

Info

- Final Exam is in **one week**-usual time and place (5:30pm)
- Quiz 11 results posted. Time is running out, please double check that everything is as it should be and that all corrections have been properly posted

General Analysis of dynamic changes

- $aA + bB \rightleftharpoons cC + dD$
- The above reaction, initially not at equilibrium, will be described at equilibrium by the following general equation

$$\frac{([C]_i + \text{or} - cx)^c ([D]_i + \text{or} - dx)^d}{([A]_i + \text{or} - ax)^a ([B]_i + \text{or} - bx)^b} = K$$

- If $Q < K$, which means the reaction will proceed L to R to reach equilibrium, then the signs in the numerator will be positive and those in the denominator, negative

$$\frac{([C]_i + cx)^c ([D]_i + dx)^d}{([A]_i - ax)^a ([B]_i - bx)^b} = K$$

- For $Q > K$, the opposite will be the case

$$\frac{([C]_i - cx)^c ([D]_i - dx)^d}{([A]_i + ax)^a ([B]_i + bx)^b} = K$$

- For the reaction below, if the initial concentrations are all 0.10 and K is as shown, write the equation that would permit you to solve for the equilibrium concentrations
 - $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g}) \quad K=2.5$
- For the reaction below, if the initial concentrations are all 0.50 and K is as shown, write the equation that would permit you to solve for the equilibrium concentrations
 - $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \quad K=0.15$
- You are expected to be able to do problems like the above on the final exam.

K_p vs K_c

- In the following problems, all species are gaseous unless otherwise noted
- Given the balanced equation and the value of K_c
 - $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$
K=1.58
T=389K

What is the value of K_p?

- Given the balanced equation and the value of K_c
 - $\text{Cl}_2 + 3\text{F}_2 \rightleftharpoons 2\text{ClF}_3$
K=8.55
T=392K

What is the value of K_p?

- Given the balanced equation and the value of K_c

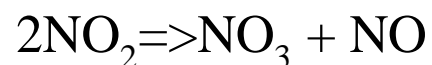


$$K = 9.42$$

$$T = 417\text{K}$$

What is the value of K_p ?

- Given the balanced equation and the value of K_c



$$K = 8.25$$

$$T = 425\text{K}$$

What is the value of K_p

Combining equilibria

- The rules
 - Reverse reaction $K_{\text{rev}} = 1/K_{\text{forward}}$
 - Multiply the reaction by $x \Rightarrow K=K^x$
- For Example
- Use the set of reactions and equilibrium constants provided to determine the value of K for the reaction:
 - $2\text{C}_2\text{H}_6\text{O}(\text{l}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{C}_2\text{H}_4\text{O}(\text{l}) + 2\text{H}_2\text{O}(\text{l})$
 - $2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_2\text{H}_6\text{O}(\text{l}) + 3\text{O}_2(\text{g}) \quad K= 0.100$
 - $2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4\text{O}(\text{l}) + 5/2\text{O}_2(\text{g}) \quad K= 0.120$
- $\text{H}_2\text{S}(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{SO}_4(\text{l})$
 - $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2\text{SO}_4(\text{l}) \quad K= 0.164$
 - $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{S}(\text{g}) + 2\text{O}_2(\text{g}) \quad K= 0.148$
 - $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) \quad K= 6.58$

- $\text{C}_2\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_2(\text{g}) + 2\text{H}_2(\text{g})$
- $\text{C}_2\text{H}_2(\text{g}) + 5/2\text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ $K = 3.60$
- $\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g})$ $K = 0.333$
- $\text{C}_2\text{H}_6(\text{g}) + 7/2\text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$ $K = 2.44$

- $\text{H}_2\text{S}(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{SO}_4(\text{l})$
- $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2\text{SO}_4(\text{l})$ $K = 0.505$
- $\text{H}_2\text{S}(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$ $K = 3.59$
- $\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$ $K = 0.162$

Messing with an equilibrium system

- If a system is at equilibrium and something is done to move it away from the equilibrium condition, what will happen and why?
- In general, how would you describe this process in terms used to date (Q and K)
- What types of stress will always disturb the equilibria?
- Changes in concentrations of species appearing in Q and temperature changes
 - Adding or removing products or reagents
 - Increasing or decreasing T
- What will never disturb the equilibria?
- Adding an inert material or something that doesn't appear in Q or adding a catalyst
- What will sometimes disturb the equilibria?
 - Volume changes
- Explain each of the above in terms of Q and K
- Handling temperature changes-a special case.
 - For an exothermic process consider heat as a product
 - For an endothermic process consider heat as a reagent

LeChatelier Effects

- The perturbing of an equilibrium system and its subsequent response is called a LeChatelier effect. The system responds in a manner that “relieves the stress” and reestablishes the equilibrium state How would the system respond to each of the following?
- Add reagent
- Add product
- Remove reagent
- Remove product
- $q > 0$
 - Increase T
 - Decrease T
- $q < 0$
 - Increase T
 - Decrease T

Volume changes-anthropomorphic view

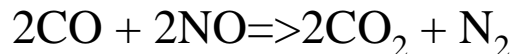
- Predicting the effect of volume changes on equilibria can be done by using the “relieve the stress “ approach.
 - If the volume increases, the system will adjust in a fashion as to occupy more volume => produce more moles
 - If the volume decreases, the system will adjust in a fashion as to occupy less volume => produce fewer moles
 - $\Delta n = \text{moles prods} - \text{moles reagents}$
 - $\Delta V = V_2 - V_1$
- special case: $\Delta n = 0$
- The four cases
- $\Delta V > 0 \quad \Delta n > 0$
- $\Delta V > 0 \quad \Delta n < 0$
- $\Delta V < 0 \quad \Delta n > 0$
- $\Delta V < 0 \quad \Delta n < 0$

Volume Changes-Q vs K view

- The preceding discussion, although it will yield the correct results, is largely baloney.
- When the volume of the system is changed, which concentrations are changed?
- If V increases, how are the concentrations changed?
- If V decreases?
- Will Q change and can you predict how? In other words, since all of the $[]$ s are changed will the effect be greater on the numerator or denominator of Q ?
- what about $\Delta n=0$ here?
- The four cases (Q vs K view)
 - $\Delta V > 0 \quad \Delta n > 0$
 - $\Delta V > 0 \quad \Delta n < 0$
 - $\Delta V < 0 \quad \Delta n > 0$
 - $\Delta V < 0 \quad \Delta n < 0$

Handling LeChatelier Quantitatively

- For the reaction below, at equilibrium with the concentrations shown. If [CO] is changed to 0.30, what will all of the concentrations be once equilibrium is reestablished?



Equilibrium Concentrations:

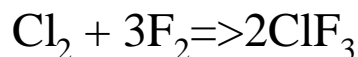
CO:0.20M

NO:0.35M

CO₂:0.40M

N₂:0.15M

- For the system below, at equilibrium with the concentrations shown, if the volume is doubled, what will the new concentrations be once equilibrium is reestablished?



Equilibrium Concentrations:

Cl₂:0.30M

F₂:0.20M

ClF₃:0.10M

Kinetics and Equilibrium

- The reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ follows the rate law: $\text{rate} = k [\text{N}_2\text{O}_4]$. If the rate constant is $6.30 \times 10^{-2} \text{sec}^{-1}$ and $K = 2.45$, how long will it take for a reaction mixture containing only N_2O_4 initially to reach equilibrium?
- At first glance, it might seem like this problem could be solved as follows:
- $[\text{N}_2\text{O}_4]_i = 1.00$ $[\text{NO}_2]_i = 0.00$
- equilibrium $[\text{N}_2\text{O}_4]_{\text{eq}} = 1.00 - x$ $[\text{NO}_2]_{\text{eq}} = 2x$
- $4x^2 / (1-x) = 2.45 \Rightarrow x = 0.534$ $[\text{N}_2\text{O}_4]_{\text{eq}} = 0.466$ (check: $4 \times (.534)^2 / .466 = 2.45$)
- $\ln(.466/1) = -kt \Rightarrow 12 \text{ secs}$ (check $t_{1/2} = 0.693 / .063 = 11 \text{ sec}$)
- What's wrong with this?
- If the molecularity of the rate laws for the forward and reverse reactions in a reversible process is the same as that in Q ($\text{rate}_{\text{rev}} / \text{rate}_{\text{for}} = Q$) then $K = k_{\text{forward}} / k_{\text{reverse}}$. Does the logic this presents with regards to the relative sizes of the k s and the resultant K make sense to you?

