

THERMODYNAMICS NOTES

Energy in Chemical Systems

Perfect Gas –

$$p = \frac{nRT}{V}$$

Realistic Gas –

Van der Waals Equation:

$$p = \frac{nRT}{V - nb} - a \frac{n^2}{V^2}$$

Where a and b are constants, a is for strength of attraction and b is for repulsive interactions. Both are independent of T.

Can be rearranged to give the **Virial Equation of State**:

$$p = \frac{nRT}{V} \left(1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \dots \right)$$

Systems

- Open, e.g. test tube. Exchange energy and matter.
- Closed, e.g. bunged test tube. Exchange energy with surroundings only.
- Isolated, e.g. bunged test tube with insulation. Exchanges nothing.

Work and Heat

Work – uniform movement of atoms. Lifting a weight.

Heat – random motion of atoms. Vibration (temperature gradients only). No transfer of heat means **adiabatic** barrier. Otherwise it is **diathermic**.

$W > 0$ when work is done *on the system*. Energy transferred to the system.

$W < 0$ when work done *by the system*, energy lost.

$q > 0$ when E transferred *to the system*, and vice versa.

Internal Energy = total energy of all particles. KE + PE.

$$\Delta U = q + W.$$

For an isolated system, $\Delta U = 0$. This is the *First Law of Thermodynamics*: that the internal energy of an isolated system is constant.

U is a state function, which means it is independent of the preparation of its state.

- Energy added to or work done on a system = positive.
- Energy removed or work done by a system = negative.

dU is an exact differential. For infinitesimal changes, **dU = dq + dW**.

$\Delta U = U_f - U_i$, whether the path is adiabatic or non-adiabatic. This is not the case for work and heat.

$$\text{Work, } W = \int_i^f dw.$$

Expansion Work –

Taking a piston, where an external pressure is pressing down on an Area so that it is lowered by a distance dz, then $dW = -p_{\text{ex}}A dz$, so:

$$dW = -p_{\text{ex}} dV$$

So, for Constant external Pressure, $W = -p_{\text{ex}} \Delta V$.
Free expansion implies $p_{\text{ex}} = 0$, so $W = 0$.

Reversible processes do maximum work. This means an infinitesimal change in conditions.
So $p \rightarrow p+dp$, or $p+dp \rightarrow p$.

Work done by a Perfect Gas:

For a reversible expansion,

$$W = - \int_{V_i}^{V_f} p dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

Since nRT is constant for Isothermal expansion,

$$\text{Work} = -nRT (\ln V_f / V_i).$$

A plot of p against V gives isotherms for each temperature. These approach p_{ex} as V increases, and are hyperbolic in shape.

Heat Capacities of Gases

These correlate the amount of energy required for heating a substance.

Amount of energy dq_v added to a gas at constant volume causes a temperature change dT , then the constant volume molar heat capacity, C_v is:

$$dq_v = C_v dT$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

Enthalpy and Thermochemistry

Describes energy changes at constant pressure. Defined as:

$$H = U + pV$$

This comes from $\Delta H = q_p = \Delta U + p \Delta V$, from the 1st Law.

$\Delta H \approx \Delta U$ for liquid / solid systems (ΔV is approximately constant).

Evolving heat \rightarrow exothermic (negative ΔH).

Absorbing heat \rightarrow endothermic (positive ΔH).

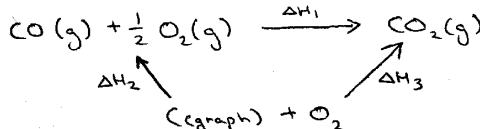
Hess' Law -

Total ΔH for the reaction is independent of the path of the reaction (true as ΔH is made up of State Functions).

$$\Delta_{\text{irs}} H = q_p$$

$$\Delta_{\text{irs}} H_{a \rightarrow b} = H_m(b) - H_m(a)$$

Enthalpy is a state function, and therefore summable (Hess Cycles). Must be at constant T.



This is only valid at constant temperature.

$$\text{Hence, } \Delta H_1 = -\Delta H_2 + \Delta H_3.$$

For infinitesimal changes in H:

$$dH = dU + Vdp + pdV$$

Hence,

$$dH = dq + Vdp$$

From this we see that $dH = dq$ (at constant p).

Also, $H_m = U_m + pV_m$ (where subscript m indicates molar).
 For a perfect gas, $H_m = U_m + RT$ (RT is constant, 2.5 kJ mol^{-1}).

Heat Capacity

$$C_p = \frac{dq}{dT}$$

C_p is the amount of energy needed to raise the temperature of 1 mol of substance by 1K at constant pressure.

$C_p > C_v$ (Gradient of q against T is higher for H than U).

$C_v = \left(\frac{\partial U}{\partial T} \right)_v$	$C_p = \left(\frac{\partial H}{\partial T} \right)_p$
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The standard state of a substance is the pure substance at 1 bar.

Using the above and Hess' Law, we can obtain:

$H_m(T_2) = H_m(T_1) + \int_{T_1}^{T_2} C_{p,m} dT$	[Kirchoff's Law]
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Thus,

$$\Delta_r H \approx \Delta_r H + (T_2 - T_1) \Delta_r C_p$$

Similarly,

$\Delta_r C_p = \sum_{(\text{prod})} n C_{p,m} - \sum_{(\text{react})} n C_{p,m}$

Enthalpies of Reaction –

Consider $R \rightarrow P$.

Enthalpy at $25^\circ\text{C} \rightarrow \Delta H_{f,298}^\circ (R)$

Enthalpy at some other temperature, T: $[\Delta H_{f,298}^\circ (R) + C_p(R)(T - 298)]$

The same is true for P.

$\Delta H_T^\circ (\text{reaction}) = \Delta H_{f,T}^\circ (P) - \Delta H_{f,T}^\circ (R) \rightarrow \Delta H_T^\circ (\text{reaction}) = \Delta H_{298}^\circ (\text{reaction}) + \Delta C_p(T - 298)$

ΔC_p is the change in mean C_p between P and R.

So far have assumed that the use of mean heat capacities gives sufficient accuracy. In fact, C_p can change significantly.

Use,

$$C_p(T) = a + bT + cT^2 + dT^3 + \dots$$

$\int_{T_1}^{T_2} dH = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} (a + bT + cT^2) dT$

Hence,

$$H_{T_2} - H_{T_1} = [a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3)]$$

Standard Enthalpy of formation is the standard reaction enthalpy for formation of the substance from its elements in their reference (most stable) states.

Entropy in Chemistry

Spontaneous – occurs without work needing to be done.

2nd Law – spontaneous processes are those which cause an increase in the entropy of the universe.

Tendency for matter to disperse – diffusion.

Internal Energy is the quantity of Energy.

Tendency for energy to disperse – conduction.

Entropy is the quality of Energy.

A spontaneous process in an isolated system gives rise to an increase in Entropy (**Clausius Inequality**).

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

dq_{rev} is inexact, so an integrating factor $1/T$ is required.
 dS is exact, and so S is a State Function.

Qualitative proof –

more heat \rightarrow more disorder, so $dS \propto dq$.

A higher temperature means the disorder is affected less by a given increase in heat, so $dS \propto 1/T$

Isothermal Reversible Expansion of a Perfect Gas:

$$\Delta S = \int_{V_i}^{V_f} \frac{dq}{T}$$

$dq = dU - dW$, and $dU/dV)_T = 0$.
 $dW = -pdV$

$dq = -dW$
 $p = nRT/V$

Thus,

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Change in Entropy when a system is heated:

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

C_p usually depends on Temperature. However, when it is constant (for a given temperature range),

$$\Delta S = C_p \ln \frac{T_f}{T_i}$$

$$S_{T_f} - S_{T_i} = \int_{T_i}^{T_f} \frac{C_p}{T} dT$$

Often the best way to find the change in entropy is by *graphical* means – the *area* under the graph of C_p/T against T between T_f and T_i .

Absolute Entropies –

3rd Law – entropy of a perfect crystal at 0K is zero.

A perfect crystal is very hard to achieve, and Residual Entropy is usually present.

Standard Entropies –

S_{298}° of a compound is the molar entropy at 298K and 1 bar.

For a gas at room temperature:

- Heat from 0 to T_m – $\Delta S_1^\circ = \int_0^{T_m} \frac{C_p(\text{solid})}{T} dT$
- Melt at T_m – $\Delta S_2^\circ = \frac{\Delta H_{fus}}{T_m}$
- Heat from T_m to T_b – $\Delta S_3^\circ = \int_{T_m}^{T_b} \frac{C_p(\text{liquid})}{T} dT$
- Vaporisation at T_b – $\Delta S_4^\circ = \frac{\Delta H_{vap}}{T_b}$
- Heat from T_b to 298K – $\Delta S_5^\circ = \int_{T_b}^{298} \frac{C_p(\text{vapour})}{T} dT$

Then sum the ΔS terms for the absolute standard entropy.

Entropy in Reactions –

$$\Delta S^{\circ}_{298} (\text{reaction}) = \sum \nu_i S^{\circ}_{298}(P) - \sum \nu_i S^{\circ}_{298}(R)$$

(as for enthalpy)

Entropy at another temperature can then be given by:

$$\Delta S_{T_2} - \Delta S_{T_1} = \int_{T_1}^{T_2} \frac{\Delta C_p}{T} dT$$

$$\Delta S_{T_2} - \Delta S_{T_1} = \Delta C_p \ln \left(\frac{T_2}{T_1} \right)$$

Free Energy

The factors governing chemical reactivity – enthalpy and entropy.

Spontaneous –

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + (\Delta H_{\text{surr}})/T > 0$$

& $\Delta H_{\text{sys}} = -\Delta H_{\text{surr}}$, hence:

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} - (\Delta H_{\text{sys}})/T > 0$$

Therefore for spontaneity,

$$\Delta H - T\Delta S < 0.$$

Gibbs and Helmholtz

Gibbs Free Energy is at constant T and p (more useful practically).

$$G = H - TS$$

This is a state function. $\Delta G < 0$ for spontaneous process.

Helmholtz is for constant V and T. $\Delta A < 0$ for a spontaneous process.

$$A = U - TS$$

i.e. for a spontaneous process, you want to *lower the free energy*.

Consider infinitesimal changes:

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

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

$$\& dU = dq + dw = dq - pdV$$

$$\& dS = dq/T \rightarrow dU = TdS - pdV.$$

Hence,

$$dG = Vdp - SdT.$$

$$\left(\frac{\partial G}{\partial T} \right)_p = -S \quad \text{i.e.} \quad \left(\frac{\partial \Delta G}{\partial T} \right)_p = -\Delta S$$

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

$$\int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} \frac{nRT}{p} dp, \quad \therefore \Delta G = nRT \ln \left(\frac{p_2}{p_1} \right)$$

Similarly,

$$dA = dU - TdS - SdT$$

$$dA = dq + dw - Tds - SdT$$

Assuming Reversible work done,

$$dA = TdS + dw_{\max} - TdS - SdT$$

$$dA = dw_{\max} \text{ at constant } T$$

Thus for a system, $w_{\max} = \Delta U - T\Delta S$. The entropy of surroundings will always increase to compensate for a decrease in the system.

$$dG = dH - TdS - SdT$$

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

$$dG = dq + dw + pdV + Vdp - TdS - SdT$$

$$dG = TdS + (dw_{\text{add}} - pdV) + pdV$$

$$dH = dU + pdV + Vdp$$

$$dU = dq + dw$$

$$dq = TdS.$$

$$dw = dw_{\text{add}} - pdV \text{ for non-expansion work.}$$

$$dG = dw_{\text{add}} + Vdp - SdT$$

$$dG = dw_{\text{add}} \text{ at constant } p \text{ and } T$$

Endoergic compound has $\Delta_f G > 0$.

Temperature dependence of G:

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

$$\left[\frac{\partial}{\partial T}\left(\frac{q}{T}\right)\right]_p = \frac{-q}{T^2} + \frac{1}{T}\left(\frac{\partial q}{\partial T}\right)_p$$

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

$$\therefore \left[\frac{\partial}{\partial T}\left(\frac{q}{T}\right)\right]_p = \frac{-H}{T^2}$$

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

This is the **Gibbs-Helmholtz Equation**.

Also,

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

And,

$$dU = T dS - p dV$$

Thus,

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

Thermodynamic Activity –

Effective concentration:

$$G = G^\circ + nRT \ln a$$

$$a = \frac{p}{p^\circ} \text{ for an ideal gas.}$$

The effect of pressure on a solid / liquid is negligible, so:

$$G \approx G^\circ \rightarrow a_{\text{pure solid}} = a_{\text{pure liquid}} = 1$$

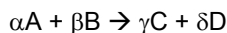
Variation of G with concentration (for a condensed phase system) –

Concentration = moles per unit volume, and $p = RT (n/V)$,

$$G_i = G_i^\circ + nRT \ln [i]$$

Equilibrium

A system comes to equilibrium when it reaches a minimum of free energy.



$$Q = \frac{(a_C)^\gamma (a_D)^\delta}{(a_A)^\alpha (a_B)^\beta} = K \text{ at equilibrium.}$$

If $\Delta G < 0$ or $Q < K_p \rightarrow$ forward reaction.
 If $\Delta G > 0$ or $Q > K_p \rightarrow$ reverse reaction.
 If $\Delta G = 0$ or $Q = K_p \rightarrow$ equilibrium.

Relating G & K:

$$A + B \rightarrow C + D$$

$$\Delta G(\text{reaction}) = (G_C + G_D) - (G_A + G_B)$$

$$G_A = G_A^\circ + RT \ln a_A$$

$$\rightarrow \Delta G(\text{reaction}) = \Delta G^\circ(\text{reaction}) + RT \ln Q$$

$\Delta G^\circ(\text{reaction}) + RT \ln K = 0$ at equilibrium.
 Hence,

$$\Delta G^\circ = -RT \ln K$$

Chemical Potential

$$G_A = G_A^\circ + RT \ln a_A$$

This implies that the free energy of a component is independent of all other components of the mixture. This is reasonable for ideal gases only.

$$G_A = \left(\frac{\partial G}{\partial n_A} \right)_{p,T,n_B} = \mu_A$$

This is the definition of the chemical potential (i.e. the partial molar free energy of component A).

Pure substance, $\mu_A = G$, i.e. $dG = \mu_A dn_A$.

Generalised to:

$$dG_{p,T} = \sum_i \mu_i dn_i$$

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

$$G_A = G_A^\circ + RT \ln \frac{P}{P^\circ}$$

$$\left(\frac{\partial G}{\partial n_A} \right) = \left(\frac{\partial G^\circ}{\partial n_A} \right) + nRT \ln \frac{P_A}{P_A^\circ}$$

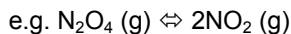
Consider **at equilibrium**,

$dG = 0$, therefore:

$$\mu_A dn = \mu_B dn \rightarrow \mu_A = \mu_B$$

i.e. at equilibrium, chemical potential of reactants = products.

ASIDE: Mole Fractions



Let 1 mole of N_2O_4 reach \rightleftharpoons at a pressure p_{tot} such that α moles of N_2O_4 have reacted.

At equilibrium, $(1-\alpha)$ moles of N_2O_4 left, and 2α moles of NO_2 formed.

Total moles of gas therefore = $(1-\alpha) + 2\alpha = (1+\alpha)$ moles.

Hence,

$$K_p = \frac{(p_{NO_2})^2}{(p_{N_2O_4})^2} = \frac{(x_{NO_2} p_{tot})^2}{(x_{N_2O_4} p_{tot})^2} = \frac{\left(\frac{2\alpha}{1+\alpha} p_{tot}\right)^2}{\left(\frac{1-\alpha}{1+\alpha} p_{tot}\right)^2} = K_p = \frac{4\alpha^2 p_{tot}}{(1-\alpha)^2}$$

x is the mole fraction, $x = \frac{\text{\# moles of component}}{\text{total \# moles present}}$

Effect of pressure on equilibrium:

K does not depend on p. Position of equilibrium does (as illustrated by the result above).

Effect of temperature on equilibrium:

$$G = \Delta H - T\Delta S \text{ and } dG_{p,T} = \sum_i \mu_i dn_i$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

Assume ΔH° and ΔS° independent of T:

$$\ln K = \text{constant} - \frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right)$$

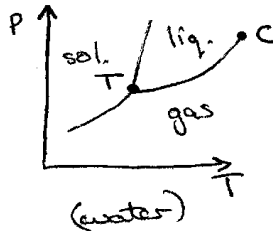
Note the linear relation between $\ln K$ and $1/T$. This is the **Van't Hoff Equation**.

Phase Equilibria

Definition: Phase – part of a system which is homogeneous throughout and separated from other phases by a definite boundary.

- Vapour → only one phase (irrespective of number of components).
- Liquid → Many phases possible (never > number of components).
- Solid → single component may exhibit many phases, e.g. carbon.

Single component phase diagrams:

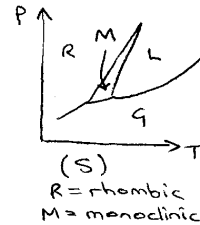
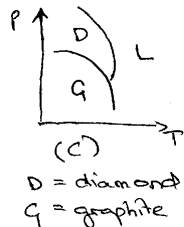
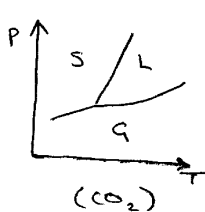


T = triple point – all 3 phases in equilibrium.

C = critical point – maximum T at which a gas can be liquefied merely by increasing pressure.

e.g. heat liquid in a sealed container – does not boil. Density of the vapour increases as more liquid evaporates until at T_C , density of vapour = density of liquid.

Fluids with temperatures and pressure above T_C are called supercritical fluids, SCFs. Properties of these phases are a mixture of vapour and liquid.



Quantitatively,

Consider 2 phases of a pure material in equilibrium, e.g. water and water vapour at fixed T, p, e.g. $p = p^\circ$, $T = 373K$.

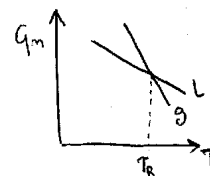
For the two phases a and b,

$$G = G^a + G^b \text{ must be at a minimum, so } dG = dG^a + dG^b = 0.$$

Hence,

$$dG = G_m^a dn + G_m^b dn = 0$$

$$dG = (G_m^b - G_m^a) dn$$



i.e. $G_m^a = G_m^b$ at equilibrium.
More generally,

$$\mu^\alpha = \mu^\beta, \mu = \left(\frac{\partial G}{\partial n} \right)_{p,T}$$

$G_m(l) < G_m(g)$ at low T

$$\left(\frac{\partial G}{\partial T} \right)_p = -S < 0$$

$S_m(l) < S_m(g)$

$$\Delta H_m = T \Delta S_m$$

(NB: applies only when system is in equilibrium).

How Does Equilibrium responds to changes in T and p?

Changing only one will shift system from equilibrium point.

Must change both to maintain $G_m^\alpha = G_m^\beta$

Using:

$$dG_m^\alpha = V_m^\alpha dp - S_m^\alpha dT$$

$$V^\alpha dp - S^\alpha dT = V^\beta dp - S^\beta dT$$

$$\frac{dp}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

This is the **Clapeyron Equation**, and is an exact relationship (applicable to all phases).

For solid to gas and liquid to gas, equilibria can be approximated:

$$\Delta V = V(g) - V(l) \approx V(g) \approx RT/p$$

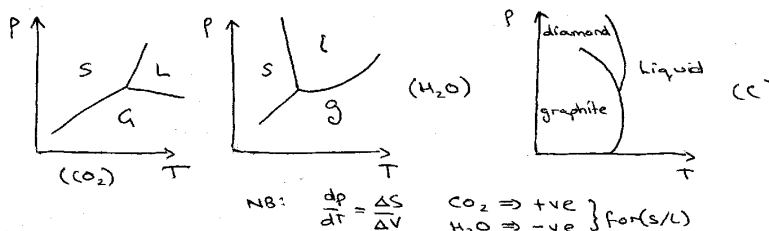
$$(dp/dT) = \rho\Delta H/RT^2$$

Using:

$$\frac{d \ln p}{dT} = \frac{1}{p} \frac{dp}{dT}$$

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}$$

This is **Clausius-Clapeyron Equation**, and is an approximation. It can be used on Phase Diagrams to quantify the gradients, e.g.



This is e.g. for CO_2 . Assuming ΔH , ΔV independent of T,
 $s \leftrightarrow l, p_2 = p_1 + \Delta H/\Delta V \ln(T_2/T_1)$
 $l \leftrightarrow g$ & $s \leftrightarrow g$,

$$\ln \frac{p_2}{p_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln p = const - \frac{\Delta H_{vap}}{R} \left(\frac{1}{T} \right)$$

Standardise – T_b and 1 bar.

$$\ln 1 = \text{const} - \frac{\Delta H_{\text{vap}}^{\circ}}{R} \left(\frac{1}{T_b} \right)$$

$$\therefore \text{const} = \frac{\Delta H_{\text{vap}}^{\circ}}{RT_b} = \frac{\Delta S_{\text{vap}}^{\circ}}{R}$$

$$\ln p = \frac{\Delta S_{\text{vap}}^{\circ}}{R} - \frac{\Delta H_{\text{vap}}^{\circ}}{RT_b}$$

Measure entropy of vaporisation from intercept of $\ln p$ vs. $1/T$.

Many liquids have $\Delta S_{\text{vap}}^{\circ} \approx 85 \text{ J K}^{-1} \text{ mol}^{-1}$. This is **Trouton's Rule**.

Rationalised as, in absence of specific structural features, most liquids have similar structures, implying same change in structural order would take place on vaporisation.

Deviations – specific features in chemical bonding of system, e.g. H-bonding.

Vapour ordered (acetic acid) $\rightarrow \Delta S_{\text{vap}}^{\circ}$ decreases compared to 85.

Liquid ordered (H_2O) $\rightarrow \Delta S_{\text{vap}}^{\circ}$ increased compared to 85.

Solutions and Mixtures

Partial Molar Gibbs Energy,

$$\mu_A = \left(\frac{\partial G}{\partial n_A} \right)_{T, p, n_B}$$

$$G = \mu_A n_A + \mu_B n_B \text{ for a binary mixture.}$$

For an open system, G dependent on p, T, n. Thus,

$$dG = V dp - S dT.$$

Allowing for change in composition,

$$dG = V dp - S dT + \mu_A dn_A + \mu_B dn_B \dots$$

At constant p, T:

$$dG = \mu_A dn_A + \mu_B dn_B + \dots \text{ (i.e. eliminates first 2 terms of the equation).}$$

So maximum amount of non-expansive work:

$$dw_{\text{max}} = \sum \mu_A dn_A$$

Since chemical potential depends on composition, for a binary system:

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

(for an infinitesimally small change).

So,

$$n_A d\mu_A + n_B d\mu_B = 0$$

Therefore, chemical potential of one component cannot change independently of the other.

Thermodynamics of Mixing –

Prior to mixing,

$$G_i = n_A \mu_A + n_B \mu_B$$

$$G_i = n_A (\mu_A^{\circ} + RT \ln p) + n_B (\mu_B^{\circ} + RT \ln p)$$

Following mixing, and using partial pressures,

$$G_f = n_A (\mu_A^{\circ} + RT \ln p_A) + n_B (\mu_B^{\circ} + RT \ln p_B)$$

Free energy of mixing, $G_f - G_i$:

$$\Delta G_{\text{mix}} = n_A RT \ln (p_A/p) + n_B RT \ln (p_B/p)$$

Using mole fractions ($n_j = x_j n$):

$$\Delta G_{\text{mix}} = nRT (x_A \ln x_A + x_B \ln x_B)$$

Hence, ΔG is always negative for perfect gases, and ΔG_{mix} is independent of total pressure.

$$\Delta S_{\text{mix}} = - \left(\frac{\partial \Delta G_{\text{mix}}}{\partial T} \right)_p$$

$$= -R (x_A \ln x_A + x_B \ln x_B)$$

$$\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T \Delta S_{\text{mix}} = 0$$

Therefore no heat absorbed or released on forming an ideal mixture

Consider 2 liquids A and B at constant p and T.

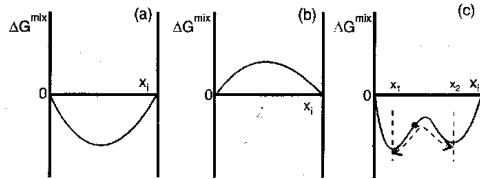
Mixing n_A of A with n_B of B:

- Gibbs before mixing = $n_A G_A + n_B G_B$
- Gibbs after mixing = $(n_A + n_B) G_{AB}$

- $\Delta G^{\text{mix}} = [(n_A+n_B)G_{AB}] - [n_A G_A + n_B G_B]$
- $\Delta G^{\text{mix}} = [G_{AB}] - [x_A G_A + x_B G_B]$

For mixing, ΔG^{mix} must be **negative**.

Three possibilities:



- $\Delta G^{\text{mix}} < 0$ for all compositions implies mix in all proportions at the specified temperature – completely **miscible**.
- $\Delta G^{\text{mix}} > 0$ for all $x \rightarrow$ **immiscible**.
- $\Delta G^{\text{mix}} < 0$, therefore expect miscible. However, if $x_1 < x < x_2$, then a less negative ΔG^{mix} will result if the mixture separates into phases with composition x_1 and x_2 . Hence, it is **partially miscible**.

How this arises – consider H and S:

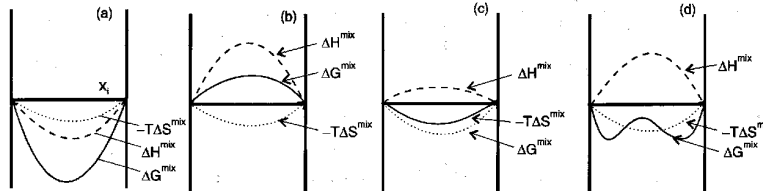
$$\Delta H^{\text{mix}} = H_{AB} - (x_A H_A + x_B H_B)$$

$$\Delta S^{\text{mix}} = S_{AB} - (x_A S_A + x_B S_B)$$

Generally, $\Delta S^{\text{mix}} > 0$ (more disordered than pure).

Thus, $-T\Delta S^{\text{mix}}$ contribution to ΔG^{mix} is favourable.

So ΔH^{mix} usually determines miscibility.



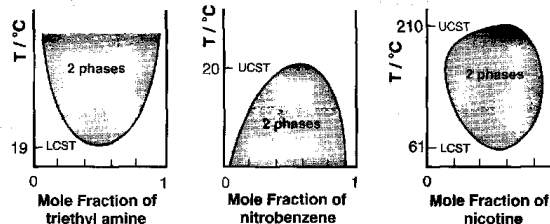
- $\Delta H^{\text{mix}} < 0$. Exothermic.
- $\Delta H^{\text{mix}} > -T\Delta S^{\text{mix}}$ (any composition \rightarrow no mixing). Endothermic.
- Endothermic but $\Delta H^{\text{mix}} < -T\Delta S^{\text{mix}}$ so $\Delta G^{\text{mix}} < 0$ so miscible also.
- Concentration dependence of ΔH^{mix} has particular form.

Temperature Dependence –

- and (c) – the $T\Delta S$ term has no effect – still miscible at all temperatures (changes magnitude of ΔG^{mix} but not sign).
- ΔS^{mix} dominates at high temperature – immiscible at low temperatures, but miscible at high temperatures. The transition temperature \rightarrow Upper Critical Solution Temperature (UCST).

Note that it is possible for ΔS^{mix} to be negative. When the 2 components have some kind of strong interaction, such as H-bonding implies higher order when mixed.

However, this is usually overcome by a high ΔH^{mix} associated with strong interactions. In this case, entropy favours phase separation as temperature increases \rightarrow a lower critical solution temperature (LCST).



Phase diagrams for two component liquid mixtures. The two-phase regions are shaded.
A: Water–triethyl amine. B: Hexane–nitrobenzene. C: Water–nicotine.

Vapour-Liquid Behaviour –

At equilibrium the chemical potential of a substance in a liquid must equal that of the vapour.

Since vapour pressure of pure liquid is p_A^*

$$\mu_A^* = \mu_A^0 + RT \ln p_A^*$$

For a solute,

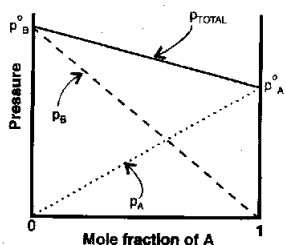
$$\mu_A = \mu_A^0 + RT \ln p_A$$

So,

$$\mu_A = \mu_A^0 + RT \ln (p_A/p_A^*)$$

If ratio of partial pressures is proportional to the mole fraction in the liquid mixture:

$$p_A = x_A p_A^* \quad \text{[Raoult's Law]}$$



$$p_A = p_A^* x_A$$

$$\mu = \mu^* + RT \ln x$$

$$G = \sum n_i \mu_{mix} - \sum n_i \mu_{pure}$$

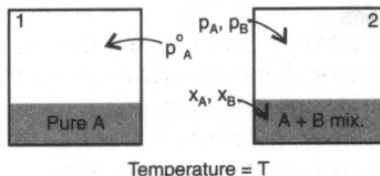
$$= \frac{n_1 RT \ln x_1 + n_2 RT \ln x_2}{n}$$

$$= RT(x_1 \ln x_1 + x_2 \ln x_2)$$

Mixtures that follow the law throughout composition range are ideal solutions.

Ideal dilute solutions obey Henry's Law at low concentrations.

Ideal Solution:



When these two are brought into equilibrium:

$$\mu_A(\text{gas}, p_A^0) = \mu_A(\text{pure liquid A})$$

$$\mu_A(\text{gas}, p_A) = \mu_A(\text{mixture at } x_A)$$

Hence,

$$\mu_A(\text{gas}, p_A) - \mu_A(\text{gas}, p_A^0) = RT \ln (p_A/p_A^0)$$

$$\mu_A(\text{mixture}, x_A) - \mu_A(\text{pure A}) = RT \ln (p_A/p_A^0)$$

$$\mu_A = \mu_A^0 + RT \ln x_A$$

Also,

$$G_{p,T} = \sum_i \mu_i n_i$$

$$\Delta G^{\text{mix}} = RT \sum_i x_i \ln x_i$$

Using:

$$\Delta G^{\text{mix}} = \Delta H^{\text{mix}} - T \Delta S^{\text{mix}} = 0 - T \Delta S^{\text{mix}}$$

i.e.

$$\Delta S^{\text{mix}} = -R \sum_i x_i \ln x_i$$

Thus, for an ideal solution, molecules must be:

- similar in chemical nature (similar intermolecular forces)
- similar in size and shape.

The 2nd of these → no overall volume change on mixing:

$$\Delta V^{\text{mix}} = \left(\frac{\partial \Delta G^{\text{mix}}}{\partial p} \right)_T = \left(\frac{\partial (RT \sum_i x_i \ln x_i)}{\partial p} \right)_T = 0$$

Non-ideality –

$$\mu_A = \mu_A^0 + RT \ln a_A$$

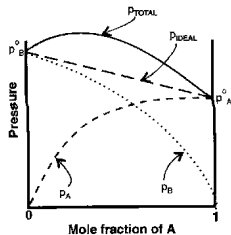
For real solutions, $a_A \neq x_A$, $a_A = \gamma_A x_A$

$$\gamma_i = \frac{a_i}{x_i} = \frac{\text{effective concentration}}{\text{actual concentration}} = \frac{p_i}{x_i p_i^{\circ}}$$

γ tells us how much it has deviated from ideality.

Generally, interactions in solution are weaker than in pure liquids – more easily escape to the vapour.

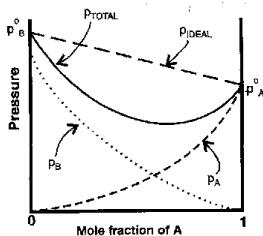
Actual vapour pressure > ideal vapour pressure.



Positive deviations from Raoult's Law.

$$p_i > p_i^{\text{ideal}} \text{ \& } \gamma_i > 1.$$

Opposite case – strong interactions e.g. H-bonding.



Negative deviations from Raoult's Law.

$$p_i < p_i^{\text{ideal}} \text{ \& } \gamma_i < 1$$

Solid-Liquid Phase Equilibrium

Solute A and solvent B.

Solid A \leftrightarrow Liquid (A+B) – solid A comes out of solution leaving a saturated solution of A in B. This represents the solubility limit of the solute in the solvent.

Solid B \leftrightarrow liquid (A+B) – solvent starts to freeze. This represents the freezing point of the solution.

Solid A \leftrightarrow Solution of A.

$$\mu_A^{\circ}(\text{solution}) = \mu_A(\text{solution}) = \mu_A^{\circ}(\text{liquid}) + RT \ln a_A.$$

$$\mu_A^{\circ}(\text{solution}) - \mu_A^{\circ}(\text{liquid}) - RT \ln a_A.$$

$$\Delta G_A^{\text{fus}} = \Delta H_A^{\text{fus}} - T \Delta S_A^{\text{fus}} = RT \ln a_A.$$

Therefore,

$$\Delta H_A^{\text{fus}} - T \left(\frac{\Delta H^{\text{fus}}}{T_{m,A}} \right) = RT \ln a_A.$$

$$\ln a_A = \frac{\Delta H^{\text{fus}}}{R} \left(\frac{1}{T_{m,A}} - \frac{1}{T} \right)$$

Ideal, $a_A = x_A$.

Note only terms involving A.