

Conditions for Thermodynamic equilibrium:

- Mechanical equilibrium ($P = \text{const}$ throughout system)
- Thermal equilibrium ($T = \text{const}$ throughout system)
- "Diffusional" equilibrium
 μ is constant for each substance throughout the system.

How do we calculate chemical potential?

→ depends on phase state of substance.

recall:

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

consider $T = \text{const}$. Then:

$dG = V dp$ so, if you have a pressure change: from $p \rightarrow p'$

$$\int_p^{p'} dG = \int_p^{p'} V dp \quad \Rightarrow \quad G(p') = G(p) + \int_p^{p'} V dp \quad (1)$$

Change in G.F.E. for a pressure change, and for $T = \text{const}$.

So, depending on the phase of substance, we can calculate changes in G by calculating the integral of equation (1).
 Let's take specific cases.

- a) Substance is solid or liquid. Then it is practically incompressible, in other words, its volume doesn't change much with pressure, i.e., $V \approx \text{const}$, so ① becomes:

$$G(p) = G(p') + V \int_p^{p'} dp = G(p') + V(p' - p)$$

↑
this is also known as "Poynting factor".

we usually take p to be = 1 atm (reference pressure). So:

$$G(p) = G(1 \text{ atm}) + V(p - 1 \text{ atm})$$

also, most often the "Poynting factor" is negligible compared to $G(1 \text{ atm})$. Hence, you can make the statement:

$$G(p) \approx G(1 \text{ atm}) \quad \text{i.e., } G \text{ is constant with respect to pressure.}$$

now, in a similar fashion, $g(p) \approx g(1 \text{ atm})$.
or, $\mu(p) = \mu(1 \text{ atm})$, and considering variations in temperature:

$$\mu(p, T) \approx \mu(1 \text{ atm}, T)$$

i.e. chemical potential for gases and liquids do not change with pressure - only with T .

b) gases

$$dg = -SdT + vdp$$

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

we know that $v = \frac{RT}{p}$

so: equation 1 (for $n=1$ mol) becomes:

$$g(p') = g(p) + \int_p^{p'} \frac{RT}{p} dp =$$

$$= g(p) + RT \ln \frac{p'}{p}, \text{ or:}$$

$$\mu(p', T) = \mu(p, T) + RT \ln(p'/p) \quad \text{assuming a reference pressure } p = 1 \text{ atm:}$$

$$\mu(p, T) = \mu(1 \text{ atm}, T) + RT \ln p$$

for a mixture of gases with a mol fraction y_i you have that the chemical potential of each component is:

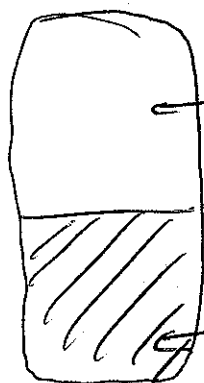
$$\mu_i(p, T) = \mu_i(1 \text{ atm}, T) + RT \ln(y_i p)$$

Partial pressure of i in gas phase.

↑
"reference" chemical potential,
always available from tables.

c) Aqueous solutions (or any solution in general)
 assume you have ^{liquid} water ("A") with some
 substance B dissolved in it. what is μ_A and
 μ_B now?

first step: consider pure water; vapor in equilibrium
 with liquid; $T = \text{const}$



$$\mu_A(\text{gas}) = \mu_A(1\text{atm}, T) + RT \ln P_A$$

partial pressure
 of A in gas phase,
 or vapor pressure of pure A.

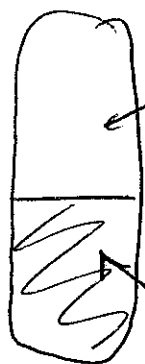
we can then directly determine $\mu_A(\text{liquid})$, because
 you know that

$$\mu_A(\text{liquid}) = \mu_A(\text{gas}) \Rightarrow$$

$$\Rightarrow \boxed{\mu_A(\text{liquid}) = \mu_A(1\text{atm}, T) + RT \ln P_A}$$

Note: vapor pressure and $\mu_A(1\text{atm}, T)$ are
 all obtained from measurements.

So, now that we have some B dissolved in A, we get:



$$\mu_A(\text{gas}) = \mu_A(P=\text{atm}, T) + RT \ln P_A^*$$

vapor pressure of A, when B is dissolved in it.

$$\mu_A(\text{liquid})$$

$$\mu_B(\text{liquid})$$

we know that $\mu_A(\text{liquid}) = \mu_A(P=\text{atm}, T) + RT \ln P_A^*$

but how can we determine P_A^* ? From Raoult's

law: $P_A^*/P_A = X_A$. So:

$$\mu_A(\text{liquid}) = \mu_A(P=\text{atm}, T) + RT \ln X_A P_A =$$

$$= \underbrace{\mu_A(P=\text{atm}, T) + RT \ln P_A}_{\mu_A(\text{liquid, pure})} + RT \ln X_A$$

$$= \mu_A(\text{liquid, pure}) + RT \ln X_A$$

So, adding a solvent changes G.F.E by a calculable amount.

Similarly, $\mu_B(\text{liquid}) = \mu_B(\text{liquid, pure}) + RT \ln X_B$

If you have nonideal solution, then you need to "correct" Raoult's law by a factor:

$$\frac{P_A}{P_A^*} = f_A X_A \quad \text{and:}$$

$$\mu_A = \mu_A^\circ(T) + RT \ln f_A X_A$$

↑
"activity coefficient"

$f_A X_A$ is also known as "activity" and expresses the "effective" concentration of A in the solution.

Temperature dependence of μ :

Gibbs-Helmholtz Equation:

The G-H Equation expresses the dependence of G on T:

$$\boxed{\frac{\partial \left(\frac{G}{T}\right)}{\partial T} = -\frac{H}{T^2}} \quad \text{G-H Equation}$$

Derivation:

$$G = -SdT + VdP$$

Applying constant P: $dG = -SdT$

$$\text{but } G = H - TS \Rightarrow -S = \frac{G - H}{T}$$

$$\Rightarrow dG = \frac{G - H}{T} dT \Rightarrow$$

$$\left(\frac{\partial G}{\partial T}\right)_P = \frac{G - H}{T} \quad (*)$$

For function $\frac{G}{T}$ dependence on T

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

$$\left(\frac{\partial (G/T)}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} \quad \text{inserting } (*)$$

$$\boxed{\left(\frac{\partial (G/T)}{\partial T}\right)_P = -\frac{H}{T^2}}$$

If we apply the above equation to a process, in other words if we have a reaction or a change in a system, then:

$$\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} = - \frac{\Delta H}{T^2} \quad \text{another form}$$

But $\Delta G \sim \mu$ so this is how you calculate changes in chemical potentials

BTW: why $\Delta G/T$?

ΔG tells us whether or not a reaction wants to go. The ultimate arbiter of how strongly the reaction wants to go depends on $\Delta G/T$

Because $\left\{ \frac{\Delta G}{T} = -\Delta S_{\text{univ}} \right\}$

The last equation tells us that the ultimate driving force in nature is entropy, that is, the drive toward disorder

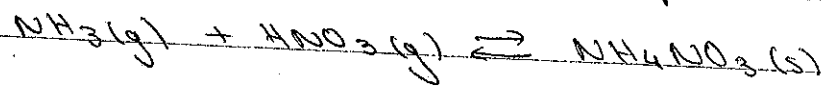
We can get reference μ 's from tables for $P=1 \text{ atm}$, $T=298 \text{ K}$. What about the μ at any temperature?

For a chemical reaction:

$$\ln K = - \frac{\sum \nu_i \mu_i^0}{RT} = - \frac{\Delta G^{\circ}_{\text{reaction}}}{RT}$$

So: $K_i = \prod_{i=1}^K a_i^{\nu_i}$ or for gases $K_i = \prod_{i=1}^K p_i^{\nu_i}$

For example consider the simple reaction:



The condition for equilibrium is:

$$\mu_{\text{NH}_3} + \mu_{\text{HNO}_3} - \mu_{\text{NH}_4\text{NO}_3} = 0$$

"a" for solids is 1 so:

$$\ln K = \frac{\mu_{\text{NH}_4\text{NO}_3}^* - \mu_{\text{NH}_3}^0 - \mu_{\text{HNO}_3}^0}{RT} \quad \text{or} \quad K = p_{\text{NH}_3} \cdot p_{\text{H}_2\text{SO}_4}$$

Now, from Gibbs-Helmholtz we have:

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

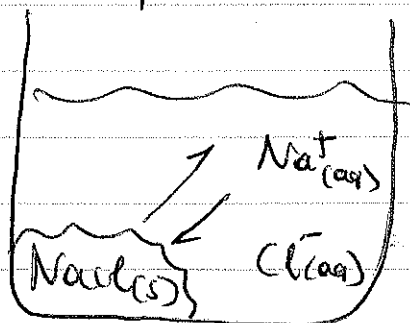
So $\frac{\partial \ln K}{\partial T} = - \frac{\Delta H}{RT^2}$ enthalpy of change of

reaction: $\Delta H(T_0) + \Delta C_p (T - T_0)$

So, we have the equilibrium constant as a function of T as

Example

Sea salt in solution being in equilibrium with a solid precipitate. Calculate relationship at equilibrium.



at equilibrium, $\mu_{\text{NaCl(s)}} = \mu_{\text{Na}^+(\text{aq})} + \mu_{\text{Cl}^-(\text{aq})}$

$$\mu_{\text{NaCl(s)}} = \mu_{\text{Na}^+(\text{aq})}^* + RT \ln X_{\text{Na}^+(\text{aq})} + \mu_{\text{Cl}^-(\text{aq})}^* + RT \ln X_{\text{Cl}^-(\text{aq})} \Rightarrow$$

$$\Rightarrow \mu_{\text{NaCl(s)}} - \mu_{\text{Na}^+(\text{aq})}^* - \mu_{\text{Cl}^-(\text{aq})}^* = RT \ln X_{\text{Na}^+} + RT \ln X_{\text{Cl}^-}$$

$$\mu_{\text{NaCl(s)}} - \mu_{\text{Na}^+(\text{aq})}^* - \mu_{\text{Cl}^-(\text{aq})}^* = RT (\ln X_{\text{Na}^+} + \ln X_{\text{Cl}^-})$$

↓

$$\mu_{\text{NaCl(s)}} - \mu_{\text{Na}^+(\text{aq})}^* - \mu_{\text{Cl}^-(\text{aq})}^* = RT \ln X_{\text{Na}^+} X_{\text{Cl}^-}$$

so $\ln X_{\text{Na}^+} X_{\text{Cl}^-} = \frac{\mu_{\text{NaCl(s)}} - \mu_{\text{Na}^+(\text{aq})}^* - \mu_{\text{Cl}^-(\text{aq})}^*}{RT}$

$$X_{\text{Na}^+} X_{\text{Cl}^-} = \exp \left\{ \frac{\mu_{\text{NaCl(s)}} - \mu_{\text{Na}^+(\text{aq})}^* - \mu_{\text{Cl}^-(\text{aq})}^*}{RT} \right\}$$

equilibrium constant, K_{sp}

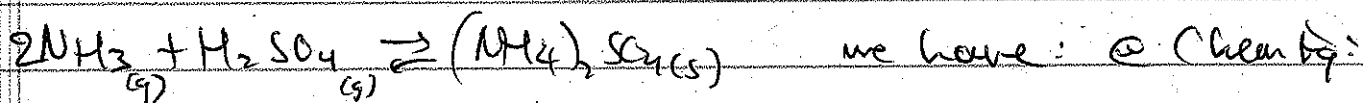
Another example

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no ap: $\mu_{\text{solid}} = \mu^{\circ}_{\text{solid}}(T)$

$$\mu_{\text{gas}} = \mu^{\circ}_{\text{gas}}(T, \text{sat}) + RT \ln P_i$$

so, for our reaction:



$$2\mu_{\text{NH}_3(g)} + \mu_{\text{H}_2\text{SO}_4(g)} - \mu_{(\text{NH}_4)_2\text{SO}_4} = 0, \text{ or:}$$

$$2\left\{\mu^{\circ}_{\text{gas}}(T, \text{sat}) + RT \ln P_{\text{NH}_3}\right\} + \left\{\mu^{\circ}_{\text{gas}}(T, \text{sat}) + RT \ln P_{\text{H}_2\text{SO}_4}\right\} - \mu^{\circ}_{(\text{NH}_4)_2\text{SO}_4} = 0 \Rightarrow$$

$$\Rightarrow -\left(2\mu^{\circ}_{\text{NH}_3(g)} + \mu^{\circ}_{\text{H}_2\text{SO}_4(g)} - \mu^{\circ}_{(\text{NH}_4)_2\text{SO}_4}\right) = RT(\ln P_{\text{NH}_3} + \ln P_{\text{H}_2\text{SO}_4}) \Rightarrow$$

$$\Rightarrow \ln P_{\text{NH}_3} P_{\text{H}_2\text{SO}_4} = -\frac{(2\mu^{\circ}_{\text{NH}_3} + \mu^{\circ}_{\text{H}_2\text{SO}_4} - \mu^{\circ}_{(\text{NH}_4)_2\text{SO}_4})}{RT} \Rightarrow$$

$$\Rightarrow P_{\text{NH}_3(g)} P_{\text{H}_2\text{SO}_4(g)} = \left\{ \exp \left\{ -\frac{\sum \nu_i \mu^{\circ}_i}{RT} \right\} \right\}$$

"
equilibrium constant K
also know T dependence

$$P_{\text{NH}_3(g)} P_{\text{H}_2\text{SO}_4(g)} = K_{(\text{NH}_4)_2\text{SO}_4}$$