Lecture 15 Chemistry 163B
Free Energy
and
Equilibrium
E&R (≈ ch 6)

$\Delta G_{reaction}$ and equilibrium (first pass, lecture 14)

here $\Delta G \Rightarrow \Delta G_{reaction}$

1. **$\Delta G < 0$ spontaneous *('natural', irreversible)***
   $\Delta G = 0$ equilibrium *(reversible)*
   $\Delta G > 0$ spontaneous in reverse direction
2. **$\Delta G_T = \Delta H - T\Delta S$**
3. **ΔG^o all reactants and products in standard states**
4. $\Delta \bar{G}_f^0 \equiv \bar{G}_f^0$ **Appendix A at 298.15K *(reaction where reactants are elements in their most stable form and in their standard states, P=1 atm, [conc]=1M, etc)***

$$\Delta \bar{G}_f^0\left(O_2(g)\right) \equiv 0 \quad \Delta \bar{G}_f^0\left(C(gr)\right) = 0$$

5.

$$\Delta G^0_{reaction} = \sum_i \nu_i \Delta \bar{H}_f^0 - T\sum_i \nu_i \bar{S}_i^0$$

$$\Delta G^0_{reaction} = \Delta H^0_{reaction} - T\Delta S^0_{reaction}$$

NOTE : *in* Appendix A: $\Delta \bar{G}_f^0$ *and* $\Delta \bar{H}_f^0$ in kJ mol^{-1} BUT $\bar{S}^0$ in J K^{-1}mol^{-1}

6. **Brief hello to thermodynamics of multicomponent systems (n_i's vary)**

7. **$\Delta G_{reaction}$ for non-standard state concentrations, pressures**

   $$\Delta G_{reaction} = \Delta G^o_{reaction} + \underline{R}T \ln Q$$

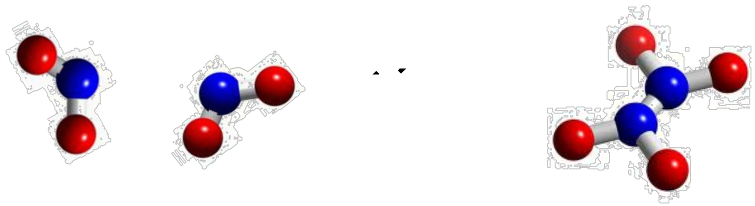
8. **K_{eq} and $\Delta G^o_{reaction}$**

9. **$\Delta G_{reaction} = \Delta G^o_{reaction} + \underline{R}T \ln Q$ is extensive**

10. **Variation of K_{eq} with T**

6.0 molar free energy and partial molar free energy (chemical potential)

$$2NO_2 \rightleftarrows N_2O_4$$



multicomponent **mixture**

n_{NO_2} moles NO_2 ;

$n_{N_2O_4}$ moles N_2O_4

$$G_{NO_2+N_2O_4\ mixture}(T,P,n_{NO_2},n_{N_2O_4})$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_{NO_2},n_{N_2O_4}} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_{NO_2},n_{N_2O_4}} dP + \left(\frac{\partial G}{\partial n_{NO_2}}\right)_{T,P,n_{N_2O_4}} dn_{NO_2} + \left(\frac{\partial G}{\partial n_{N_2O_4}}\right)_{T,P,n_{NO_2}} dn_{N_2O_4}$$

$$\mu_{NO_2} = \left(\frac{\partial G_{(NO_2+N_2O_4\ \text{mixture})}}{\partial n_{NO_2}}\right)_{T,P,n_{N_2O_4}}$$

partial molar Gibbs free energy or chemical potential (of NO_2)

more generally $G_{mixture}(T,P,n_1,...,n_N)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum_{i=1}^{N}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i = -SdT - VdP + \sum_{i=1}^{N}\mu_i dn_i$$

6.0 molar free energy and partial molar free energy (chemical potential)

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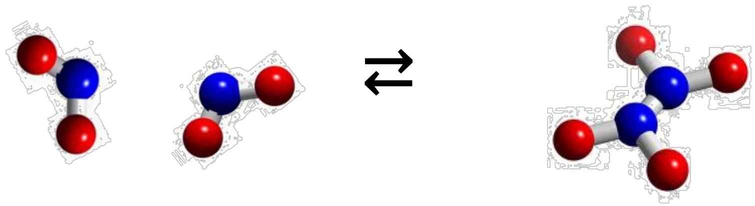

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$$G_{NO_2+N_2O_4\ mixture}(T,P,n_{NO_2},n_{N_2O_4})$$

$$dG=\left(\frac{\partial G}{\partial T}\right)_{P,n_{NO_2},n_{N_2O_4}}dT+\left(\frac{\partial G}{\partial P}\right)_{T,n_{NO_2},n_{N_2O_4}}dP+\left(\frac{\partial G}{\partial n_{NO_2}}\right)_{T,P,n_{N_2O_4}}dn_{NO_2}+\left(\frac{\partial G}{\partial n_{N_2O_4}}\right)_{T,P,n_{NO_2}}dn_{N_2O_4}$$

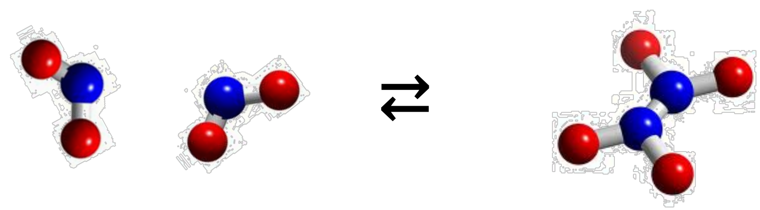
$$\mu_{NO_2}=\left(\frac{\partial G_{(NO_2+N_2O_4\ \text{mixture})}}{\partial n_{NO_2}}\right)_{T,P,n_{N_2O_4}}$$

partial molar Gibbs free energy or chemical potential (of NO_2)

more generally $G_{mixture}(T,P,n_1,...,n_N)$

$$dG=\left(\frac{\partial G}{\partial T}\right)_{P,n_i}dT+\left(\frac{\partial G}{\partial P}\right)_{T,n_i}dP+\sum_{i=1}^{N}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}dn_i=-SdT-VdP+\sum_{i=1}^{N}\mu_i dn_i$$

$2NO_2 \rightleftarrows N_2O_4$



multicomponent **mixture**

n_{NO_2} moles NO_2 ;

$n_{N_2O_4}$ moles N_2O_4

$$\mu_{NO_2} = \left(\frac{\partial G_{(NO_2 + N_2O_4 \text{ mixture})}}{\partial n_{NO_2}} \right)_{T,P,n_{N_2O_4}}$$

partial molar Gibbs free energy

or chemical potential

$\bar{G}_{NO_2}$ molar Gibbs free energy of pure NO_2 $\left[(\bar{G}_{NO_2} \equiv \left(\Delta \bar{G}_f \right)_{NO_2} \right]$

μ_{NO_2} molar Gibbs free energy of NO_2 in environment where other molecules are present

thermodynamics of multicomponent systems
E&R section 6.4 (later)

$\mu_i \approx \bar{G}_i$

$$\textit{for}\ \text{now}\ \mu_i \approx \bar{G}_i$$

$$\Delta\mu_{reaction} \approx \Delta G_{reaction}$$

$$\Delta\mu_{reaction} = \sum_i \nu_i \mu_i \approx \sum_i \nu_i \bar{G}_i = \Delta G_{reaction}$$

7. How does $\Delta G_{reaction}$ ($\Delta\mu$) vary as the concentration of reactants and products varies?

example : 'concentration' of gas = partial pressure P_i

$P_i = X_i P_{total}$ where X_i is mole fraction of species i

$$d\bar{G} = -\bar{S}dT + \bar{V}dP \Rightarrow \left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$$

for ideal gas:

$$P_{total} = n_{total}\frac{RT}{V}$$

$$P_i = n_i \frac{RT}{V}$$

7.1 $\Delta G_{reaction}$ as a function of concentration

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$$

for ideal gas

$$P_{total} = n_{total}\frac{RT}{V}$$

$$P_i = n_i\frac{RT}{V}$$

$$\left(\frac{\partial \bar{G}_i}{\partial P_i}\right)_T = \bar{V}$$

$$\bar{G}_i\left(P_i\right) - \bar{G}_i\left(P_i = 1\,bar\right) = \int_{1\ bar}^{P_i}\left(\frac{\partial \bar{G}_i}{\partial P_i^{'}}\right)_T dP_i^{'} = \int_{1\ bar}^{P_i}\bar{V}dP_i^{'} = \int_{1\ bar}^{P_i}\frac{RT}{P_i^{'}}dP_i^{'}$$

$$\bar{G}_i\left(P_i\right) - \bar{G}_i\left(P_i = 1\,bar\right) = RT\ln\left(\frac{P_i}{1\,\mathrm{bar}}\right)$$

7.2 $\Delta G_{reaction}$ as a function of concentration (ideal gas)

$$\bar{G}_i\left(P_i\right)-\bar{G}_i\left(P_i=1\,bar\right)=RT\ln\left(\frac{P_i}{1\,\mathrm{bar}}\right)$$

$$\bar{G}_i\left(P_i\right)-\bar{G}_i^0=RT\ln\left(\frac{P_i}{1\,\mathrm{bar}}\right)$$

$$\bar{G}_i\left(P_i\right)=\bar{G}_i^0+RT\ln\left(\frac{P_i}{1\,\mathrm{bar}}\right)$$

$$later\;\;\mu_i\left(P_i\right)=\mu_i^0+RT\ln\left(\frac{P_i}{1\,\mathrm{bar}}\right)$$

7.3 $\Delta G_{reaction}$ as a function of concentration

$$\bar{G}_i(P_i) = \bar{G}_i^0 + RT\ln\left(\frac{P_i}{1\,\text{bar}}\right)$$

$$\Delta G_{reaction} = \sum_i \nu_i \bar{G}_i$$

$$\Delta G_{reaction} = \sum_i \nu_i \left(\bar{G}_i^0 + RT\,ln\left(\frac{P_i}{1\ bar}\right)\right)$$

$$\Delta G_{reaction} = \sum_i \nu_i \bar{G}_i^0 + \sum_i \nu_i RT\,ln\left(\frac{P_i}{1\ bar}\right)$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i \nu_i RT\,ln\left(\frac{P_i}{1\ bar}\right)$$

$$\underline{R}T\sum_i \bar{\nu}_i\,ln\left(\frac{P_i}{1\ bar}\right) = \underline{R}T\,ln\left[\prod_i \left(\frac{P_i}{1\ bar}\right)^{\bar{\nu}_i}\right] = \underline{R}T\ln Q_P$$

for 'persnickety' units notation

$\underline{R} = R(mol) = [J\,K^{-1}]$

$\bar{\nu}_i = \nu_i\left(mol^{-1}\right) = [unitless]$

$$Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\bar{\nu}_i}$$

7.4 $\Delta G_{reaction}$ as a function of concentration

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q_P$$

reaction quotient $Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\bar{\nu}_i} = \frac{\prod_{q=prod}\left(\frac{P_q}{1\ bar}\right)^{\bar{n}_q}}{\prod_{r=react}\left(\frac{P_r}{1\ bar}\right)^{\bar{n}_r}}$ *Q* is UNITLESS

1 bar is P^0, *std* state for P

$$n_aA + n_bB \rightleftarrows n_cC + n_dD$$

$Q_P = \frac{\left(\frac{P_C}{1\ bar}\right)^{\bar{n}_c}\left(\frac{P_D}{1\ bar}\right)^{\bar{n}_d}}{\left(\frac{P_A}{1\ bar}\right)^{\bar{n}_a}\left(\frac{P_B}{1\ bar}\right)^{\bar{n}_B}}$ 'like' an equilibrium constant

for solutes in soln $Q_C = \prod_i \left(\frac{[i]}{1\ M}\right)^{\bar{\nu}_i}$ $Q_C = \frac{\left(\frac{[C]}{1\ M}\right)^{\bar{n}_c}\left(\frac{[D]}{1\ M}\right)^{\bar{n}_d}}{\left(\frac{[A]}{1\ M}\right)^{\bar{n}_a}\left(\frac{[B]}{1\ M}\right)^{\bar{n}_b}}$ *Q* is UNITLESS

HW6 prob 39

1 M is std state for solute

7.5 Q and units (persnicketyness)

$$\Delta G_{reaction} = \Delta G^0_{reaction} + RT\ ln\ Q_P$$

reaction quotient $Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\bar{\nu}_i}$ **Q is UNITLESS**

$$Q_C = \prod_i \left(\frac{[i]}{1\ M}\right)^{\bar{\nu}_i}$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i \nu_i RT\ ln\left(\frac{P_i}{1\ bar}\right)$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i \frac{\nu_i}{1\ mol}(1\ mol\ R)T\ ln\left(\frac{P_i}{1\ bar}\right)$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i (1\ mol\ R)T\ ln\left(\frac{P_i}{1\ bar}\right)^{\frac{\nu_i}{1\ mol}}$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \sum_i (\underline{R})T\ ln\left(\frac{P_i}{1\ bar}\right)^{\bar{\nu}_i}$$

unitless exponent

$$[R \times 1\ mol] = [\underline{R}] = J\ K^{-1}$$

7.6 $\Delta G_{reaction}$ as a function of concentration

$$\Delta G_{reaction} = \Delta G^{0}_{reaction} + \underline{R}T\ ln\ Q$$

$$Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\bar{\nu}_i} \qquad Q_C = \prod_i \left(\frac{[i]}{1\ M}\right)^{\bar{\nu}_i}$$

evaluates ΔG for ANY set of pressures, concentrations

ΔGº gives free energy change for standard conditions,
***R̲T ln Q* corrects ΔG for actual P's and [conc's]**

at equilibrium ΔG= ?

8. $\Delta G_{reaction}$ at equilibrium

at equilibrium $\Delta G = 0$

$$0 = \Delta G^0_{reaction} + \underline{R}T \ln Q_{eq}$$

$$\Delta G^0_{reaction} = -\underline{R}T \ln Q_{eq}$$

$$at\ given\ T \quad Q_{eq} = constant \equiv K_{eq}$$

$$\Delta G^0 = -\underline{R}T \ln K_{eq}$$

$$K_{eq} = e^{-\frac{\Delta G^0}{\underline{R}T}}$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q$$

$$Q_P = \prod_i \left(\frac{P_i}{1\ bar}\right)^{\bar{\nu}_i} \qquad Q_C = \prod_i \left(\frac{[i]}{1\ M}\right)^{\bar{\nu}_i}$$

$$\Delta G_{reaction} = \Delta G^0_{reaction} + \underline{R}T \ln Q \quad any\ concentrations\ \text{for}\ Q$$

$$Q_{eq} \equiv K_{eq}\ \ for\ equilibrium\ \text{concentrations}$$

$$\text{that satisfy}\ \ \Delta G^0_{reaction} = -\underline{R}T \ln K_{eq}$$

9. $\Delta G_{reaction} = \Delta G^o + \underline{R}T \ln Q$ is extensive

$$\Delta G_1 \quad n_aA + n_bB \rightleftarrows n_cC + n_dD$$

$$\Delta G_2 \quad 2n_aA + 2n_bB \rightleftarrows 2n_cC + 2n_dD$$

$$?? \; \Delta G_2 = 2\Delta G_1 \; ??$$

$$Q_1 = \frac{\left(P_C/1\ bar\right)^{\bar{n}_c}\left(P_D/1\ bar\right)^{\bar{n}_d}}{\left(P_A/1\ bar\right)^{\bar{n}_a}\left(P_B/1\ bar\right)^{\bar{n}_b}} \qquad Q_2 = \frac{\left(P_C/1\ bar\right)^{2\bar{n}_c}\left(P_D/1\ bar\right)^{2\bar{n}_d}}{\left(P_A/1\ bar\right)^{2\bar{n}_a}\left(P_B/1\ bar\right)^{2\bar{n}_b}}$$

$$Q_2 = Q_1^{\ 2}$$

$$\Delta G_1 = \Delta G_1^0 + \underline{R}T \ln Q_1$$

$$\Delta G_2 = \Delta G_2^0 + \underline{R}T \ln Q_2$$

$$\Delta G_2 = 2\Delta G_1^0 + \underline{R}T \ln Q_1^2 = 2\left(\Delta G_1^0 + \underline{R}T \ln Q_1\right)$$

$$\Delta G_2 = 2\Delta G_1$$

- $(\Delta G_{rxn})_{T,P}$ ⇨ reaction carried out isothermally a P

- Vary T: $(\Delta G_{rxn})_{T_1,P}$ vs $(\Delta G_{rxn})_{T_2,P}$

- Need $\left(\frac{\partial G}{\partial T}\right)_P$ and $\left(\frac{\partial \Delta G_{rxn}}{\partial T}\right)_P$

10.2 variation of K_{eq} with T

$$d\overline{G} = -\overline{S}dT + \overline{V}dP$$

$$\left(\frac{\partial \overline{G}}{\partial T}\right)_P = -\overline{S} \quad but \text{ remember } S(T)$$

a few manipulations which lead to simpler final relationships

$$\Delta G_{rxn} = \Delta G^0_{rxn} + \underline{R}T\ ln\ Q \qquad \Delta G^0_{rxn} = -\underline{R}T\ ln\ K_{eq}$$

$$\frac{\Delta G}{T} = \frac{\Delta G^0}{T} + \underline{R}\ ln\ Q \qquad \frac{\Delta G^0}{T} = -\underline{R}\ ln\ K_{eq}$$

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

10.3 variation of K_{eq} with T

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

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

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

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

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

$$\left(\frac{\partial \frac{\Delta G^0}{T}}{\partial T}\right)_P = \left(\frac{\partial\left(-\underline{R}\ln K\right)}{\partial T}\right)_P = -\underline{R}\left(\frac{\partial \ln K}{\partial T}\right)_P = -\frac{\Delta H^0}{T^2}$$

$$\boxed{\left(\frac{\partial \ln K}{\partial T}\right)_P = +\frac{\Delta H^0}{\underline{R}T^2}}$$

10.5 variation of K_{eq} with T

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = +\frac{\Delta H^0}{\underline{R}T^2}$$

$$\int_{T_1}^{T_2} d\ln K = \int_{T_1}^{T_2} +\frac{\Delta H^0}{\underline{R}T^2}\,dT$$

$$\ln K_{T_2} - \ln K_{T_1} = -\frac{\Delta H^0}{\underline{R}}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \frac{\Delta H^0}{\underline{R}}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{\Delta H^0}{\underline{R}}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

10.6 variation of K_{eq} with T

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{\Delta H^0}{\underline{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$T_2 > T_1$$

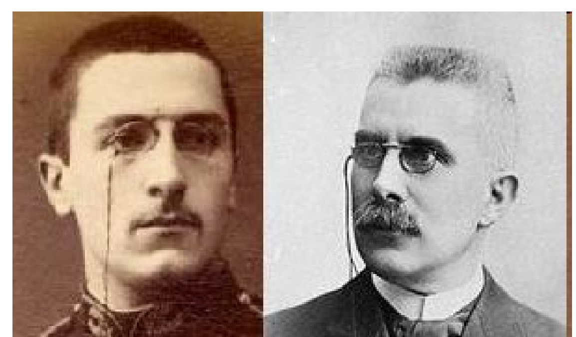
endothermic, $\Delta H^0 > 0 \quad \Rightarrow \quad \ln\frac{K_{T_2}}{K_{T_1}} > 0 \quad \Rightarrow \quad K_{T_2} > K_{T_1}$

higher T moves equilibrium to right (products)   reactants + heat $\rightleftarrows$ products

exothermic $\Delta H^0 < 0 \quad \Rightarrow \quad \ln\frac{K_{T_2}}{K_{T_1}} < 0 \quad \Rightarrow \quad K_{T_2} < K_{T_1}$

higher T moves equilibrium to left (reactants)   reactants $\rightleftarrows$ products + heat

Le Chatelier's Principle
"for heat"



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free *End of Lecture 15* *energy*

persnickity

per·snick·et·y

/pərˈsnikədē/

Learn to pronounce

adjective INFORMAL • NORTH AMERICAN

placing too much emphasis on trivial or minor details; fussy.

"she's very persnickety about her food"

Similar: fussy | difficult to please | difficult | finicky | overfastidious

- requiring a particularly precise or careful approach.