- If Clausius Clapeyron fails

$$\left(\frac{dP}{dT}\right)_{pb} = \frac{l}{T(v_2 - v_1)} = 0/0$$

- Second order phase transition ($\Delta S, \Delta v = 0$)

$$\left(\frac{dP}{dT}\right)_{pb} = \frac{c_{P,1} - c_{P,2}}{Tv(\beta_1 - \beta_2)}$$

- Two phases intermingled
- Ferromagnet (Excess "spin-up" atoms)
- Superfluid Helium (Many particles in quantum ground state)
- Superconductor (Many "paired" electrons in same quantum state)

Open systems

How to deal with particle exchange?

Extra particles $N \to N + dN$

Energy gained by adding a particle?

$$dU = TdS - PdV + \mu dN \qquad \text{with } \mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}$$

Mathematically μdN equivalent to including an extra type of work.

Chemical Potential μ and thermodynamic potentials

Definitions unchanged

$$F = U - TS$$

$$H = U + PV,$$

$$G = H - TS = F + PV$$

Therefore $dG = -SdT + VdP + \mu dN$ etc.

$$\boxed{\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P}}$$

Also, for many species

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_{j\neq i}}$$

μ is useful with ANY boundary condition

Chemical potential and Gibbs Free Energy

Consider the two ways to write the free energy of αN particles:

$$\Rightarrow \alpha G(P, T, N) = G(P, T, \alpha N)$$

Take the derivative of both sides with respect to α:

$$
\begin{aligned}
G &= \left(\frac{\partial G(P, T, \alpha N)}{\partial \alpha} \right)_{P,T} \\
&= N \left(\frac{\partial G(P, T, \alpha N)}{\partial (\alpha N)} \right)_{P,T} \\
&= \frac{N}{\alpha} \left(\frac{\partial G(P, T, \alpha N)}{\partial N} \right)_{P,T} \\
&= N \left(\frac{\partial G(P, T, N)}{\partial N} \right)_{P,T}
\end{aligned}
$$

$$\boxed{\mathbf{G} = \mathbf{N}\mu} \qquad \text{for a pure substance}$$

State functions in terms of μ

$$\boxed{G = N\mu \qquad \text{for a pure substance}}$$

The chemical potential for one species is the specific Gibbs free energy!
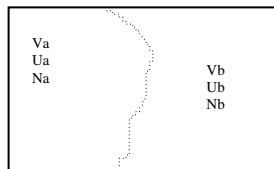$\mu = G(T, P, N)/N$ we find that:

$$d\mu = -sdT + vdP$$

μ **can be written as a function of P and T only** for a pure substance.

$$\boxed{s = -(\partial\mu/\partial T)_{p,N} \qquad v = (\partial\mu/\partial p)_{T,N}; \qquad \text{for a pure substance}}$$

Be careful with extensive ($\propto N$) and intensive quantities.

A closed system equilibrates

Closed system, two parts initially out of equilibrium.

Conservation Laws: $dU_A + dU_B = 0$, $dN_A + dN_B = 0$, $dV_A + dV_B = 0$.

Second law: $dS_A + dS_B \geqslant 0$

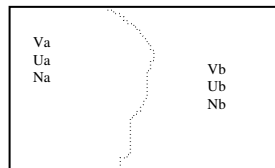$$dS(U, V, N) = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$$

Which, when applied to the two-part system gives

$$\Big(\frac{1}{T_A} - \frac{1}{T_B}\Big)dU_A + \Big(\frac{P_A}{T_A} - \frac{P_B}{T_B}\Big)dV_A - \Big(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\Big)dN_A \geqslant 0$$

,

Hold that thought ...

Flow of heat and particles
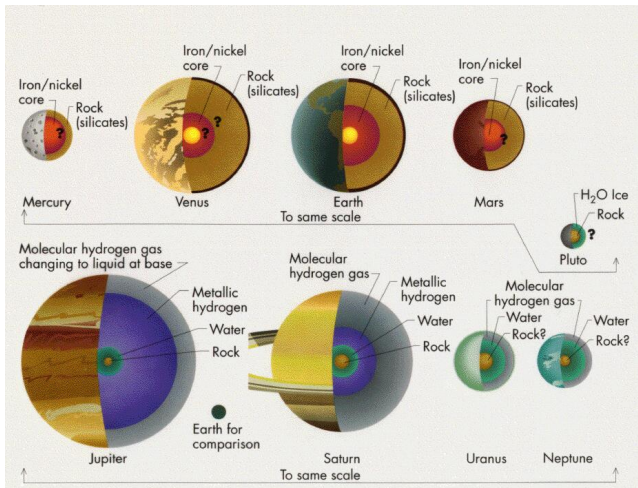

From previous slide ...

$$\Big(\frac{1}{T_A} - \frac{1}{T_B}\Big)dU_A + \Big(\frac{P_A}{T_A} - \frac{P_B}{T_B}\Big)dV_A - \Big(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\Big)dN_A \geqslant 0$$

At equilibrium $T_A = T_B$, $P_A = P_B$ and $\mu_A = \mu_B$.

- energy flows from hot to cold until $T_A = T_B$.
- volume moves from high to low pressure (for equal T)
- particles flow from high to low chemical potential (for equal T).

Particles (mass) flow along gradients of the chemical potential .

Phase separation in Planets

Chemical potential includes gravity: $\mu = u - Ts + Pv + mg_{\mathbf{r}}h$.
Heavy atoms fall to the bottom: can be drawn up if soluble (u)

Chemical Potential for single component ideal gas

$$dG = VdP - SdT + \mu dN$$

For constant N, integrating g from T=0, P=P_0 , we get

$$
\begin{aligned}
d\mu = dg &= \left(\frac{d(G/N)}{dT}\right)_{P,N} dT + \left(\frac{d(G/N)}{dP}\right)_{T,N} dP \\
&= (S/N)dT + (V/N)dP = c_P dT + \frac{RT}{P} dP
\end{aligned}
$$

$$\mu = c_P T + RT \ln(P/P_0)$$

Note dependence on P ($=nRT/V$):
adding more stuff (n) at fixed (V, T) increases μ

Stating the obvious

Non-interacting objects in the same system can be treated as *independent* ideal gases, thanks to ...
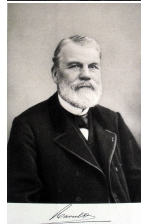
Dalton's Law

Total pressure is the sum of partial pressures

$$P = \sum_i p_i$$

Raoult's Law

Partial pressure is proportional to concentration

$$p_i V = N_i RT$$

e.g. dilute chemicals in solution, photons in a cavity etc.

Entropy/free energy of very dilute system

Recall the entropy of an ideal gas

$$S - S_0 = c_p \ln T - R \ln P$$

For multiple components i

$$S = \sum N_i s_i = c_V \ln T - R \sum (p_i/P) \ln p_i$$

So at *very low* $p_i \to 0$, pressure term is

$$0 \times \ln 0$$

Contribution to entropy is zero, but *per particle* it is near infinite.
Systems can always lower their Gibbs free energy by having a tiny amount
of a component.

Solubility: Find concentration, c_x, of x at equilibrium?

Boundary conditions: $T_0, P_0, \mu_x^{(0)}$,
Chemistry: specific enthalpy of solution δh_i.

Consider system in Eqm with boundary:
$T = T_0$, $\mu = \mu_x^{(0)}$, and Raoult's Law

$$p_x = P_0 N_x / N = c_x P_0$$

with ideal gas entropy:

$$\mu_x^{(0)} = \mu_x = h - Ts = \delta h + RT \ln p_x / P_0$$

Rearranging: $\qquad c_x = \exp\left[(\mu_x^{(0)} - \delta h)/RT\right]$

If insoluble: $\delta h \gg \mu_x^{(0)}$ there is still some x in solution,
If soluble, $\delta h < \mu_x^{(0)}$ (x is "soluble") concentration larger than 1 (not ideal gas).

"Do I really have to do all these?"

Thermodynamics in Chemistry

Molecules react to form other molecules.
A chemical potential can be defined for each.

$$dU = TdS - PdV + \sum_i \mu_i dN_i$$
$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

Total Gibbs, G is also the sum of the chemical potentials

$$G = \sum_i \mu_i N_i \implies dG = \sum_i N_i d\mu_i + \mu_i dN_i$$

Equating these expressions for dG yields the **Gibbs-Duhem relation**:

$$\boxed{\sum_i N_i \; d\mu_i = -S \; dT + V \; dp}$$

This gives balance of concentration of components i

Chemical equilibrium of a reacting system

Closed system, fixed (T, P) boundary
Minimise G (set $dG = 0$)

$$dG = \sum_i \mu_i dN_i = 0 \qquad \text{closed system at equilibrium, fixed T}$$

N_i are all internal degrees of freedom.
dN_i are constrained by the reaction equation $\sum_i b_i dN_i = 0$
e.g. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ leads to $dN_{H_2} + \frac{1}{2}dN_{O_2} - dN_{H_2O} = 0$

Combining minimisation of G and constraint: chemical process equilibrium:

$$\sum_i b_i \mu_i = 0$$

$$\text{e.g. } \mu_{H_2} + \frac{1}{2}\mu_{O_2} = \mu_{H_2O}$$

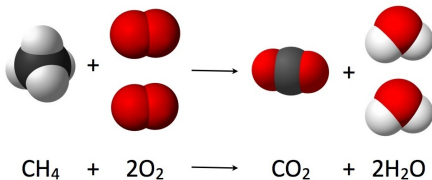At Eqm, chemical potential of reagents and products are equal
If we start with "too high" concentration a reagent, it will react away

Reaction between ideal gases at fixed T, N

- Dilute solution $\approx$ Ideal Gas = "Ideal Solution".
- Ideal gas mixture: $P = \sum p_i$
- Raoult's Law: $p_i V = N_i RT$

$$CH_4 \;+\; 2O_2 \;\longrightarrow\; CO_2 \;+\; 2H_2O$$

$$dG = V \sum_i dp_i - SdT + \sum_i \mu_i dN_i$$

For isothermal reaction (fixed T boundary)

$$dG \equiv \sum_i d\mu_i = \sum_i \frac{RT}{p_i} dp_i$$

Get change in μ_i with pressure by integrating from reference state μ_i^0,

$$\mu_i = \mu^0{}_i + RT \ln[p_i/p_i^0]$$

Substituting into equilibrium condition $\sum b_i \mu_i = 0$

Equilibrium constant (Generalization of solubility)

...From previous

$$\sum_i b_i(\mu_i^0 + RT \ln[p_i/p_i^0]) = 0$$

Each reaction has an "Equilibrium constant" (which depends on T).

$$\ln(K) \equiv \ln\left[\prod_i (p_i/p_0)^{b_i}\right] = -\frac{\sum_i b_i \mu_i^0}{RT}$$

$$\implies \quad K(T) \equiv \prod_i (p_i/p_0)^{b_i} = \exp[-\frac{\sum_i b_i \mu_i^0}{RT}] \quad (=0 \text{ @ reference state})$$

At low temperature (compared with chemical energy)

- TS is negligible, so μ equals Enthalpy
- $\sum_i b_i \mu_i$ becomes the enthalpy of reaction.
- K(T) looks like the Boltzmann factor $\exp -\Delta E/kT$.

Chemistry made easy

Need only measure Chemical Potential μ_i for each component (N measurements), not K for every possible reaction (N! measurements)

The Chemical Potential is ...

- The extra energy from adding a particle $dU = TdS - PdV + \mu dN$
- The specific Gibbs $\mu = g$ for a pure substance.
- The quantity which drives particle flow.
- The quantity which defines chemical equilibrium

All of the above!