_2^o is the vapour pressure of the pure liquefied solute

i.e., Ideal mole fraction solubility
(at $p_2 = 1$ atm) $= 1/p_2^o$

Hence the ideal solubility can be readily calculated for any gas whose p_2^o versus T relationship is known in the liquid state and can be extrapolated to room temperature.

_____

The temperature variation of ideal solubility is the inverse of the temperature dependence of the vapour pressure.

Ideal solubility decreases with increasing temperature – gradient is $\dfrac{d\left((\ln N_2\right)}{d\left(1/T\right)}$ of the same

value $\left(= \dfrac{\Delta H}{R} \right)$ but opposite in sign from that of the vapour pressure dependence

i.e., $\Delta H_{soln} = \Delta H_{vap.}$

_____

Example: for permanent gases p_2^o at 298 K will be large: for $CH_4 = 370$ atmospheres. Hence the ideal solubility is small - $1/370 = 0.0027$ mole fraction. The value found in non-polar solvents are $0.002 – 0.003$.

EQUILIBRIUM BETWEEN IDEAL SOLUTION AND SOLID

(Solubility Equation, Temperature Dependence of Solubility and
Freezing Point Depression)

The consideration of a system with these components allows us to develop a solubility equation and the dependence on temperature of the solubility if the solid is the solute. But if we choose the solid to be the solvent then we can develop equations to quantify the freezing point of an ideal solution.

Solution	N_1 solvent	Equilibrium Condition
	N_2 solute	μ_i crystal = μ_i solution
Crystal	$N_i = 1$	

_____

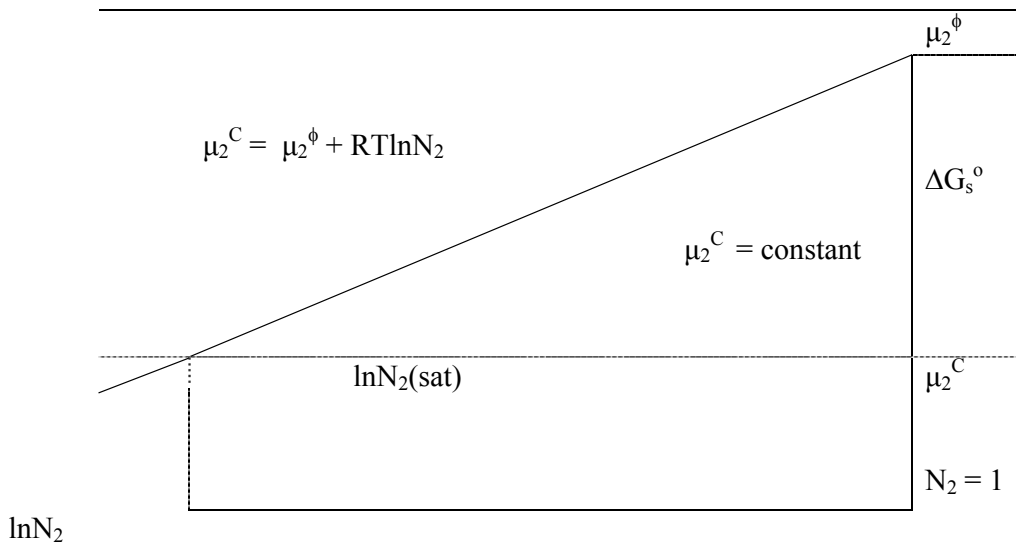**FIRST CASE**: some of the solute precipitates out to provide the solid phase

Consider first the case where the solute is crystal – this represents a **solubility** equilibrium. The superscript C denotes a crystal (solid) phase.

$$\mu_2{}^C = \mu_2{}^\phi + RT\ln N_2 \qquad \text{for saturated solution}$$

$$\ln N_2 = (\mu_2{}^C \, \mu_2{}^\phi)/RT = -\Delta G^o s/RT$$

where $\Delta G^o s$ is the free energy of solution

and is $\equiv \mu_2{}^\phi - \mu_2{}^C$

$\mu_2{}^\phi$

$\mu_2{}^C = \mu_2{}^\phi + RT\ln N_2$

$\Delta G_s{}^o$

$\mu_2{}^C$ = constant

$\ln N_2(\text{sat})$

$\mu_2{}^C$

$N_2 = 1$

$\ln N_2$

Temperature dependence of ideal solubility

$$\frac{d(\ln N_2)}{dT} = \frac{d}{dT}\left(-\Delta G^o{}_s\Big/RT\right)$$

$$= \frac{1}{R}\frac{d}{dT}\left(-\Delta G^o{}_s\Big/T\right) = \Delta H^o{}_s/RT^2$$

Where $\Delta H^o{}_s$ is the enthalpy of solution.

The integrated form is $\ln N_2(sat) = -\Delta H^o{}_s/kT + constant$.

or $\quad \ln\left(\dfrac{N_2{}'}{N_{2''}}\right) = -\dfrac{\Delta H^o{}_s}{R}\{\dfrac{I}{T'} - \dfrac{I}{T''}\}$

_____

Now if T″ is the melting point of the solute then $N_2{}'' = 1$.

Ideal liquids mix in all proportions and $\Delta H^o s = \Delta H_f$ (fusion of solute)

For **IDEAL** solutions

$$\ln N_2 = -\frac{\Delta H_f}{R}\{\frac{1}{T} - \frac{1}{T_f}\}$$

$$= -\frac{\Delta H_f}{R}\{\frac{T_f - T}{T T_f}\} = \frac{\Delta S_f}{R}\{\frac{T_f - T}{T}\}$$

IDEAL solubilities of solids determined only by their m.p. and enthalpy (or entropy) of fusion.

 Note: that no properties of the ideal solvent are relevant. Why is this true?

_____

SECOND CASE the solvent freezes and provides the solid phase

This is where the solvent is the crystal (at the freezing point of the solution) – this allows us to calculate the freezing point depression of the solution. At equilibrium we have:

$$\mu_1{}^c = \mu_1{}^\phi + RT\ln N_1$$

Using the same argument as above but now in terms of the solvent (species (1)) leads to the same equation for the composition of the solution N_1 in equilibrium with the melting (solvent) crystal.

$$\ln N_1 \quad = \quad -\frac{\Delta H_f}{R}\{\frac{T_f - T}{T\,T_f}\}$$

$$\cong \quad -\frac{\Delta H_f}{R}\frac{\Delta T_f}{T_f^{\ 2}} \qquad \text{When } T \approx T_f \text{ so that } \Delta T_f \text{ is small}$$

So that the Freezing Point Depression, ΔT_f, is given as

$$\Delta T_f \quad \approx \quad (-RT_f^2/\Delta H_f)\ \ln N_1$$

$$\approx \quad (-RT_f^2/\Delta H_f)(1-N_2)$$

$$\approx \quad (-RT_f^2/\Delta H_f)\ (-N_2) \qquad \text{where } N_2 \text{ is small}$$
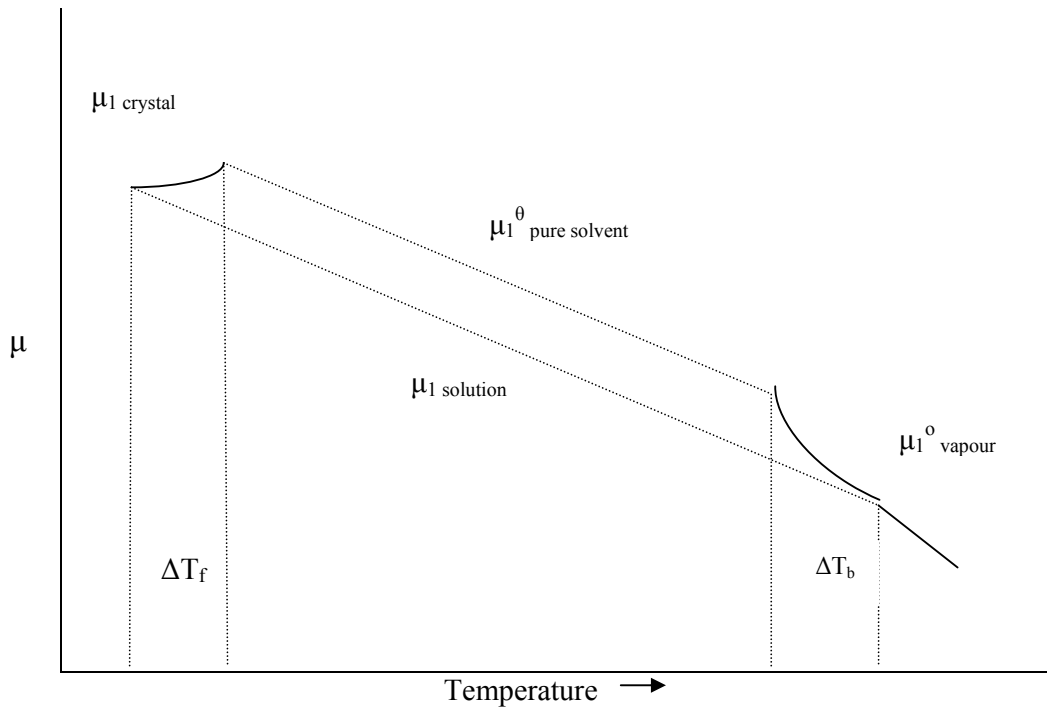
so that $\qquad \Delta T_f \approx \dfrac{RT_f^2}{\Delta H_f}\ N_2 \qquad$ i.e., is proportional to the

mole fraction of the solute

$$\approx \quad \left(\frac{RT_f^{\ 2}}{\Delta H_f}\ \frac{M_1}{1000}\right)\ n_2 \quad \text{for } n_2 \text{ moles of solute in 1000g solvent}$$
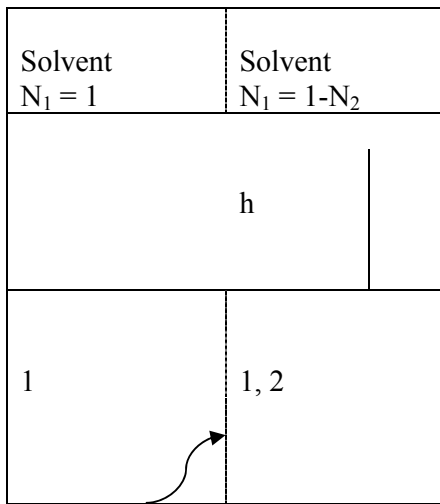
so that the cryoscopic constant of the solvent K_f can be calculated without ever making a measurement of a freezing point depression and is given by:

$$K_f \quad \approx \quad \left(\frac{RT_f^{\ 2}}{\Delta H_f}\ \frac{M_1}{1000}\right)$$

All properties of the solvent – we can evaluate the cryoscopic constant (ideal) if ΔH_f, T_f and M_1 are known. Note that these are all properties of the solvent.

$\mu_{1\ crystal}$

$\mu_1^{\theta}{}_{pure\ solvent}$

μ

$\mu_{1\ solution}$

$\mu_1^{o}{}_{vapour}$

ΔT_f

ΔT_b

Temperature →

IDEAL SOLUTION – SOLVENT EQUILIBRIUM
(Osmotic Pressure)

Solvent $N_1 = 1$	Solvent $N_1 = 1-N_2$
h	
1	1, 2

$h\rho g = \pi$

Semi permeable membrane

The osmotic pressure of ideal solutions

The chemical potential in the pure solvent is higher so that the solvent passes through the membrane

$\mu_1^{soln.} = \mu_1^{\phi} + RT\ln N_1$

Pure   Negative term
Solvent $N_1 < 1$
Osmosis – the passage of solvent through the membrane takes place

---

When this osmosis is stopped by the application of an additional osmotic pressure on the solution – μ_1(solution) is raised to μ_1^{ϕ}

μ_1 is solution with π = μ_1 in solvent (1 atm)

$$\mu_1^{\phi}(\pi) + RT\ln N_1 \quad = \quad \mu_1 \text{ in solvent at 1 atm}$$

54

$$\mu_1^{\circ}(\pi) - \mu_1^{\circ}(1 \text{ atm}) = -RT\ln N_1$$

_____

Work of compression of 1 mole from pressure 1 to pressure π

$$= \int_1^{\pi} V_1 dp \qquad \approx \qquad V_1 \int_1^{\pi} dp \qquad \approx \quad V_1\pi$$

$\therefore$ Ideal solution comes to osmotic equilibrium when at a pressure

$$\pi = \frac{-\dfrac{RT}{V_1}\ln N_1}{} \qquad = \qquad -\frac{RT}{V_1}\ln(1-N_2)$$

$$\pi \approx \frac{\dfrac{RT}{V_1}(N_2)}{} \qquad \text{for } N_2 \text{ small}$$

$$\approx \frac{RT}{V_1}\frac{n_2}{n_1+n_2} \qquad \approx \qquad \frac{RT}{V_1}\frac{n_2}{n_1}$$

i.e., the osmotic pressure $\qquad \pi \approx RTC_2$ where $C_2 = \dfrac{n_2}{n_1 V_1}$ {molar concentration}

Note: This equation has the same form as the equation of state for an ideal gas.

$$\pi V = \pi\, RT$$