

The Daily News

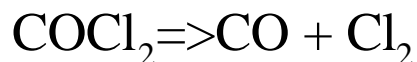
- Quiz 10 and HW#4 are posted-remember that the Feb 17 assignment includes the “Ice and Water” page
- Correction on Tuesday’s notes:
 - $2\text{PBr}_3(\text{g}) + 3\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{PCl}_3(\text{g}) + 3\text{Br}_2(\text{g})$
- I will be out of town until late Monday night-feel 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:



Equilibrium Concentrations:

COCl_2 : 0.0699M

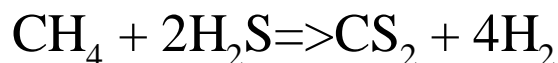
CO: 0.340M

Cl_2 : 0.151M

What is the value of K?

$$K = \frac{[\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}}{[\text{COCl}_2]_{\text{eq}}} = \frac{(0.340)(0.151)}{(0.0699)} = 0.734$$

- Given the balanced equation and the equilibrium concentrations shown:



Equilibrium Concentrations:

CH_4 : 0.437M

H_2S : 0.122M

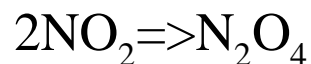
CS_2 : 0.0891M

H_2 : 0.482M

What is the value of K?

$$K = \frac{[\text{CS}_2]_{\text{eq}}[\text{H}_2]_{\text{eq}}^4}{[\text{CH}_4]_{\text{eq}}[\text{H}_2\text{S}]_{\text{eq}}^2} = \frac{(0.0891)(0.482)^4}{(0.437)(0.122)^2} = 7.39$$

- Given the balanced equation and the equilibrium concentrations shown:



Equilibrium Concentrations:

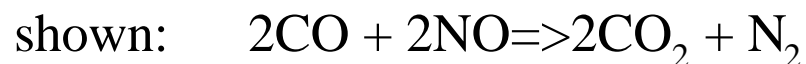
NO_2 : 0.339M

N_2O_4 : 0.0705M

What is the value of K?

- $K = \frac{[\text{N}_2\text{O}_4]_{\text{eq}}}{[\text{NO}_2]_{\text{eq}}^2} = \frac{(0.0705)}{(0.339)^2} = 0.613$

- Given the balanced equation and the equilibrium concentrations shown:



Equilibrium Concentrations:

CO: 0.482M

NO: 0.238M

CO_2 : 0.275M

N_2 : 0.448M

What is the value of K?

- $K = \frac{[\text{CO}_2]_{\text{eq}}^2 [\text{N}_2]_{\text{eq}}}{[\text{CO}]_{\text{eq}}^2 [\text{NO}]_{\text{eq}}^2} = \frac{(0.275)^2 (0.448)}{(0.482)^2 (0.238)^2} = 2.57$

Calculating []_{eq}

Given the balanced equation, the K value and the partial set of equilibrium concentrations shown:



$$K = 1.61 \times 10^{-1}$$

Equilibrium Concentrations:

$$\text{NO}: 0.194\text{M}$$

$$\text{Br}_2: 0.0965\text{M}$$

What is the concentration of NOBr

- $K = 0.161 = \frac{[\text{NO}][\text{Br}_2]^2}{[\text{NOBr}]^2} \Rightarrow$
 - $0.161 = \frac{(0.194)(0.0965)^2}{[\text{NOBr}]^2} = \frac{.00181}{[\text{NOBr}]^2}$
 - $[\text{NOBr}]^2 = .0112 \quad [\text{NOBr}] = .106$
 - Checking $\frac{(0.194)(0.0965)^2}{(.106)^2} = .161$
-
- Given the balanced equation, the K value and the partial set of equilibrium concentrations shown:
$$2\text{CO} + 2\text{NO} \rightleftharpoons 2\text{CO}_2 + \text{N}_2$$
$$K = 1.82 \times 10^1$$
Equilibrium Concentrations:
$$\text{CO}: 0.0325\text{M}$$
$$\text{NO}: 0.247\text{M}$$
$$\text{N}_2: 0.113\text{M}$$
What is the concentration of CO₂?
 - $K = 18.2 = \frac{[\text{CO}_2]^2[\text{N}_2]}{[\text{CO}]^2[\text{NO}]^2} = \frac{[\text{CO}_2]^2(0.113)}{(0.0325)^2(0.247)^2}$
 - $18.2 = \frac{[\text{CO}_2]^2 \cdot 1750}{\Rightarrow [\text{CO}_2]^2 = .0104 \quad [\text{CO}_2] = .101}$
 - Checking $\frac{(.101)^2(.113)}{(.0325)^2(.247)^2} = 17.9$

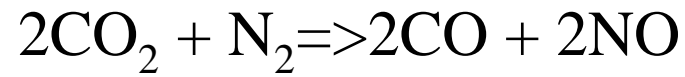
Suppose You're not at Equilibrium

- 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?

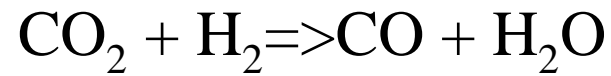


	[] _i	[] _{eq}
SO ₃	0.00	0.20
SO ₂	0.33	
O ₂	0.40	

How many variations can you see on this?



	[] _I	[] _{eq}
CO	0.00	
NO	0.00	0.053
CO ₂	0.440	
N ₂	0.110	



	[] _I	[] _{eq}
CO	0.00	
H ₂ O	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, in 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?

- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ $K=0.80$
- 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 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ 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?

K_c and K_p

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

Mathematics of K

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