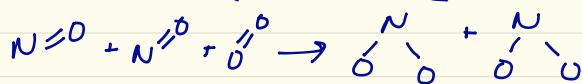
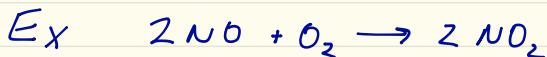


## Lecture 11 - Chemical Reactions

What's a chemical reaction?

Rearrangement of Atoms from some initial state to some final.



Atoms/bonds change partners

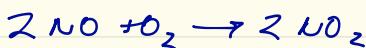
Internal, potential energy changes associated with these rearrangements

Entropic changes associated with changes in # available states, DOFs

Manifest themselves in changes in thermodynamic quantities, U, H, S, ...

Chemical reactions always conserve mass  
always " Atom types

Reactions always follow some fixed stoichiometry



$$\nu_{\text{NO}} = -2 \quad \nu_{\text{O}_2} = -1 \quad \nu_{\text{NO}_2} = 2$$

Thermodynamics can tell us about

- state function changes between fully specified initial and final states of a reaction
- what reactions are/are not spontaneous
- what the equilibrium state is under some specified constraints

Thermodynamics can tell us what is possible/impossible. Cannot tell us what will happen, or what rate of change will be. These are the domain of kinetics.

Kinetics intersects with thermodynamics, but we have no time to cover.

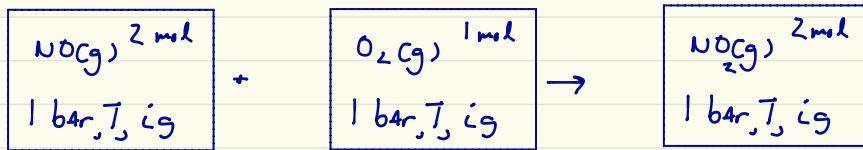
To apply thermo, must fully specify initial and final states of system. Eg



In principle could be mixed in any proportion, does not have to go to completion.

Let's go on here - reaction, mixing, T, P change

Conventional to define a standard state reaction:



Standard states are pure substances at 1 bar, specified T, ideal gas

Because std state specifies P, enthalpy is natural function for capturing energy change.

$$\Delta H_{rxn}^{\circ(T)} = Z_m H_{NO_2}^{\circ}(T) - Z_m H_{NO}^{\circ}(T) - n H_{O_2}^{\circ}(T)$$

$$\Delta H_{rxn}^{\circ} = \sum_j 2j H_j^{\circ}(T) \quad \text{molar std rxn energy}$$

Enthalpy change corresponds to heat flow in/out of thermal reservoir holding T constant

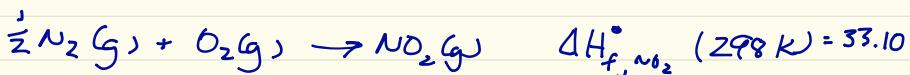
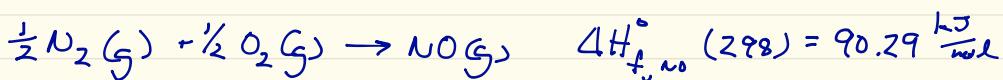
Can then connect to real situation by mixing, pressurizing, converting (using eg departure functions) to real conditions; ...

These  $H^{\circ}$  and  $\Delta H^{\circ}$  are not readily inferred. Can in principle be computed from QM or modelled using eg group additivity. Most reliable usually are tabulations.

Zero of enthalpy is not defined. Important, though, to specify a common zero in any tabulation. Get to set one zero for each atom type. Conventional to define enthalpy of elements in their most common states @ 1 bar, 298 K, to be 0.

$$H_{C(s)}^{\circ} (298\text{ K}) = 0 \quad H_{O_2(g)}^{\circ} (298\text{ K}) = 0 \quad \dots$$

With this convention, can define formation rxn + corresponding formation enthalpy of any substance.



It is these formation enthalpies that are tabulated in standard references.

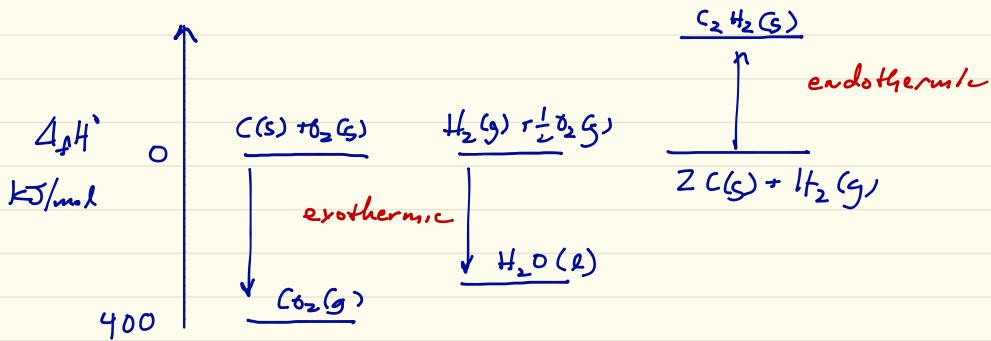
Because enthalpy is a state function, formation enthalpies can be combined to get standard enthalpy of any reaction:



$$\begin{aligned} \Delta H_r^{\circ} &= 2\Delta H_{f, NO_2}^{\circ} - 2\Delta H_{f, NO}^{\circ} - \Delta H_{f, O_2}^{\circ} \\ &= 2(33.10) - 2(90.29) - 0 = -114.38 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

$$\text{In general, } \Delta H_r^{\circ}(298) = \sum_j \nu_j \Delta_f H_j^{\circ}$$

Fun comparisons:



All well & fine. What if we want  $\Delta H_r^\circ$  @ some T other than 298 K?

$$\text{Recall } H^\circ(T_2) - H^\circ(T_1) = \int_{T_1}^{T_2} C_p^\circ(T) dT$$

$$\text{Then } \Delta H_r^\circ(T) = \Delta H_r^\circ(298) + \int_{298}^T \Delta C_p^\circ(T) dT$$

$$\Delta C_p^\circ = \sum_j n_j C_{p,j}^\circ(T)$$

Works as long as T change does not go across a phase change. If it did, would have to add in latent heat (enthalpy) of phase change.

$$H^\circ(T_2) = H^\circ(T_1) + \int_{T_1}^{T_2} C_p^\circ(T) dT + \Delta H_{\text{phase change}}^\circ + \int_{T_p}^{T_2} G^\circ(T) dT$$

Very similar statements apply to entropy.

Again conventional to define a standard state entropy  $S^\circ$  of a material at 1 bar and ( $\text{f}_{\text{orgas}}$ ) in ideal gas state. Key

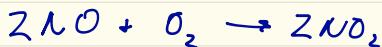
difference is that entropy has a well-defined zero,  $S(0\text{K}) = 0$ . No need to define a  $\Delta_f S$ .

$$\Delta S_r^\circ = \sum_j n_j S_j^\circ \quad S_{\text{O}_2}^\circ(298) \neq 0 !$$

Learned how to calculate this for gases!

If we want T other than 298 K

$$\Delta S_r^\circ(T) = \Delta S_r^\circ(298) + \int_{298}^T \frac{\Delta C_p^\circ(T)}{T} dT$$



$$S_{\text{NO}}^\circ = 210.76 \text{ J/mol K} \quad S_{\text{O}_2}^\circ = 205.152$$

$\sim$  same number!

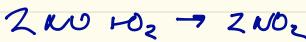
$S_{\text{NO}_2}^\circ = 240.04$   
slightly larger, more NOFs

$$\begin{aligned} \Delta S_r^\circ &= 2(240.04) - \{2(210.76) + 205.152\} \\ &= -146.59 \text{ J/mol K} \end{aligned}$$

$\leftarrow$  entropy favors reactants over products

Particularly important quantity for consideration of equilibrium is Gibbs energy of reaction.

$$\Delta G_r^\circ(T) = \Delta H_r^\circ(T) - T\Delta S_r^\circ(T)$$



$$\Delta G_r^\circ = -114.38 - 298\text{K} \left( \frac{-146.59}{1000} \right) = -70.69 \text{ kJ/mol}$$

enthalpy trumps entropy @ 298 K

Can also write in terms of formation free energies:

$$\Delta G_r^\circ = \sum_j v_j \Delta G_f^\circ$$

Like enthalpy, Gibbs energy has an arbitrary zero.  
Many compilations define a formation free energy to be zero for elements in their standard states.

$$\Delta_f G_{\text{O}_2}^\circ(298) = 0 \quad \Delta_f G_{\text{graphite}}^\circ(298) = 0$$

Can be confusing because  $\Delta_f G^\circ \neq \Delta_f H^\circ + S^\circ$  in tables.  
I have seen other conventions, eg in CRC.  
Important to look closely @ source.

JANAF tables [kinetics.nist.gov / janaf](http://kinetics.nist.gov/janaf)

Webbook [webbook.nist.gov](http://webbook.nist.gov)

CODATA key values CRC  
+ other compilations

(8)

T dependence of  $\Delta G_r^\circ$ :

$$\text{Already learned Gibbs-Helmholtz : } \frac{\partial (G/T)}{\partial T} = -\frac{H}{T^2}$$

$$\Rightarrow \frac{\partial (\Delta G_r^\circ(T)/T)}{\partial T} = -\frac{\Delta H_r^\circ(T)}{T^2}$$

$$\int d\left(\frac{\Delta G_r^\circ(T)}{T}\right) = - \int \frac{\Delta H_r^\circ(T)}{T^2} dT$$

$$\frac{\Delta G_r^\circ(T_2)}{T_2} - \frac{\Delta G_r^\circ(T_1)}{T_1} = - \int \frac{\Delta H_r^\circ(T)}{T^2} dT \approx \Delta H_r^\circ(T) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

NO example @ 348 K

$$\Delta H_r^\circ \approx -114 \text{ kJ/mol} \quad \Delta G_r^\circ(298) = -70.69 \text{ kJ/mol}$$

$$\Delta H_r^\circ \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = (-114 \text{ kJ/mol}) \cdot \left( \frac{1}{348} - \frac{1}{298} \right) = 0.0550$$

$$\begin{aligned} \Delta G_r^\circ(348) &= 348 \text{ K} \left( \frac{-70.69}{298 \text{ K}} + 0.0550 \text{ kJ/mol/K} \right) \\ &= -63.4 \text{ kJ/mol} \end{aligned}$$

reaction "driving force" decreases as T ↑  
Generally true for exothermic reactions

JANAF tables give  $\Delta_f G_{\text{no}_2}^\circ(350) = 85.955$  (600) = 82.822

$\text{no}_2(350) = 54.445$  70.230

$\text{o}_2(350) = 0$  0

$\Delta G_r^\circ = -63.02 \text{ kJ/mol}$  = -25.18 kJ/mol

Common problem is to determine equilibrium state of some mixture undergoing reaction.



At constant  $T, P$ , minimization of Gibbs energy is most convenient.

$$dG = -SdT + VdP + \sum_j \mu_j dN_j$$

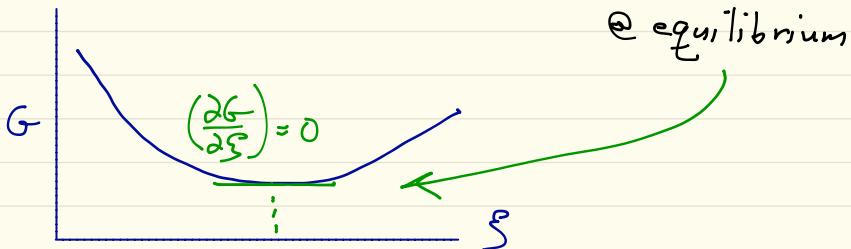
$$\text{have } dG = \sum_j \mu_j dN_j \quad @ \text{const } T, P$$

Need some way to relate amounts of material. Can write

$$N_j = N_{j0} + v_j \xi \quad \xi: \text{advancement (units moles)}$$

$$dN_j = v_j d\xi$$

$$\hookrightarrow dG = dS \left( \sum_j \mu_j v_j \right) \quad \left( \frac{\partial G}{\partial S} \right)_{T, P} = 0 \rightarrow \boxed{\sum_j v_j \mu_j = 0}$$



In lecture 10, said in general  $M_j(T, p) = M_j^\circ(T) + RT \ln a_j$

where activity  $a_j(T, p, v_j)$  is relative to some reference state. (ideal gas, Raoult's Law, Henry's Law, ...)

$$\sum_j v_j M_j = \underbrace{\sum_j v_j M_j^\circ}_{\Delta G_r^\circ(T)} + RT \sum_j v_j \ln a_j = 0 \text{ @ equilibrium}$$

Define equilibrium "constant"  $K_{eq}(T) = e^{-\Delta G_r^\circ(T)/RT}$

$$K_{eq}(T) = \prod_j a_j^{v_j}$$

unless, but defined wrt underlying standard states.



$$\Delta G^\circ(298) = -70.69 \text{ kJ/mol} \Rightarrow K_{eq}(298) = 2.46 \times 10^{12}$$

All gases,  $a_j = \bar{f}_j/f_j^\circ = y_j p/p^\circ$  for ideal gas

$$\begin{aligned} \prod_j a_j^{v_j} &= \left(\frac{y_{NO} p}{p^\circ}\right)^{-2} \left(\frac{y_{O_2} p}{p^\circ}\right)^{-1} \left(\frac{y_{NO_2} p}{p^\circ}\right)^2 \\ &= \left(\frac{y_{NO_2}^2}{y_{NO}^2 y_{O_2}}\right) \left(\frac{p}{p^\circ}\right)^{-1} = 2.46 \times 10^{12} \end{aligned}$$

$$N_j = N_{j_0} + \nu_j \xi \quad N_T = \sum_j N_j = \sum_j N_{j_0} + \xi \sum_j \vec{v}_j = N_{T_0} - \xi$$

$$y_j = \frac{N_j}{N_T} = \frac{N_{j_0} + \nu_j \xi}{N_{T_0} - \xi} = \frac{y_{j_0} + \nu_j \xi'}{1 - \xi'} \quad \xi' = \xi / N_{T_0}$$

dimensionless  
advancement

$$y_{NO} = \frac{y_{NO_0} - 2\xi'}{1 - \xi'} \quad y_{O_2} = \frac{y_{O_20} - \xi'}{1 - \xi'} \quad y_{NO_2} = \frac{y_{NO_20} + 2\xi'}{1 - \xi'}$$

$$K_{eq} = \frac{y_{NO_2}^2}{y_{NO} y_{O_2}} \left( \frac{P}{P_0} \right) \text{ solve for } \xi \quad \begin{matrix} \text{3rd order polynomial!} \\ \text{Mathematica} \\ \text{equilibrium.eb} \end{matrix}$$

$$\text{Suppose } y_{NO_20} = 0, \quad y_{NO_0} = \frac{1}{3}, \quad y_{O_20} = \frac{2}{3}$$

3 roots :  $\xi' = 0.1667, 0.1667, 0.667$       why  
degenerate?

Which is it? Only first two give positive values of  
all  $y_j$ :

$$y_{NO} = 3 \times 10^{-7} \quad y_{O_2} = 0.6 \quad y_{NO_2} = 0.4 \quad \sim 100\% \text{ completion}$$

$$348 \text{ K} \quad \Delta G_r^\circ \approx -63.4 \text{ kJ/mol} \rightarrow K_{eq}(348) = 3.3 \times 10^9$$

$$y_{NO} = 9 \times 10^{-6} \quad y_{O_2} = 0.6 \quad y_{NO_2} = 0.4 \quad \text{a little to the left}$$

$$600 \text{ K} \quad \Delta G_r^\circ = -25.184 \text{ kJ/mol} \rightarrow K_{eq}(600) = 155.8$$

$$\xi' = \underline{0.15113}, 0.186067, 0.662804$$

$$y_{NO} = 0.037 \quad y_{O_2} = 0.607 \quad y_{NO_2} = 0.356$$

This approach requires an algebraic to be solved.  
Gets messier if system is non-ideal, or multiple rxns.

Let's look @ minimizing  $G$  itself.  $G = \sum_j n_j \mu_j$

$$\mu_j(T) = \mu_j^\circ(T) + RT \ln \gamma_j = \mu_j^\circ(T) + RT \left[ \ln \gamma_j + \ln P \right]$$

ideal gas

$$G = \sum_j n_j \mu_j^\circ + RT \sum_j n_j (\ln \gamma_j + \ln P), \quad n_j = n_{j0} + \nu_j \xi$$

$$G = \sum_j n_{j0} \mu_{j0} + \xi \sum_j \nu_j \mu_j^\circ + RT \sum_j n_j (\ln \gamma_j + \ln P)$$

all fns of  $\xi$

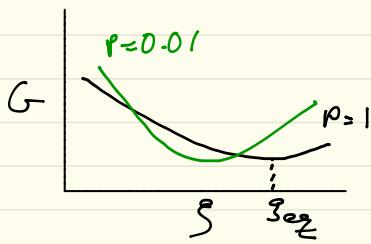
$$\frac{G - \sum_j n_{j0} \mu_{j0}}{RT n_{j0}} = \xi' \frac{\Delta G_r^\circ}{RT} + \sum_j \frac{n_j}{n_{j0}} (\ln \gamma_j + \ln P)$$

$$\tilde{G} = -\xi' \ln K_{eq} + \sum_j (\gamma_{j0} + \nu_j \xi') (\ln \gamma_j + \ln P)$$

all fns of  $\xi'$

$\tilde{G}$  is simply shifted and scaled from  $G$ , has same shape + same extrema. Can plot vs  $\xi'$  and minimize. See Mathematica.

@ 600 K,  $\xi' = 0.152$ , pretty close



$P$  dependence enters directly. Compare solution when  $P = 10^{-2}$ . Which direction does reaction go?  $\leftarrow$

This minimization technique is numerically more powerful than algebraic approach

T-dependence of  $K_{eq}$  follows directly from Gibbs-Helmholtz:

$$\frac{\partial(\Delta G_r^\circ(T)/T)}{\partial T} = -\frac{\Delta H_r^\circ(T)}{T^2} + K_{eq} = e^{-\Delta G_r^\circ/RT}$$

$$\Rightarrow \left( \frac{\partial \ln K}{\partial T} \right)_{P, n_j} = \frac{\Delta H_r^\circ(T)}{R T^2}$$

$$\text{or often } \left( \frac{\partial \ln K}{\partial T} \right) = -\frac{\Delta H^\circ}{K}$$

van't Hoff equation

Over range that  $\Delta H^\circ \approx \text{constant}$

$$\ln \left( \frac{K(T_2)}{K(T_1)} \right) = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Observation of  $K(T)$  one way to infer  $\Delta H^\circ$

$$\tilde{G}(T) = -\xi' \left[ \underbrace{\ln K(T_1)}_{-\Delta C^\circ(T_1)} - \frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right] + \sum_j (y_{j0} + v_j \xi') (\ln y_j + \ln P)$$

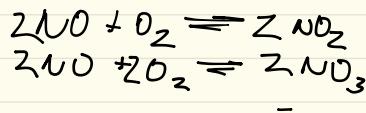
Sce Mathematica plots

## Parallel Reactions

Very similar ideas apply.

j reactants, i reactions  $\sum_j \nu_{ij} \alpha_j = 0 \quad \forall i$

### Example

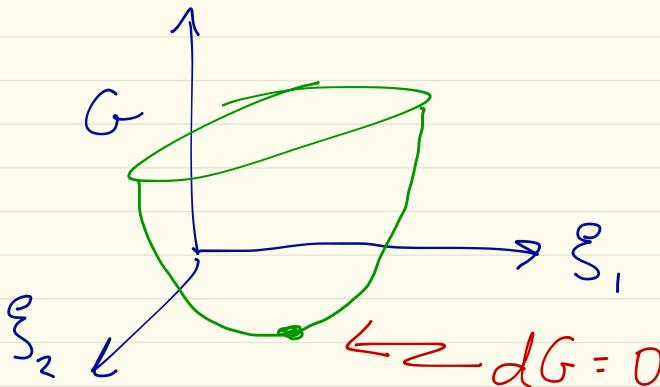


Have to express  $\alpha_j$  in terms of  $\xi_i$  and either solve algebraically or do optimization of G over allowed  $\xi_i$ .

Write  $n_j = n_{j0} + \sum_i \nu_{ij} \xi_i$ ,  $\xi_i$ : Advancement of rxn i

$$G = \sum_j n_j \mu_j = \sum_j (n_{j0} + \sum_i \nu_{ij} \xi_i) (\mu_j^\circ + RT \ln \alpha_j)$$

$$dG = \sum_i \sum_j \nu_{ij} \mu_j d\alpha_j = 0 \quad \Rightarrow \quad K_i = \prod_j \alpha_j^{\nu_{ij}} = e^{-\Delta G_i^\circ(t)/RT}$$



## Reaction phase diagrams

In those examples, assumed closed system,  $N_j$  relax to find equilibria. What if one of the  $N_j$  is fixed somehow?

Eg v large  $x_S$ , or controlled electrochemically,

$$\sum_j \nu_j \mu_j = 0 \rightarrow \mu_{NO_2} - \mu_{NO} = \frac{1}{2} \mu_{O_2} \quad @ \text{equilibrium}$$

$$(\mu_{NO_2}^{\circ}(T) - \mu_{NO}^{\circ}(T) + RT \ln \frac{y_{NO_2}}{y_{NO}}) = \frac{1}{2} (\mu_{O_2}^{\circ} + \Delta \mu_{O_2})$$

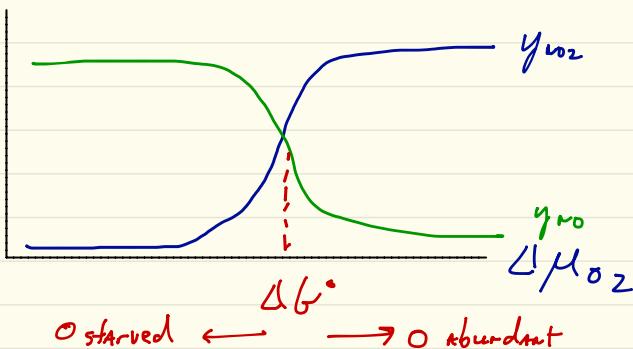
$$RT \ln \frac{y_{NO_2}}{y_{NO}} = \frac{1}{2} (-\Delta G_r^{\circ} + \Delta \mu_{O_2})$$

$$y_{NO_2}/y_{NO} = \exp \left[ \frac{\Delta \mu_{O_2} - \Delta G_r^{\circ}}{2RT} \right]$$

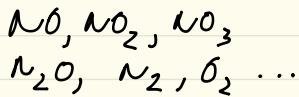
$$y_{NO_2} + y_{NO} = 1 \rightarrow \frac{y_{NO_2}}{1-y_{NO_2}} = \exp [ " ]$$

$$y_{NO_2} = \frac{\exp [ " ]}{1 + \exp [ " ]}$$

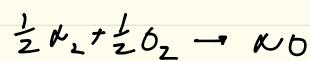
see  
mathematica



What if there were multiple products possible? Eg,  
 $\text{NO}_x$  system includes



Consider  $\text{NO}_x$  only:



$$\begin{aligned} \Delta G &= \mu_{\text{NO}} - \frac{1}{2}\mu_{\text{N}_2} - \frac{1}{2}\mu_{\text{O}_2} \\ &= (\mu_{\text{NO}}^{\circ} - \frac{1}{2}\mu_{\text{N}_2}^{\circ} - \frac{1}{2}\mu_{\text{O}_2}^{\circ}) \\ &\quad - \frac{1}{2}\Delta\mu_{\text{N}_2} - \frac{1}{2}\Delta\mu_{\text{O}_2} \\ \Delta_f G_{\text{NO}}^{\circ} &= \frac{1}{2}\Delta\mu_{\text{N}_2} - \frac{1}{2}\Delta\mu_{\text{O}_2} \end{aligned}$$

In general,

$$\Delta G_{\text{NO}_x}(T) = \Delta_f G_{\text{NO}_x}^{\circ}(T) - \frac{x}{2}\Delta\mu_{\text{N}_2} - \frac{y}{2}\Delta\mu_{\text{O}_2}$$

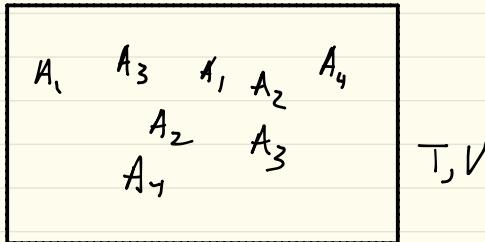
$$\Delta\mu_{\text{N}_2} = RT \ln \frac{P_{\text{N}_2}}{P_{\text{N}_2}^{\circ}}$$

Form surfaces in  $\Delta\mu_{\text{N}_2}$ ,  $\Delta\mu_{\text{O}_2}$  space.

Species that minimize  $\Delta G$  @ a given condition is the most abundant.

## The molecular picture

Suppose we have a box containing a mixture of ideal gases,  $A_1, A_2, A_3, A_4$ , fixed  $T, V$



What is partition function of mixture?

$$Q(N_1, N_2, \dots, N_i, T) = \prod_i Q_i(N_i, V, T) \quad \text{ideal gas, separable}$$

$$= \prod_i \frac{\xi_i^{(V, T)}{}^{N_i}}{N_i!}$$

What's chemical potential of each component?

$$\mu_i - \mu_i^\circ = -RT \ln \left( \underbrace{\frac{\xi_i^{(V, T)}}{N_i}}_{\text{activity!}} \right)$$

Suppose species connected by reaction  $\sum_i \nu_i A_i = 0$

@ chemical equilibrium  $\sum_i \nu_i \mu_i = 0$

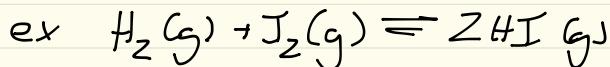
$$\Rightarrow \sum_i \nu_i (\mu_i^\circ - RT \ln \left( \frac{\xi_i}{N_i} \right)) = 0$$

$$\Rightarrow \prod_i N_i^{\nu_i} = e^{-\Delta \mu_i^\circ / RT} \prod_i \xi_i^{\nu_i}$$

What is  $\xi_i$ ?  $\xi_i = \underbrace{\xi_{i,\text{trans}} \cdot \xi_{i,\text{rot}} \cdot \xi_{i,\text{vib}}}_{V/N(T) \cdot f(T) \cdot f(T)}$

Divide thru by V:

$$\prod_i \left(\frac{\xi_i}{V}\right)^{\nu_i} = \prod_i c_i^{\nu_i} = e^{-\Delta \mu^\circ / RT} \underbrace{\prod_i \left(\frac{\xi_i}{V}\right)^{\nu_i}}_{\text{stat mech equilibrium const}} = K_c(T)$$



$$K(T) = \frac{\left(\frac{\xi_{HI}}{V}\right)^2}{\left(\frac{\xi_{H_2}}{V}\right)\left(\frac{\xi_{I_2}}{V}\right)} e^{-\Delta \mu^\circ / RT}$$

$$= \left( \frac{\frac{m_{HI}^2}{m_{H_2} m_{I_2}}}{\Theta_{\text{rot}}^{HI^2}} \right) \left( \frac{4 \Theta_{\text{rot}}^{H_2} \Theta_{\text{rot}}^{I_2}}{\Theta_{\text{rot}}^{HI^2}} \right) \frac{(1 - e^{-\Theta_{\text{vib}}^{H_2} \beta})(1 - e^{-\Theta_{\text{vib}}^{I_2} \beta})}{(1 - e^{-\Theta_{\text{vib}}^{HI} \beta})^2} e^{-\Delta \mu^\circ \beta}$$

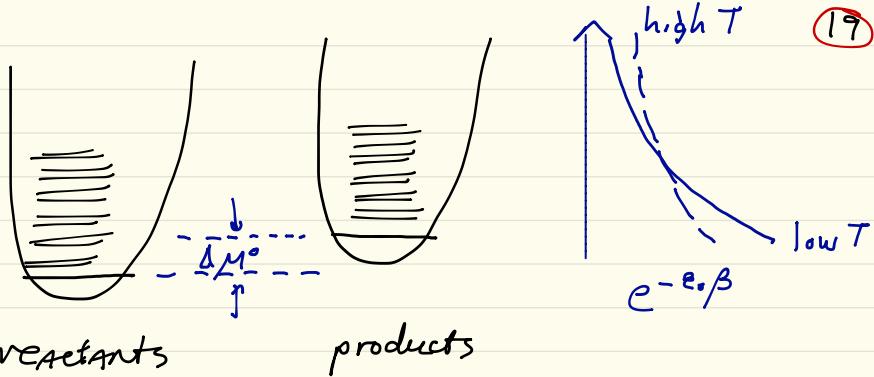
all molecular quantities

$\Delta \mu^\circ$ ? Difference in 0K energies/enthalpies/free energies (all the same!)

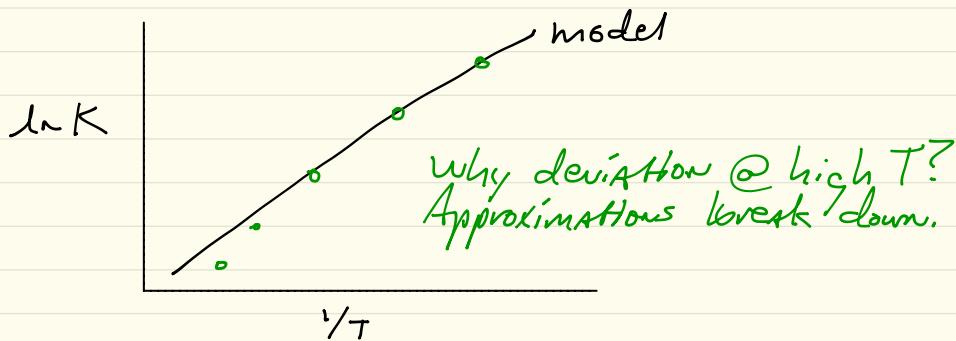
Eg from bond dissociation energies

$$-\Delta \mu^\circ = 2 D_b^{HI} - D_b^{H_2} - D_b^{I_2}$$

$$= 2(294.7) - 432.1 - 150.3 = 7.0 \text{ kJ/mol}$$



Changing  $T$  changes probability distribution  
Changing  $V$  changes density of states



Standard state here is  $\#/\text{V}$ , through  $1/\text{V}^3$  term.  
Convert to pressure standard state using

$$K_p = K_c \left( \frac{c^\circ R T}{p^\circ} \right)^{\leq 2} \quad c^\circ = 1 \text{ mol/dm}^3$$

$$p^\circ = 1 \text{ bar}$$

$$\Rightarrow \left( \frac{c^\circ R T}{p^\circ} \right) = \frac{RT}{1 \cdot \text{bar/mol}}$$

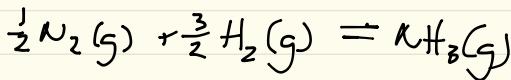
Non-ideality  
In general write

$$\mu_j(x_j, P, T) = \mu_j^\circ(T) + RT \ln \alpha_j(x, T, P)$$

gases:  $\alpha_j = \bar{f}_j / f_j^\circ$      $\bar{f}_j = \bar{\phi}_j \cdot p_j$   
 $= \bar{\phi}_j y_j p$

$$K_{eq}^T(T) = \frac{\prod_j \bar{f}_j^{v_j}}{\prod_j f_j^\circ} = \underbrace{\prod_j p_j^{v_j}}_{K_p} \underbrace{\prod_j \bar{\phi}_j^{v_j}}_{K_\phi}$$

ex NH<sub>3</sub> synthesis



<u>P/bar</u>	<u>K<sub>p</sub>/10<sup>-3</sup></u>	<u>K<sub>f</sub>/10<sup>-3</sup></u> @ 450°C
10	6.59	6.55
30	6.76	6.59
50	6.96	6.50
100	7.25	6.36
300	8.84	6.08
600	12.94	6.42

- NOT  
constant!

~ constant

solutions

Raoult's Law  $a_j = x_j \gamma_j$   $\lim_{x_j \rightarrow 1} \gamma_j = 1$

$$\mu_j^\circ = \mu_j^*$$

Henry's Law  $a_j = x_j \gamma_j$ ,  $c_j \gamma_j$ ,  $m_j \gamma_j$   
 $\lim_{x_j \rightarrow 0} \gamma_j = 1$  dilute ideal

$\mu_j^\circ$ : chemical potential of ideal solute  $j$   
@ unit concentration.

ionic solutions require special treatment

pure liquid/solid

$$d\mu = RT d\ln a \quad d\mu = v dp$$

$$d\ln a = \frac{v}{RT} dP$$

$$\int_1^P d\ln a = \int_1^P \frac{v}{RT} dP$$

$$\ln a \approx \frac{v}{RT} \int_1^P dP \quad \text{if } \sim \text{incompressible}$$

$$= \frac{v}{RT} (P - 1)$$

22

$$\rho \sim 1 \text{ g/cm}^3 \rightarrow \nu \sim 10 \text{ cm}^3/\text{mol} \rightarrow \frac{\nu}{RT} \sim 10^{-4} \text{ bar}^{-1}$$

$$\text{eg } \ln a = (100 \text{ bar} - 1 \text{ bar}) \cdot 10^{-4}$$

$$= 10^{-2} \Rightarrow a = \underline{1.01}$$

Activity very insensitive to  $P$

ex C(graphite)  $\rightarrow$  C(diamond)

$$\Delta G^\circ = 2.900 \text{ kJ/mol} @ 298.15 \text{ K}$$

$$\rho_{\text{graphite}} = 2.27 \text{ g/cm}^3 \quad \rho_{\text{diamond}} = 3.52 \text{ g/cm}^3$$

At what  $P$  does graphite  $\rightarrow$  diamond

$$\Delta G^\circ = -RT \ln K_p = -RT \ln \frac{a_{\text{diamond}}}{a_{\text{graphite}}}$$

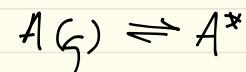
$$\ln \frac{a_{\text{diamond}}}{a_{\text{graphite}}} = \frac{\Delta \nu}{RT} (P - 1)$$

$$\Delta G^\circ = -\Delta \nu (P - 1)$$

$$P = 1 + \frac{\Delta G^\circ}{\Delta \nu} = 1 + \Delta G^\circ \Delta \rho / \text{MW}$$

$$= 1 \text{ bar} + 2.9 \frac{\text{kJ}}{\text{mol}} (3.52 - 2.27) / 12 \frac{\text{mol}}{\text{cm}^3}$$

$$= \underline{1.54 \times 10^4 \text{ bar}}$$

Surfaces

Langmuir model

finite sites, single occupancy

$$\mu_A(T, \theta) = \underbrace{\mu_A^\circ(T)}_{\text{isolated}} + RT \ln \frac{\theta}{1-\theta} + \underbrace{\text{immobile}}_{\text{adsorbate}}$$

What's equilibrium coverage @  $T, P$ ?

$$\mu_g(T, P) = \mu^\circ(T) + RT \ln P$$

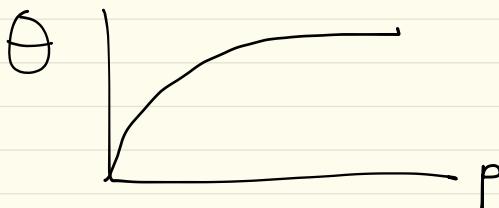
$$\sum_j \mu_j = 0 \rightarrow \mu_g = \mu_A$$

$$\mu^\circ(T) + RT \ln P = \mu_A^\circ(T) + RT \ln \frac{\theta}{1-\theta}$$

$$\ln P - \ln \frac{\theta}{1-\theta} = \Delta G_{\text{ads}}^\circ / RT$$

$$P \left( \frac{1-\theta}{\theta} \right) = e^{\Delta G_{\text{ads}}^\circ / RT} = 1/K_{\text{ads}}(T)$$

$$KP = \frac{\theta}{1-\theta} \rightarrow \theta = \frac{K_{\text{ads}} P}{1+K_{\text{ads}} P}$$

Langmuir  
isotherm

dissociative adsorption  $A_2 \rightarrow 2A^*$

$$\mu_{A_2} = 2\mu_A$$

$$\mu_{A_2}^\circ + RT \ln P = 2(\mu_A^\circ + RT \ln \frac{\theta}{1-\theta})$$

$$\ln P - 2 \ln \frac{\theta}{1-\theta} = \Delta G_{ads}^\circ / RT$$

$$P \left( \frac{\theta}{1-\theta} \right)^2 = e^{\Delta G_{ads}^\circ / RT} = 1/K_{ads}$$

$$\frac{1-\theta}{\theta} = (KP)^{1/2} \Rightarrow \theta = \frac{(K_{ads}P)^{1/2}}{1+(K_{ads}P)^{1/2}}$$

Saturates @ same level, rises more slowly.