

## Review for Exam 3

MT3.1

Where have we come from and why did we go that way?

We started by looking at  $PV=nRT$  and realizing it was an Equation of State, relating the thermodynamic variables to one another.

This showed us the goal of thermo: get the variables!

$P, V, T + N$  are good variables but not for reactions. We needed 2 more:  $S$  and especially  $\mu \rightarrow$  chem. pot.

To get  $\mu$ , we started with internal energy,  $U$ , and stripped away work energy (the subject of PHY 113) and heat energy (the subject of thermo, but less widely seen\* relative to particle energy) leaving behind only the particle energy - specifically the potential of particles to release energy as useful, non-PV work.

This stripped down potential energy is  $G$ , Gibbs Free energy.

To get  $\mu$  we stripped down  $U$  once more to get the Gibbs-Duhem eqn:  $SdT - Vdp + \sum N_i d\mu_i = 0$  i.e.  $\mu$  is a function of  $T + P \rightarrow \mu(T, P)$

\*The flow of heat is the only thermodynamic flow not governed by a force that depends on the chemical potential.

## MT3.2

The fact that  $\mu$  is a function of  $T + p$  is also seen in an equation that expresses the "stripped-down" nature of  $G$ :

$$G = U - ST - PV = \sum \mu_k N_k \quad \text{or} \quad \bar{G}_k = \mu_k$$

Since  $G$  is a function of  $P, T, + N$ ,  $\bar{G}$  (i.e.  $\mu$ ) is a function of only  $P + T$ .

So we have  $\mu(P, T)$  for pure components, what about mixtures?  $\rightarrow \mu_i(P, T, x_i)$

What happens for multiple phases, e.g. liq + gas?

$\rightarrow \mu_{i,l} = \mu_{i,g}$  ← What about reactions?

$\rightarrow \mu_{\text{products}} = \mu_{\text{reactants}}$

These give us Gibbs Phase Rule:  $Dof = C - P - R + 2$

So, how does  $\mu_i$  depend on  $P, T + x_i$ ? Go back to

Gibbs-Duhem:  $d\mu_i = -\bar{S}_i dT + \bar{V}_i dP$  compare to:  $d\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_P dT + \left(\frac{\partial \mu_i}{\partial P}\right)_T dP$

We see that:  $\left(\frac{\partial \mu_i}{\partial T}\right)_P = -\bar{S}_i$  and  $\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i$

The first expression is useful for phase transitions\*, the second is useful to find how  $\mu_i$  depends on  $p$  (and  $x$ , it turns out)

\* we don't directly use this to get  $T$  dependence, instead we take  $\left(\frac{\partial(\mu_i/T)}{\partial T}\right)_P = -\bar{H}_i/T^2$  (Gibbs-Helmholtz) and integrate

How does  $\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i$  give us  $P + x_i$  dependence?

First write:  $d\mu_i = \bar{V}_i dP = \frac{RT}{P} dP$  for ideal gases  
 then integrate:  $\mu_i(P) - \mu_i(P_0) = RT \int_{P_0}^P \ln P' \leftarrow \text{"dummy" variable of integration}$

so we get:  $\mu_i(P) = \mu_i(P_0) + RT \ln \frac{P}{P_0}$  (looks familiar!)  
 and for partial pressure:  $P = P_i = x_i P_{\text{tot}} \Rightarrow \mu_i(P_i, x_i) = \mu_i(P_{\text{tot}}) + RT \ln x_i$

For non ideal gases, solids, etc we set  $\int_{P_0}^P \bar{V}_i dP' = RT \ln a_i$  correction factor included: e.g.  $\gamma_i x_i$  or  $\gamma_i P_i$  etc.  
 so our expressions will look ideal-like.

As mentioned,  $T$  dependence is obtained from  $\left(\frac{\partial(\frac{\mu_i}{T})}{\partial T}\right)_P = -\frac{\bar{H}_i}{T^2}$

by integrating:  $\frac{\mu_i(T)}{T} - \frac{\mu_i(T_0)}{T} = \int_{T_0}^T \frac{\bar{H}_i}{T^2} dT'$

keeping in mind that  $\bar{H}_i(T) - \bar{H}_i(T_0) = \int_{T_0}^T C_p(T') dT'$   
 and  $C_p(T) = \alpha + \beta T + \gamma T^2$ , where  $\alpha, \beta, \gamma$  can be found in tables\*

So, we have  $T, P + x_i$  dependence, is there anything else?  
 $\rightarrow \mu$  as a function of external field!

Now  $\mu_i(\text{field}) = \tilde{\mu}_i = \mu_i(\text{no field}) + \tau_i \phi$   
 $\tau_i \rightarrow$  coupling const. potential

$\phi$  itself is often a position dependent chem. pot:  $\mu(x)$   
 but it can also be the gravitational or electric potential

\* if we had started with  $\left(\frac{\partial \mu_i}{\partial T}\right)_P = -\bar{S}_i$  we would have used eq 6.3.7:  
 $\bar{S}_i(T) - \bar{S}_i(T=0K) = \int_0^T \frac{C_p(T')}{T'} dT'$  and ended up at the same place, but  
 our book uses the above method to get  $T$  dependence (p. 137)

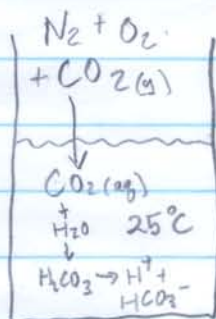
## Putting it all together

The  $P, T, x_i$ , and field dependences of  $\mu$  give us an equation of state far more useful than  $PV=nRT$ , and the corrections for non-ideality ( $a_i, \gamma_i$ , etc.) that can be obtained from thermodynamic tables makes this equation of state (like V.d Waals) match reality.

so how do we actually use  $\mu_i(P, T, x_i, \Phi)$ ?

We start with  $\mu_i(P_0, T_0, x_i=1, \Phi=0) = \Delta_f G_i$

and work our way from there. For example: Exc 9.9



the questions that  $\mu$  can answer are:

① What is the partial pressure of CO<sub>2</sub>?

② How much CO<sub>2</sub> goes into H<sub>2</sub>O?

③ How much CO<sub>2(aq)</sub> goes to H<sub>2</sub>CO<sub>3</sub>?

④ How much H<sub>2</sub>CO<sub>3</sub> becomes H<sup>+</sup>? pH?

⑤ How does Temperature affect things?

Questions ①-⑤ are dealt with in 9.9 (question ① involves knowing the volume fraction of CO<sub>2</sub> in the atmosphere, then  $\mu$  and  $M_{CO_2}$  can be used to find  $P_{CO_2}$  at various altitudes) but other questions could be asked that  $\mu$  can answer. (how does adding NaCl affect things? what about an electric field? etc) many of which are physiological.

The bottom line is that  $\Delta_f G$  (i.e.  $\mu^\circ$ ) tells us most of what we need to know about any system