

February 13, 2002

• Exam #1

• *TONITE!*, 2/13, 7 pm, B104 Angell

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On to ΔG !

Next: Find Q

$$Q = \frac{a_{\text{CH}_3\text{OH}}}{(a_{\text{CO}})(a_{\text{H}_2})^2} = \frac{1}{(5.0)(3.0)^2} = 2.222 \times 10^{-2}$$

Finally: Calculate ΔG

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = -2.920 \times 10^4 \text{ J} + (8.3145 \text{ J/mol}\cdot\text{K})(298.15 \text{ K}) \ln(2.222 \times 10^{-2})$$

$$\Delta G = -2.920 \times 10^4 \text{ J} + (-9.4366 \times 10^3 \text{ J})$$

$$\Delta G = -3.864 \times 10^4 \text{ J} = \text{-39. kJ} \leftarrow \text{Spontaneous!}$$

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How Does ΔG Change as the Reaction Proceeds?

Let's make it simple:



So, we can write:

$$G_A = G_A^\circ + RT \ln(a_A)$$

$$G_B = G_B^\circ + RT \ln(a_B)$$

So, we start at:

$$G_A > G_B$$

As the reaction proceeds:

a_A decreases $\rightarrow G_A$ DECREASES

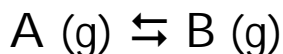
a_B increases $\rightarrow G_B$ INCREASES

$\Delta G \rightarrow 0$

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Equilibrium

- Reaction will proceed until $\Delta G = 0$
- System is then at Equilibrium:



• Equilibrium is *dynamic*:

• Rate of forward rxn = rate of reverse rxn

• Relationship with ΔG :

Equilibrium Constant

$$\Delta G = \Delta G^\circ + RT \ln Q = 0$$

$\Delta G^\circ = -RT \ln K$

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ΔG and K

$$\Delta G^\circ = -RT \ln K$$

$\Delta G^\circ = 0$ then $K = 1$ (rxn at *equilibrium* when all in std states)

$\Delta G^\circ < 0$ then $K > 1$ (fwd rxn *spontaneous* from std states)

$\Delta G^\circ > 0$ then $K < 1$ (rev rxn *spontaneous* from std states)

K quantifies the relative balance between products and reactants *at equilibrium*.

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Calculating K from ΔG°

Rearrange equation to solve for K:

$$\ln K = \frac{\Delta G^\circ}{-RT}$$

For our CH_3OH formation example:

$$\ln K = \frac{-2.92 \times 10^4 \text{ J}}{-(8.3145)(298.15\text{K})} = 11.7791$$

only 1 sig fig!

$$K = e^{11.7791} = 1.30496 \times 10^5 = 1. \times 10^5$$

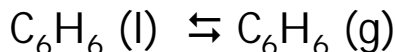
So: at equilibrium, *product* (CH_3OH) should predominate:

$$K = 1. \times 10^5 = 1/[(a_{\text{CO}})(a_{\text{H}_2})^2]$$

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How about an example?

What is the vapor pressure of benzene at 25 °C, if $\Delta G^\circ = 5.16 \text{ kJ/mol}$ for:



What is K?

$$K = a_{\text{gas}}/a_{\text{liquid}} = P_{\text{gas}} \quad (\text{vapor pressure of benzene!})$$

Knowing that: $\Delta G^\circ = -RT \ln K$

$$\ln K = (5.16 \times 10^3 \text{ J/mol}) / [(-8.3145 \text{ J/mol}\cdot\text{K})(298.15 \text{ K})]$$

$$\ln K = -2.08151 \Rightarrow K = 0.12474 = P_{\text{gas}}$$

$$P_{\text{benzene}}^\circ = 0.12474 \text{ atm} = \underline{\underline{95. \text{ torr}}}$$

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Effect of Temperature on K

■ ΔG is temperature dependent, so:

At T_1 : $\Delta G_1^\circ = \Delta H^\circ - T_1 \Delta S^\circ = -RT_1 \ln K_1$

Solve for ΔS° : $\Delta S^\circ = R \ln K_1 + \Delta H^\circ / T_1$

At T_2 : $\Delta S^\circ = R \ln K_2 + \Delta H^\circ / T_2$

Combine, collect terms, rearrange:

$$\ln(K_2/K_1) = -(\Delta H^\circ/R)(1/T_2 - 1/T_1)$$

Van't Hoff
Equation

Endothermic: K *increases* with increasing temp

Exothermic: K *decreases* with increasing temp

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