Remember next exam is 1 week from Friday. This week will be last quiz before exam.

Outline:

Extent of reaction Reaction equilibrium $\Delta_{rxn}G$ at non-standard state Relating G and ξ and K and p K and ξ as fctn of p

Review

Partition function values for typical molecule (HCl) huge for translational (10²⁶) a handful for rotational (20) just over 1 for vibrational (1.0000007) and exactly 1 for electronic (1)

I'm not going to write it all down, but remember that we had that nice table that summarized the heat capacities of molecules. Where is the temperature dependence? **all of them technically, but usually just vibration**.

And Chapt 12

- 1) Density of States:
- 2) Fluctuations are critical:
- 3) Negative temp:
- 4) Graphical connection between energy functions. Check out p.226 carefully.

Now on to Chapt 13

We have done a lot recently figuring out how to relate microscopic information (energy levels and such) to macroscopic quantities (H, T, S, U...) through the partition function. Today we are going to start really applying this to find out some useful chemical information. We are getting into some real freshman chemistry – equilibrium constants. Of course, we'll do it in just a bit more detail than you saw in CHEM111.

Let's define the simplest possible reaction:

 $aA \rightarrow zZ$

If we started with n_{A0} and n_{Z0} moles of A and Z then let's define the amounts of A and Z at any time...

$$n_A = n_{A0} - a\xi$$
$$n_Z = n_{Z0} + z\xi$$

 ξ (xi or squiggle) is the **extent of reaction**. It measures the progress of the reaction and has units of moles. Subtraction is because A is a reactant.

For instance:	H_2 +	$^{1}/_{2}O_{2} \leftrightarrow$	H_2O
At start:	n _{H2}	n _{O2}	$n_{\rm H2O}$
Later:	$n_{H2} - \xi$	$n_{O2} - \frac{1}{2}\xi$	$n_{\rm H2O}$ + ξ

Of course, we are really interested in the **change** in the amount of the substances: $dn_I = i d\xi$ (negative if reactant)

We can substitute this expression into what is called the Gibbs-Duhem equation: Gibbs-Duhem is for constant T and p (recall $dG = -SdT + Vdp + \mu_A dN_A + \mu_Z dN_Z$)

$$dG = \sum_{J} \mu_{J} dn_{J}$$

So, rewriting Gibbs-Duhem in terms of ξ gives: $dG = \sum_{I} j\mu_{J} d\xi$

(where products have positive and reactants negative coefficients)

This can be rewritten as: $\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \sum_{J} j\mu_{J}(\xi) = \Delta_{r}G$

where $\Delta_r G$ is the **reaction Gibbs energy.** This is defined for a balanced chemical equation and the reactants and products at their standard states. (add products, subtract reactants)

Let's look at a simple case: Isomerization Reaction: 11-cis retinal ↔ all trans retinal Everyone know what this does? vision

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_{trans}(\xi) - \mu_{cis}(\xi)$$

Both of these chemical potentials change as the rxn proceeds, so this differential depends on the extent of reaction.

When $\mu_A > \mu_Z$, or $\left(\frac{\partial G}{\partial \xi}\right)_{p,T} < 0$ the reaction A -> Z is spontaneous (ξ must increase to minimize G)

When $\mu_A < \mu_Z$, or $\left(\frac{\partial G}{\partial \xi}\right)_{p,T} > 0$ the reaction Z -> A is spontaneous (ξ must decrease to minimize G)

The minimum in $\left(\frac{\partial G}{\partial \xi}\right)_{p,T}$ occurs when its value is zero, or $\mu_A = \mu_Z$. (really $a\mu_A = z\mu_Z$. This is when

the reaction is at equilibrium! The reaction "stops."

All right then, we can see that equilibrium is determined by the chemical potential. Another way of saying this is that the chemical potential is the molar G for each product/reactant. (Note that chemical potential depends on concentration, p, T, etc.)

Note that the **standard molar** reaction Gibbs energy is different than the reaction Gibbs energy because for the standard energy, the composition of reactants and products are fixed at their standards states (1 M or 1 atm), rather than an arbitrary composition:

$$\Delta_{\rm r} {\rm G}^0 = z \mu_Z^0 - a \mu_{\rm A}^0$$

Calculating the composition of reactions at equilibrium (what is the yield?)

Remember that we are talking about equilibrium constants, so we want to try and get back to this. If A and Z are assumed to be perfect gases, we can calculate $\Delta_r G$ just as we have done before (constant p and T):

$$\Delta_{\rm r}G = z\mu_Z - a\mu_A$$

We now need to make use of another expression that shows the pressure (concentration) -dependence of the chemical potential.

$$\mu_{Z} = \mu_{Z}^{\varnothing} + RT \ln\left(\frac{p_{Z}}{p^{\varnothing}}\right) \quad \text{(comes from Chapt 11: } \mu_{Z} = -k_{B}T \ln\left(\frac{q_{Z}}{N_{Z}}\right)\text{)}$$

$$\Delta_r G = z \left(\mu_Z^{\varnothing} + RT \ln\left(\frac{p_Z}{p^{\varnothing}}\right) \right) - a \left(\mu_A^{\varnothing} + RT \ln\left(\frac{p_A}{p^{\oslash}}\right) \right)$$
$$\Delta_r G = z \mu_Z^0 - a \mu_A^0 + RTz \ln\left(\frac{p_Z}{p^0}\right) - RTa \ln\left(\frac{p_A}{p^0}\right)$$

$$\Delta_r G = \left(\Delta_r G^0 + RT \ln\left(\frac{p_Z^z}{p_A^a}\right)\right) \text{ where } \Delta_r G^0 = z\mu_Z^0 - a\mu_A^0$$

We will find it convenient (for more complicated reactions) to denote the argument of the logarithm as the reaction quotient, Q

(Terrible notation of course. Q is not the partition function.)

$$\Delta_r G = \left(\Delta_r G^0 + RT \ln Q\right)$$

At equilibrium $\Delta_r G = 0$ and Q is equal to the equilibrium constant K (by definition):

$$\Delta_{\rm r} {\rm G}^0 = - \, {\rm RT} \, \ln \, {\rm K}$$

This is one of the most useful equations in chemical thermodynamics because it provides a direct relationship between all that thermodynamic data and information on how **actual chemical reactions** proceed.

Obviously, when K < 1 (the reactant is favored), $\Delta_r G > 0$ and the reaction is not spontaneous and when K > 1 (the product is favored), $\Delta_r G < 0$ and the reaction is spontaneous in the direction A \rightarrow Z. (If we have equal concentrations of products and reactants.)

<PAUSE>

Exergonic and endergonic reactions

 $\Delta_r G < 0$: reaction is spontaneous and exergonic (work-producing); could drive other processes. e.g. ATP \rightarrow ADP or glucose combustion

 $\Delta_r G > 0$: reaction is not spontaneous; it is endergonic (work-consuming) e.g. ADP \rightarrow ATP or electron transfer

Discussion of the general form of G vs. ξ

If $\Delta_r G^0$ for a reaction is negative, the products are more thermodynamically stable than the reactants. **Everyone agree? Do most reactions go all the way to products, or stop somewhere in equilibrium?** Most stop short of 100 % yield. **Why?**

The standard molar reaction Gibbs energy ($\Delta_r G^0$) does not account for the additional entropy introduced when substances are mixed together. In other words, $\Delta_r G^0$ does not include contributions from $\Delta_{mix} G$.

 $\Delta_{\min} \mathbf{G} = \mathbf{?} \operatorname{nRT}(\mathbf{X}_{\mathrm{A}} \ln \mathbf{X}_{\mathrm{A}} + \mathbf{X}_{\mathrm{B}} \ln \mathbf{X}_{\mathrm{B}})$

(Think back to chapt 6 homework) (X is mole fraction, ignore enthalpy)

So, the **minimum in** Δ_{mix} **G occurs when?** our A \rightarrow B reaction is 50 % complete. After that point, our devious friend entropy 'fights' the continued conversion of reactants to products.



Depending on the relative magnitudes of $\Delta_r G^0$ and $\Delta_{mix} G$, the extent of reaction can vary dramatically.

Now that we have a relationship between equilibrium constants and thermodynamic data, we can calculate the extent of reactions (ξ) for real systems.

Use this format:

	$N_2O_4(g) <->$	$2 \operatorname{NO}_2(g)$	
Initial amounts	1	0	
Equilibrium amounts	1 - ξ	2ξ	Total amount = $1 + \xi$
Equilibrium mole fractions	$(1 - \xi)/(1 + \xi)$	$2\xi/(1+\xi)$	-

(Note that in this case ξ is now unitless and must be between 0 and 1 because of how we have set up our initial conditions in relation to the stoichiometry.)

OK so break into groups – tell me what K_p is for this rxn in terms of pressure of NO₂ and N₂O₄, and then solve for K_p in terms of ξ and P_{tot} .

What should the equilibrium constant look like in terms of pressures?

$$K_p = \frac{\text{products}}{\text{reactants}} = \frac{(P_{NO2})^2}{(P_{N2O4})}$$

Using Dalton's law and neglecting non-ideal effects:

$$K_{p} = \frac{\text{products}}{\text{reactants}} = \frac{(P_{NO2})^{2}}{(P_{N2O4})} = \frac{(X_{NO2}P_{Tot})^{2}}{X_{N2O4}P_{Tot}} = \frac{\{[2\xi/(1+\xi)] \times P\}^{2}}{[(1-\xi)/(1+\xi)] \times P} = \frac{4\xi^{2}P}{1-\xi^{2}}$$

K clearly is **constant.** So if p changes, ξ must change to compensate (Le Chatelier)!

Solving for ξ

$$\xi = \frac{1}{\left[1 + (4/K)P\right]^{\frac{1}{2}}}$$

This is an interesting result. The equilibrium constant does not depend on total pressure, but the extent of the reaction does. We will discuss this further later

For the above reaction mixture at 1 bar total pressure and 298 K and using the equilibrium expression: $\Delta_r G^0 = -RT \ln K$ to calculate K ($\Delta_r G^0 = 4.73 \text{ kJ mol}^{-1}$):

$$K = 0.148$$

 $\xi = 0.191$

So at room temperature and one atmosphere pressure, only about 20 % to the product gets used up. Perhaps the surprise is that any NO₂ gets consumed at all since $\Delta_r G^0$ is positive.