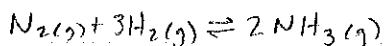
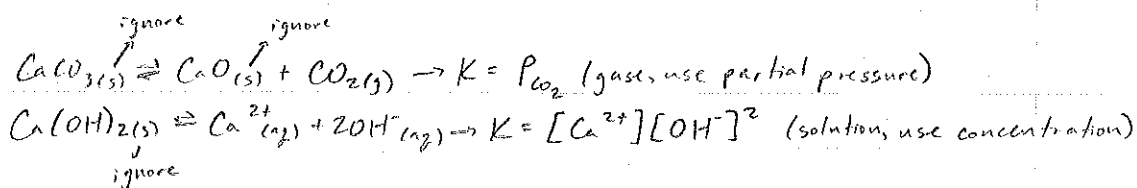


Unit 6,  
Day 2

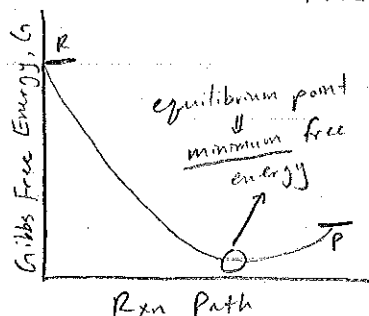


reactants: 4 total moles / products: 2 total moles

$$\hookrightarrow K_p = K_c(RT)^{\Delta n} \rightarrow \Delta n = 2 - 4 = -2 \rightarrow \boxed{K_p = K_c(RT)^{-2}}$$

- Where is the free energy lower? @ initial concentrations or after mixing?
  - $\hookrightarrow$  [after mixing  $\rightarrow$  mixing  $\uparrow$  entropy which  $\downarrow$  free energy]
  - $\hookrightarrow$  reactions always go toward lower free energy  $\rightarrow$  spontaneity
- Time can be correlated w/ reaction path (mount from reactants to products)

### Free Energy + Equilibrium



$$\Delta G_r^\circ = G_p^\circ - G_r^\circ \rightarrow \text{pure products + reactants}$$

$\hookrightarrow$  not always the case

\*  $\Delta G_r^\circ$  more negative  $\rightarrow$  favors products

\*  $\Delta G_r^\circ$  more positive  $\rightarrow$  favors reactants

slope of the line is  $\Delta G_r$  (instantaneous difference b/t reactants + products in mixture)

$\hookrightarrow$  where slope = 0,  $\Delta G_r = 0$

$$\textcircled{*} \Delta G_r = \Delta G_r^\circ + RT \ln Q \rightarrow \text{key formula used to go b/t } \Delta G_r^\circ \text{ and } Q$$

-  $Q$  = concentrations / partial pressures we have right now relative to equilibrium

$\hookrightarrow Q > K \rightarrow$  move towards reactants     $\hookrightarrow Q < K \rightarrow$  move towards products

$\Delta G_r^\circ$  units: 1M / 1atm

$R$  units: 8.314 J/molK

$$-\Delta G_r^\circ = 0 \text{ @ equilibrium} \rightarrow \boxed{\Delta G_r^\circ = -RT \ln K}$$

$$-Q = K \text{ @ equilibrium} \rightarrow \boxed{K = e^{\left(\frac{-\Delta G_r^\circ}{RT}\right)}}$$

$\hookrightarrow$  use tables to find  $\Delta H^\circ / \Delta S^\circ$  or  $\Delta G_r^\circ$  from tables

$$10,000 \text{ J/mol}$$

$$\text{Ex 1: } \Delta H^\circ = 10 \text{ kJ/mol} / \Delta S^\circ = 20 \text{ J/Kmol}$$

- assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  don't change w/  $T$ , does this reaction favor the products or the reactants @ 400K?

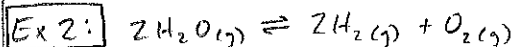
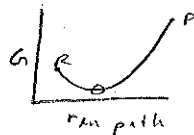
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= (10,000) - 400(20) = \boxed{2000} \rightarrow (+) \rightarrow \text{favors reactants}$$

$$\Delta G^\circ < 0 \rightarrow K > 1 \rightarrow \text{favors products}$$

$$\Delta G^\circ > 0 \rightarrow K < 1 \rightarrow \text{favors reactants}$$

$$\Delta G^\circ = 0 \rightarrow K = 1 \rightarrow \text{equilibrium point}$$



What is  $K$  for this reaction @ 298K? Extremely small Why?

$\hookrightarrow$  not a spontaneous reaction (little  $\text{H}_2$  gas compared to the amt. of  $\text{H}_2\text{O}$  in the world).

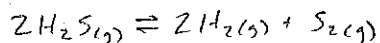
What is  $K$  for this equation @ 298K given that  $\Delta G_r^\circ = +113.4 \text{ kJ/mol}$

$$\hookrightarrow \Delta G_r^\circ = 113.4(1000) = 113400 \text{ J/mol (since } R \text{ is in J/molK units)}$$

$$\hookrightarrow K = e^{\left(\frac{-\Delta G_r^\circ}{RT}\right)} = e^{\left(\frac{-113400}{(8.314)(298)}\right)} = \boxed{1.3 \times 10^{-20}}$$

such a tiny value that we would typically say that the rxn doesn't happen

Ex 3: @ 313K,  $\Delta G^\circ = +41 \text{ kJ/mol} \rightarrow (41,000 \text{ J/mol})$  for:

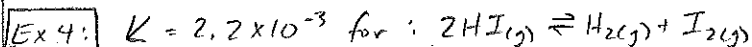


You find that @ 313K,  $\text{H}_2$  is 1atm,  $\text{S}_2$  is 1atm,  $\text{H}_2\text{S}$  is 2atm. How will this reaction proceed? Step ①: Find  $Q$  / Step ②: Find  $K$  / Step ③: compare

$$\text{① } Q = \frac{(P_{\text{H}_2})^2 (P_{\text{S}_2})}{(P_{\text{H}_2\text{S}})^2} = \frac{(1)^2 (1)}{(2)^2} = 0.25$$

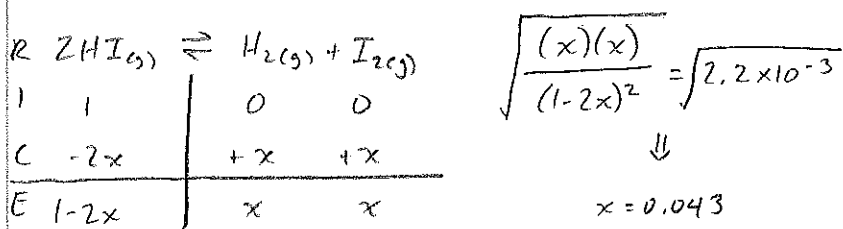
$$\text{② } K = e^{\left(\frac{-\Delta G_r^\circ}{RT}\right)} = e^{\left(\frac{-41,000}{(8.314)(313)}\right)} = 1.4 \times 10^{-7}$$

$$\text{③ } 0.25 > 1.4 \times 10^{-7} \rightarrow \boxed{Q > K} \rightarrow \text{move towards the reactants}$$



You start w/ a pp of 1atm of HI; what are the pps @ a constant  $P$  of 1atm and constant  $T$ ?

Ex 4  
cont.



$$\frac{(x)(x)}{(1-2x)^2} = \sqrt{2.2 \times 10^{-3}}$$

↓

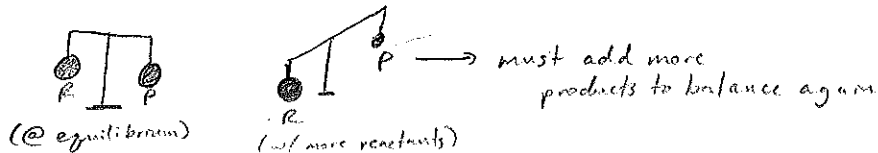
$$x = 0.043$$

$$\textcircled{1} \underline{\text{HI}} = 1 - 2(0.043) = \underline{0.914} \quad \textcircled{2} \underline{\text{H}} = \underline{\text{I}} = \underline{0.043}$$

Ex 5: Consider the previous example @ equilibrium. Add 0.5 atm of HI(g)

↳ What happens to the rxn mixture? **Shift Right** Why?

↳ adding more to the left side → must move to the right to balance it out → think of a balance:



Ex 6: Consider the previous example @ equilibrium. Add 0.5 atm of HI(g) and 0.5 atm of H<sub>2</sub>(g). What happens to the rxn mixture? **Shift Left**

Remember that:  $Q = \frac{(0.543)(0.043)}{(1.414)^2} \Rightarrow$  changing H<sub>2</sub>(g)'s pp by a huge amount

⊛ Le Chatelier's Principle: When a stress is added to a system, the system will tend to move in such a way that will return to equilibrium

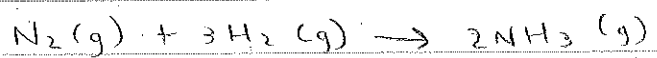
↳ changing pressure, concentration, or temperature  
volume

① Introducing inert gas: does not affect the partial gas of gases → no effect on Q  
↳ does affect total pressure no shift ←

② Expansion: composition will change in a way to increase the pressure

③ Compression: " " to minimize the resulting P in pressure

Temperature and Equilibrium: inverse relationship (dramatic) b/t K and T  
exothermic relationship (direct relationship for endothermic)



$$K_c = 0.06$$

5 moles  $\text{N}_2$ , 5 moles  $\text{H}_2$ , 10 moles  $\text{NH}_3$  in 5L cont

- A) RXN will go to products
- B) RXN will go to reactants** b/c  $Q > K$
- C) RXN is at equilibrium

$$[\text{N}_2] = \frac{5 \text{ moles}}{5 \text{ L}} = 1 \text{ M}$$

$$[\text{H}_2] = 1 \text{ M}$$

$$[\text{NH}_3] = 2 \text{ M}$$

$$Q = \frac{(2)^2}{(1)(1)^3} = 4$$

$Q > K$  to reactants!

X c1) write equilibrium constant expressions for the following



$$K = P_{\text{CO}_2}$$

$$K = [\text{Ca}^{2+}][\text{OH}^-]^2$$

c2) +10 points (pull)  
calculate  $K_c$  given  $K_p$  for



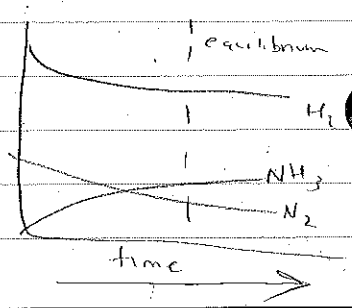
$$K_c = K_p (RT)^{\Delta n}$$

$$K_p = (RT)^{\Delta n} K_c$$

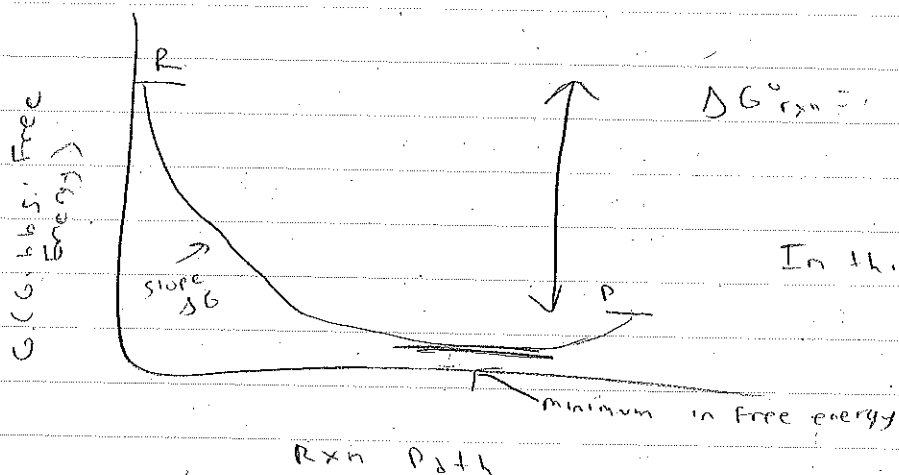
$$\Delta n = n_{\text{gas, P}} - n_{\text{gas, R}}$$

$$\Delta n = -2$$

c3) +10 points (pull)  
which is lower in free energy?  
- mixture at end  
b/c rxn always go towards lower free energy spontaneously



## Free energy and equilibrium



$$\Delta G^{\circ}_{rxn} = G^{\circ}_P - G^{\circ}_R$$

In this case,  $\Delta G^{\circ}_{rxn} < 0$

- Equilibrium favors products.
- The slope of line is  $\Delta G$  (difference between products and reactants at that specific point).
- Pure products are lower in free energy than pure reactants.

$$\Delta G_r = \Delta G^{\circ}_r + RT \ln Q$$

$Q = \frac{\text{activities of products}}{\text{activities of reactants}}$

$$\Delta G_{rxn} = \Delta G^{\circ}_{rxn} + RT \ln Q$$

at equilibrium  $\Delta G = 0$  ;  $Q = K$

$$0 = \Delta G^{\circ}_{rxn} + RT \ln K$$

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

-  $K$  depends on  $\Delta_r G^{\circ}$

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

(4) + 10 points (part)

$$\Delta_r H^\circ = 10 \text{ kJ mol}^{-1} \text{ and } \Delta_r S^\circ = 20 \text{ J K}^{-1} \text{ mol}^{-1}$$

Assuming  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  don't change with temp. does this rxn favor the products or the reactants at 400 K  
- reactants

$$\Delta G = \Delta H - T \Delta S$$

$$10,000 - (400)(20)$$

$$\Delta G = +2000 \text{ J}$$

$$\Delta G > 0$$

IF  $\Delta G < 0$ ,  $K > 1$

$\Delta G > 0$ ,  $K < 1$

(5) + 10 points (part)

what is  $K$  for this reaction at 298 K?



- extremely small

spont? No

$$\Delta G > 0$$

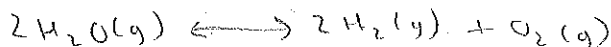
$$K < 1$$

very small

(6) + 10 points (part)

what is  $K$  for this reaction at 298 K given that  $\Delta_r G^\circ = +113.4 \text{ kJ mol}^{-1}$ ?

$$\Delta G^\circ_{\text{rxn}} = -RT \ln K$$



$$113.4 \times 10^3 = -8.314 \times 298 \ln K$$

$$\ln K = \frac{(113.4 \times 10^3)}{-8.314 \times 298}$$

$$K = 1.3 \times 10^{-20}$$

Reverse rxn  $\frac{1}{K}$

(7) +10 points (part)

At 313 K,  $\Delta_r G^\circ = +41 \text{ kJ mol}^{-1}$  for this rxn:



You find the following partial pressures at

313 K.  $\text{H}_2$  is 1 atm,  $\text{S}_2$  is 1 atm,  $\text{H}_2\text{S}$  is 2 atm

How will rxn proceed? what should you do first?

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

→ move towards the reactants

$$41 \times 10^3 = -8.314 \cdot 313 \ln K$$

$$K = 1.44 \times 10^{-7}$$

$$Q = \frac{P_{\text{H}_2}^2 P_{\text{S}_2}}{P_{\text{H}_2\text{S}}^2} = \frac{(1)^2 (1)}{2^2} = \boxed{0.25} \quad Q > K$$

$K = 2.2 \times 10^{-3}$  for this rxn at some T



Start w/ partial pressure of 1 atm of HI  
what are partial pressures at a constant P of 1 atm and constant T

R	2HI	→	H <sub>2</sub>	+	I <sub>2</sub>
E	1		0		0
C	-2x		+x		+x
E	1-2x		x		x

$$K = \frac{P_{\text{H}_2} \cdot P_{\text{I}_2}}{P_{\text{HI}}^2}$$

$$\frac{(x)(x)}{(1-2x)^2} = 2.2 \times 10^{-3} \quad \boxed{x = 0.043}$$

1 - (2)(0.043) = $\boxed{0.914}$	2 HI
0.043	H <sub>2</sub>
0.043	I <sub>2</sub>

c8) + 10 points (poll)

Consider previous example at equilibrium

Add .5 atm of  $\text{HI(g)}$ .

what is going to happen to reaction mixture?

shift right

$$Q = \frac{P_{\text{H}_2} P_{\text{I}_2}}{(P_{\text{HI}})^2} = \frac{(0.043)(0.043)}{(0.914 + .5)^2} = 9.25 \times 10^{-4}$$
$$K = 2.2 \times 10^{-3}$$

$Q < K$

c9) + 10 points (poll)

Consider previous example at equilibrium.

Add .5 atm of  $\text{HI(g)}$  and .5 atm of  $\text{I}_2(\text{g})$

what is going to happen to reaction mixture?

$$Q = \frac{P_{\text{H}_2} P_{\text{I}_2}}{(P_{\text{HI}})^2} = \frac{(0.543)(0.043)}{(1.414)^2} = 1.88 \times 10^{-2}$$
$$K = 2.2 \times 10^{-3}$$

$Q > K$  shift left

Le Chatelier when stress is applied to a system in dynamic equilibrium, it tends to minimize effect of stress.

Types of stress

- add/remove reagents
- change volume of gas phase
- add/remove heat (changing temp)

Consider equilibrium  $5 \text{O}_2(\text{g}) + \text{N}_2(\text{g}) \leftrightarrow 5 \text{NO}(\text{g}) + \text{NO}_2(\text{g})$   
- addition of  $\text{NO}_2$

c10) + 10 points (poll)