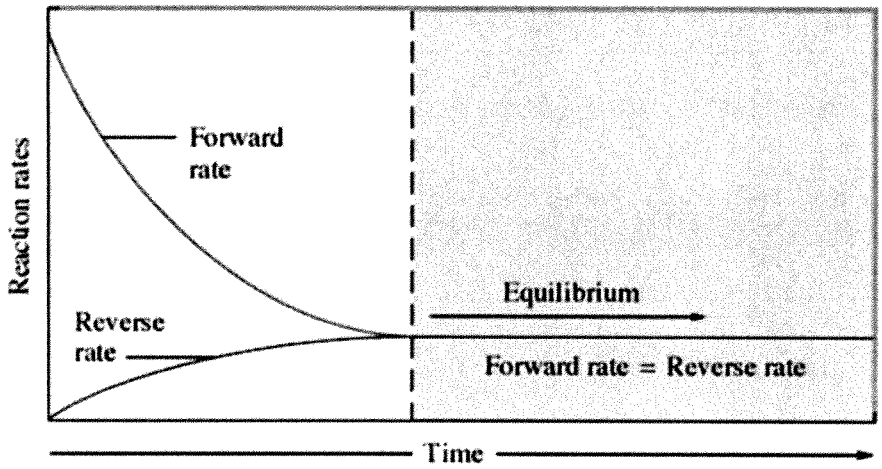
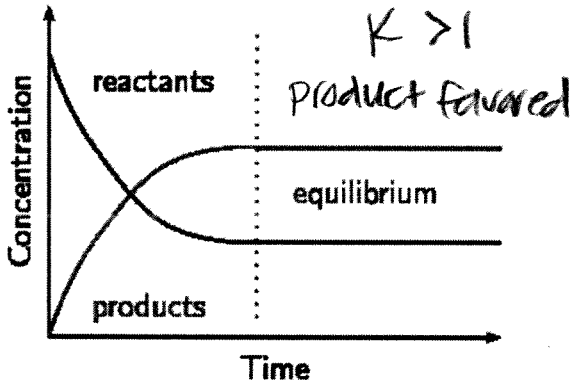
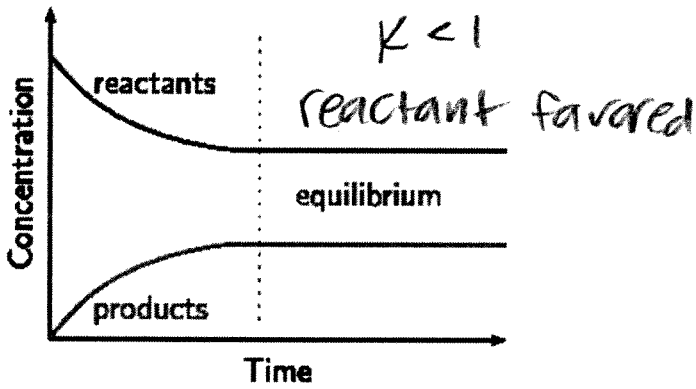
Based on the graph below, how can we define equilibrium?

equilibrium occurs when forward rate = reverse rate



Based on the graphs below, how can we define equilibrium?





[reactants] is constant at equilibrium

[products] is constant at equilibrium

Write the reaction quotient, Q, expression for each rxn.
Think back to electro... No solids or liquids in Q

1) $6\ H^+(aq) + 2\ Al(s) \rightarrow 2\ Al^{3+}(aq) + 3\ H_2(g)$

2) $3\ Cu(s) + 2\ NO^{3-}(aq) + 8\ H^+(aq) \rightarrow 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(l)$

1) $Q = \dfrac{[Al^{3+}]^2[H_2]^3}{[H^+]^6}$

2) $Q = \dfrac{[Cu^{2+}]^3[NO]^2}{[NO_3^-]^2[H^+]^8}$

How do we write equilibrium constant, K, expressions?

Same formula as Q

How do K expressions differ from Q expressions?

K is used for equlibrium concentrations/pressures

Q is used for NON equilibrium concentrations/pressures

What information does K tell us about a reaction?

$K > 1$ product favored

$K < 1$ reactant favored

Let's practice...NO CALCULATORS

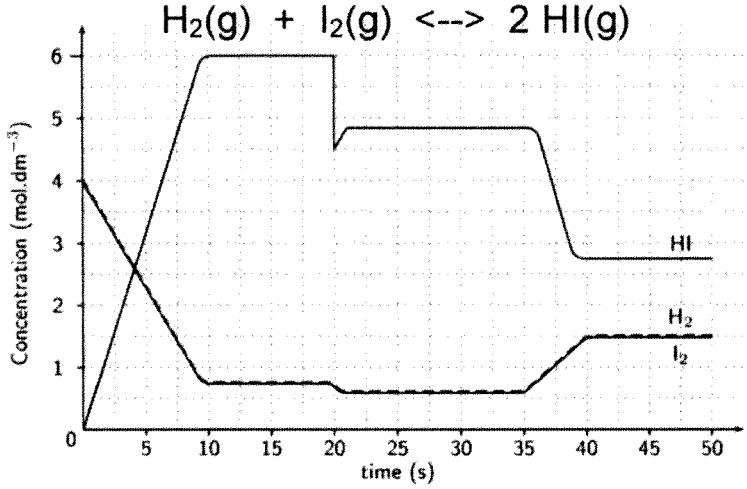
Example 1

a) Write the equilibrium constant, Kc, expression.
b) Write the pressure equilibrium constant, Kp, expression.
c) Is the rxn reactant or product favored?
d) Is K greater than, less than, or equal to 1?

a) $K_c = \frac{[HI]^2}{[H_2][I_2]}$

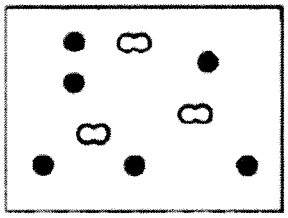
b) $K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})}$

$H_2(g) + I_2(g) \leftrightarrow 2\ HI(g)$



Let's practice...NO CALCULATORS

Example 2



6
NO_2 = ●
N_2O_4 = ∞
3

The diagram above represents a mixture of $NO_2(g)$ and $N_2O_4(g)$ in a 1.0 L container at a given temperature. The two gases are in equilibrium according to the equation $2\ NO_2(g) \rightleftharpoons N_2O_4(g)$. Which of the following must be true about the value of the equilibrium constant for the reaction at this temperature?

More reactant than product
∴ reactant favored

A) $K = 0$
B) $0 < K < 1$
C) $K = 1$
D) $K > 1$
E) Thee is not enough information to determine the relative value of K.

Let's practice...NO CALCULATORS

Example 3

$$2\,X(g) + Y(g) \leftrightarrows 3\,Z(g)$$

The reaction mixture represented above is at equilibrium at 298 K, and the molar concentrations are $[X] = 2.0\ M$, $[Y] = 0.5\ M$, and $[Z] = 4.0\ M$. What is the value of the equilibrium constant for the reaction at 298K?

A) 0.50
B) 2.0
C) 4.0
D) 16
E) 32

$$K_c = \frac{[Z]^3}{[X]^2[Y]} = \frac{(4)^3}{(2)^2(0.5)} = \frac{(4)(4)(4)}{(4)(0.5)}$$

$$= \frac{16}{0.5} = 16(2) = 32$$

Example 4 $CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g)$

2.00 M of CO and 2.00 M of H_2O are placed in an evacuated flask at 900 K. Kc = 1.56 for this reaction at 900 K.

a) Is the reaction reactant or product favored? Justify your answer.

$K > 1$

b) In which direction will the system shift to reach equilibrium? Explain your reasoning. Shift Forward b/c [products] is initially zero

c) The reaction is repeated, this time the initial concentrations are:
$[CO]_0 = [H_2O]_0 = 1.00$ M
$[CO_2]_0 = [H_2]_0 = 3.00$ M

In which direction will the system shift to reach equilibrium? Justify your answer with a calculation.

$$Q = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(3)(3)}{(1)(1)} = 9$$

$K < Q$
$1.56 \quad 9$

Shift reverse

$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g)$$

d) The reaction is repeated, this time the initial concentrations are:
$[CO]_0 = [H_2O]_0 = 1.00$ M
$[CO_2]_0 = [H_2]_0 = 1.00$ M

In which direction will the system shift to reach equilibrium? Justify your answer with a calculation.

$$Q = \frac{(1)(1)}{(1)(1)} = 1$$

$K > Q$
1.56 1

SHIFT FORWARD

How can we use K and Q to determine the direction in which a rxn will shift to establish equilibrium?

$K < Q$ SHIFT Reverse (Make more reactants)

$K > Q$ SHIFT FORWARD (Make more products)

$K = Q$ Rxn is @ equilibrium ; NO SHIFT

What other types of K exist? What do all K's have in common?

THIS UNIT

K_c - concentration
K_p - pressure
K_{sp} - solubility product

K_a - acid
K_b - base
K_w - water

Next UNIT

☆ All K's are $\frac{\text{products}}{\text{reactants}}$

☆ K is constant @ constant temp.

How do we convert between Kc and Kp?

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

☆ R = 0.0821

☆ T = Kelvin

☆ Δn = change in moles of gas

Δn = mols gas products − mols gas reactants

Add coefficients of all gas products

Add coefficients of all gas reactants

Example 5 $H_2(g) + I_2(g) \longleftrightarrow 2\,HI(g)$ K = 64

0.100 M H_2, 0.100 M I_2, and 0.700 M HI are mixed in a container. If tempearture is held constant, what are the concentrations of all species at equilibrium?

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.700)^2}{(0.100)(0.100)} = 49$$

$K > Q$ ∴ rxn shifts forward to establish equilibrium

64 49

	$H_2(g)$	$+\ I_2(g)$	$\rightleftharpoons\ 2HI(g)$
I	0.100 M	0.100 M	0.700 M
C	$-x$	$-x$	$+2x$
E	0.100 M − x	0.100 M − x	0.700 M + 2x

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

$$\sqrt{64} = \sqrt{\frac{(0.700\ M + 2x)^2}{(0.100\ M - x)(0.100\ M - x)}}$$

$$8 = \frac{0.700\ M + 2x}{0.100\ M - x}$$

$$0.800\ M - 8x = 0.700\ M + 2x$$

$$0.100\ M = 10x$$

$$x = 0.0100\ M$$

Equilibrium Concentrations

$[H_2] = [I_2] = 0.100\ M - x$

$= 0.100\ M - 0.0100\ M$

$= \boxed{0.090\ M = [H_2] = [I_2]}$

$[HI] = 0.700\ M + 2x$

$= 0.700\ M + 2(0.0100\ M$

$= \boxed{0.720\ M = [HI]}$

Example 6 $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$

0.500 mol SO_2 and 0.300 mol O_2 are placed into an evacuated 5.0 L vessel at 398 K. Once equilibrium is established, 0.100 mol of SO_3 are in the vessel.

a) What are the equilibrium concentrations of SO_2 and O_2?
b) What is the value of Kc at 398 K?
c) What is the value of Kp at 398 K?

Initial

$$[SO_2]_0 = \frac{0.500 \text{ mol } SO_2}{5.0 \text{ L}} = 0.10 \text{ M } SO_2$$

$$[O_2]_0 = \frac{0.300 \text{ mol } O_2}{5.0 \text{ L}} = 0.060 \text{ M } O_2$$

$$[SO_3] \text{ @ equilibrium} = \frac{0.100 \text{ mol } SO_3}{5.0 \text{ L}} = 0.020 \text{ M } SO_3$$

	$2\ SO_2(g)$	$+\ O_2(g)$	$\rightleftharpoons\ 2\ SO_3(g)$
I	0.10 M	0.060 M	0
C	$-2x$	$-x$	$+2x$
E	$0.10\text{ M} - 2x$	$0.060\text{ M} - x$	$2x$

Equilibrium $[SO_3] = 0.020 \text{ M} = 2x$

$\therefore x = 0.010 \text{ M}$

a) $\therefore$ Equilibrium $[SO_2] = 0.10 \text{ M} - 2x = 0.10 \text{ M} - 2(0.010 \text{ M}) = \boxed{0.08 \text{ M}}$

Equilibrium $[O_2] = 0.060 \text{ M} - x = 0.060 \text{ M} - 0.010 \text{ M} = \boxed{0.05 \text{ M}}$

b) $$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.020)^2}{(0.08)^2(0.05)} = \boxed{1.25}$$

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

$$K_p = 1.25\left[(0.0821)(398 \text{ K})\right]^{2-3} = \boxed{0.0383}$$

Example 7 $SbCl_3(g) + Cl_2(g) \leftrightarrow SbCl_5(g)$

A reaction starts with 5.00 mol each of $SbCl_3$ and Cl_2 in a 2.00 L flask at 350 degress C. When equilibrium is established at 350 degrees C, the moles of $SbCl_5$ present are 1.67 mol.

a) What are the equilibrium concentrations of $SbCl_3$ and Cl_2?
b) What is the value of Kc at 350 degrees C?
c) What is the value of Kp at 350 degress C?

$$[SbCl_3]_0 = [Cl_2]_0 = \frac{5.00 \text{ mol}}{2.00 \text{ L}} = 2.50 \text{ M}$$

$$[SbCl_5] \text{ @ equilibrium} = \frac{1.67 \text{ mol}}{2.00 \text{ L}} = 0.835 \text{ M}$$

	$SbCl_3(g)$ +	$Cl_2(g)$ $\rightleftharpoons$	$SbCl_5(g)$
I	2.50 M	2.50 M	0
C	$-x$	$-x$	$+x$
E	$2.50 \text{ M} - x$	$2.50 \text{ M} - x$	x

Equilibrium $[SbCl_5] = 0.835 \text{ M} = x$

a) $\therefore$ Equilibrium $[SbCl_3] = [Cl_2] = 2.50 \text{ M} - x = 2.50 \text{ M} - 0.835 \text{ M}$
$= 1.665 \text{ M} = \boxed{1.67 \text{ M}}$

b) $$K_c = \frac{[SbCl_5]}{[SbCl_3][Cl_2]} = \frac{0.835}{(1.67)(1.67)} = \boxed{0.299}$$

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

$$K_p = 0.299 \left[(0.0821)(623 \text{ K})\right]^{1-2} = \boxed{5.85 \times 10^{-3}}$$

Example 8 $CO_2(g) + C(s) \leftrightarrow 2\,CO(g)$

An evacuated vessel contains a small amount of powered graphite (C) and is heated to 1080 K. Then CO_2 is added to a pressure of 0.458 atm. Once the CO_2 is added, the system starts to produce CO. After equilibrium is reached, the total pressure inside the vessel is 0.757 atm. Calculate Kp for this reaction.

Initial $P_{CO_2} = 0.458$ atm

Equilibrium $P_T = 0.757$ atm

	$CO_2(g)$	+ $C(s)$	$\rightleftharpoons$ $2\,CO(g)$
I	0.458 atm	SOME	0
C	$-x$	doesn't matter	$+2x$
E	0.458 atm $-x$	b/c C is a solid	$2x$

Equilibrium Pressures

$P_{CO_2} = 0.458 \text{ atm} - x$

$P_{CO} = 2x$

$P_T = 0.757$ atm

$P_T = P_{CO_2} + P_{CO}$

$0.757 \text{ atm} = 0.458 \text{ atm} - x + 2x$

$0.757 \text{ atm} = 0.458 \text{ atm} + x$

$x = 0.299$ atm

$\therefore$ Equilibrium $P_{CO_2} = 0.458 \text{ atm} - 0.299 \text{ atm} = 0.159$ atm

$P_{CO} = 2(0.299 \text{ atm}) = 0.598$ atm

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(0.598)^2}{(0.159)} = \boxed{2.25}$$

Example 9 $H_2(g) + I_2(g) \leftrightarrow 2\,HI(g)$

$H_2(g)$, $I_2(g)$, and $HI(g)$ are placed into a 5.25 L container at 698 K. The initial partial pressure of $H_2(g)$ is 3.27 atm, I_2 is 3.27 atm and HI is 32.7 atm. Kc is 54.3 at 698 K.

a) What is the value of Kp at 698 K?
b) What is the equilibrium partial pressure of each gas in the reaction vessel?

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

$K_p = 54.3\,[(0.0821)(698\,K)]^{2-2}$

$K_p = 54.3\,[(0.0821)(698\,K)]^{0}$

$K_p = 54.3\,(1)$ * When $\Delta n = 0$, $K_p = K_c$

$\boxed{K_p = 54.3}$

b) $Q = \dfrac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \dfrac{(32.7)^2}{(3.27)(3.27)} = 100$

$K_p < Q_p$
54.3 100
∴ shift reverse ←

	$H_2(g)$ +	$I_2(g)$ ⇌	$2\,HI(g)$
I	3.27 atm	3.27 atm	32.7 atm
C	+x	+x	−2x
E	3.27 atm +x	3.27 atm +x	32.7 atm −2x

SHIFT Reverse ← Make reactants

$K_p = \dfrac{(P_{HI})^2}{(P_{H_2})(P_{I_2})}$

$\sqrt{54.3} = \sqrt{\dfrac{(32.7\text{ atm} - 2x)^2}{(3.27\text{ atm} + x)^2}}$

$7.3689 = \dfrac{32.7\text{ atm} - 2x}{3.27\text{ atm} + x}$

$24.096\text{ atm} + 7.3689x = 32.7\text{ atm} - 2x$

$9.3689x = 25.331$

$x = 2.7037\text{ atm}$

At equilibrium

$P_{H_2} = P_{I_2} = 3.27\text{ atm} + 2.7037 = \boxed{5.97\text{ atm}}$

$P_{HI} = 32.7\text{ atm} - 2(2.7037) = \boxed{27.3\text{ atm}}$

Example 10 $CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)$

Kc = 23.2 at 600 K

0.100 moles of each reactant and product species are placed into a 5.00 L flask, equilibrium is established at 600 K.

a) What is the equilibrium concentration of H_2?

b) Once equilibrium has been established, 0.0150 moles of both $CO_2(g)$ and $H_2(g)$ are added to the reaction vessel.

i) Calculate Q after this addition.
ii) Calculate the concentration of CO(g) once equilibrium has been reestablished after this addition.
iii) In which direction did the reaction shift to reestablish equilibrium? Why do you think it shifted in this way?

a) $[CO]_0 = [H_2O]_0 = [CO_2]_0 = [H_2]_0 = \frac{0.100 \text{ mol}}{5.00 \text{ L}} = 0.0200 \text{ M}$

$Q = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0200)(0.0200)}{(0.0200)(0.0200)} = 1$ $\quad K > Q$ (23.2 > 1)

∴ shift Forward →

	$CO(g)$ +	$H_2O(g)$ ⇌	$CO_2(g)$ +	$H_2(g)$
I	0.0200 M	0.0200 M	0.0200 M	0.0200 M
C	−x	−x	+x	+x
E	0.02 M − x	0.02 M − x	0.02 M + x	0.02 M + x

$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$

$\sqrt{23.2} = \sqrt{\frac{(0.02 \text{ M} + x)^2}{(0.02 \text{ M} - x)^2}}$

$4.8166 = \frac{(0.02 \text{ M} + x)}{(0.02 \text{ M} - x)}$

$0.09633 - 4.8166x = 0.02 + x$

$0.07633 = 5.8166x$

$x = 0.0131 \text{ M}$

Equilibrium $[H_2] = 0.02 \text{ M} + x$

$= 0.02 \text{ M} + 0.0131 \text{ M}$

$= \boxed{0.0331 \text{ M}}$

10b) 0.0150 mol CO_2 added and 0.0150 mol H_2 added

$$[CO_2]\text{ added} = [H_2]\text{ added} = \frac{0.0150\text{ mol}}{5\text{ L}} = 0.00300\text{ M added}$$

$$\text{New }[CO_2] = \text{New }[H_2] = 0.0331\text{ M} + 0.00300\text{ M}$$
$$= 0.0361\text{ M}$$

i) $$\text{New } Q = \frac{(0.0361)^2}{(0.02 - 0.0131)^2} = \frac{(0.0361)^2}{(0.0069)^2} = 27$$

iii) $\underset{23.2}{K} < \underset{27}{Q}$ ∴ SHIFT Reverse to reestablish equilibrium ← Make more reactants

ii)

	$CO_{(g)}$	+ $H_2O_{(g)}$	⇌ $CO_{2(g)}$	+ $H_{2(g)}$
I	0.0069 M	0.0069 M	0.0361 M	0.0361 M
C	+x	+x	−x	−x
E	0.0069 M +x	0.0069 M +x	0.0361 M − x	0.0361 M − x

$$\sqrt{23.2} = \sqrt{\frac{(0.0361\text{ M} - x)^2}{(0.0069\text{ M} + x)^2}}$$

$$4.8166 = \frac{(0.0361\text{ M} - x)}{(0.0069\text{ M} + x)}$$

$$0.0332\text{ M} + 4.8166x = 0.0361\text{ M} - x$$
$$5.8166x = 0.002865\text{ M}$$
$$x = 4.93 \times 10^{-4}\text{ M}$$

$$[CO] = 0.0069\text{ M} + x$$
$$= 0.0069\text{ M} + 4.93 \times 10^{-4}\text{ M}$$
$$= \boxed{0.00739\text{ M}}$$