The Daily News

- Quiz 10 and HW#4 are posted-remember that the Feb 17 assignment includes the “Ice and Water” page
- Correction on Tuesday’s notes:
  - $2PBr_3(g) + 3Cl_2(g) \Leftrightarrow 2PCl_3(g) + 3Br_2(g)$
- I will be out of town until late Monday night-feel free to send your usual warm and cuddly emails, but don’t expect any replies until Tuesday.

Equilibrium to Date

- “Reversible” chemical reactions must reach a point where the rates of the forward and reverse processes become equivalent.
- At that point, all the concentrations become static, despite the continuing chemical changes
- This is the **equilibrium state**
- A general function Q describes the reaction system under all conditions. Only species with variable [ ]s appear in Q
- When the system is at equilibrium Q=K
- A reversible system is either at equilibrium or moving toward equilibrium.
- Combining kinetics and equilibrium: The kinetics tell us how long it will take for a reversible reaction to reach equilibrium.

Calculating K

- Given the balanced equation and the equilibrium concentrations shown:
  $COCl_2$=>CO + Cl_2
  Equilbrium Concentrations:
  $COCl_2$:0.0699**M**
  CO:0.340**M**
  Cl_2:0.151**M**
  What is the value of K?

$K= [CO]_{eq}[Cl_2]_{eq}/[COCl_2]_{eq}=(0.340)(0.151)/(0.0699)=0.734$

- Given the balanced equation and the equilibrium concentrations shown:
  $CH_4 + 2H_2S$=>$CS_2 + 4H_2$
  Equilbrium Concentrations:
  CH_4:0.437**M**
  H_2S:0.122**M**
  CS_2:0.0891**M**
  H_2:0.482**M**
  What is the value of K?
- $K=[CS_2]_{eq}[H_2]^4_{eq}/[CH_4]_{eq}[H_2S]^2_{eq}=(.891)(.482)^4/(.437)(.122)^2=7.39$

- Given the balanced equation and the equilibrium concentrations shown:
  $2NO_2 => N_2O_4$
  Equilbrium Concentrations:
  NO_2:0.339**M**
  N_2O_4:0.0705**M**
  What is the value of K?
- $K=[N_2O_4]_{eq}/[NO_2]^2_{eq}=(.0705)/(.339)^2=0.613$

- Given the balanced equation and the equilibrium concentrations shown: $2CO + 2NO => 2CO_2 + N_2$
  Equilbrium Concentrations:
  CO:0.482**M**
  NO:0.238**M**
  CO_2:0.275**M**
  N_2:0.448**M**
  What is the value of K?
- $K= [CO_2]_{eq}^2[N_2]_{eq}/[CO]_{eq}^2[NO]_{eq}^2=(.275)^2(.448)/(.482)^2(.238)^2=2.57$

Calculating [ ]$_{eq}$

Given the balanced equation, the K value and the partial set of equilibrium concentrations shown:
$2NOBr \Rightarrow NO + 2\ Br_2$
$K=1.61*10^{-1}$
Equilbrium Concentrations:
NO:0.194**M**
Br_2:0.0965**M**
What is the concentration of NOBr

- $K=0.161= [NO][Br_2]^2/[NOBr]^2 \Rightarrow$
- $0.161=(.194)(0.0965)^2/[NOBr]^2= .00181/[NOBr]^2$
- $[NOBr]^2 =.0112$ $[NOBr]=.106$
- Checking $(.194)(0.0965)^2/(.106)^2=.161$

- Given the balanced equation, the K value and the partial set of equilibrium concentrations shown:
$2CO + 2NO \Rightarrow 2CO_2 + N_2$
$K=1.82*10^{1}$
Equilbrium Concentrations:
CO:0.0325**M**
NO:0.247**M**
N_2:0.113**M**
What is the concentration of CO_2?
  - $K=18.2= [CO_2]^2[N_2]/[CO]^2[NO]^2= [CO_2]^2(0.113)/(0.0325)^2(0.247)^2$
  - $18.2= [CO_2]^2*1750 \Rightarrow [CO_2]^2=.0104$ $[CO_2]=.101$
  - Checking $(.101)^2(.113)/(.0325)^2(.247)^2=17.9$

Suppose You're not at Equilibrium

- The preceding treatments deal with a system wherein equilibrium has already been established. What sort of analysis can/should be made for a non equilibrium state?
- First, let's exam a bit of a transition case
- The table provides concentration data for the reaction shown going to equilibrium. Use the data to calculate the value of K?
  $2SO_2 + O_2 \Rightarrow 2SO_3$

	$[\ ]_i$	$[\ ]_{eq}$
SO_3	0.00	0.20
SO_2	0.33	
O_2	0.40	

How many variations can you see on this?

$2CO_2 + N_2 \Rightarrow 2CO + 2NO$

	$[\ ]_I$	**$[\ ]_{eq}$**
CO	0.00	
NO	0.00	0.053
CO_2	0.440	
N_2	0.110	

$CO_2 + H_2 \Rightarrow CO + H_2O$

	$[\ ]_I$	**$[\ ]_{eq}$**
CO	0.00	
H_2O	0.00	
CO_2	0.210	
H_2	0.370	0.226

Q vs K-the key to everything

- If a system is not at equilibrium, then it must be moving toward it. Thus, there are two issues in analyzing reversible systems
  - Is it at equilibrium?
  - If not, is which direction is the reaction occurring?
- For any system which is not at equilibrium, Q is constantly changing due to the net chemical change which is occurring.
- The proper evaluation of Q is the key to analyzing a nonequilibrium state. If one rephrases the earlier statement using Q and K it reads: “Q is either equal to K or changing in such a fashion as to eventually equal K.” Q can no more diverge from K than a system can move away from equilibrium.
- Q=K-equilibrium state
- Q>K or Q<K: System is not at equilibrium and a net reaction is occurring.
- Q>K what’s happening and why?
- Q<K ditto

How Complex Can Things Become?

- $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ K=0.80
- Assume all of the initial concentrations are 0.500.
- What is Q?
- In what direction is the reaction occurring?
- When equilibrium is established-what are the concentrations

Kinetics and Equilibrium

- The reaction $N_2O_4(g) \Leftrightarrow 2NO_2(g)$ follows the rate law: rate=k $[N_2O_4]$.   If the rate constant is $6.30*10^{-2}$sec-1 and K=2.45, how long will it take for a reaction mixture containing only N_2O_4 initially to reach equilibrium?

K_c and K_p

- aA + bB ⇔ cC + dD
- $K_c=[C]^c[D]^d/[A]^a[B]^b$
- $K_p=P_C{}^c*P_D{}^d/P_A{}^a*P_B{}^b$
- P=nRT/V n/V=**M**
- $K_p=([C]*RT)^c([D]*RT)^d/([A]*RT)^a([B]*RT)^b$
- Δn=(c+d)-(a+b) or moles gaseous prods-moles gaseous reagents
- $K_c=[C]^c[D]^d/[A]^a[B]^b(RT)^{\Delta n}= K_c* (RT)^{\Delta n}$
- Δn=0 $K_p=K_c$

Mathematics of K

- aA + bB ⇔ cC + dD K=2.4
- What is K for the following
- cC + dD ⇔ aA + bB
- 2aA + 2bB ⇔ 2cC + 2dD
- 1/3*cC +1/3* dD ⇔ 1/3*aA + 1/3*bB
- Where do you think this is heading?