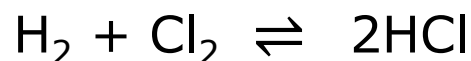# Outline

- Equilibrium Condition

- Equilibrium Constant

- Reaction Quotient

- Equilibrium Problems

- Le Chatelier's Principle

Equilibrium Condition

All reactions proceed in both directions...

$$H_2 + Cl_2 \rightleftharpoons 2HCl$$

The rate of the forward and reverse rxns depend on <u>temperature</u> and the <u>concentrations</u>

$R_f = k_f [H_2][Cl_2]$

$R_r = k_r [HCl]^2$

The net direction of the reaction is determined by the rates of the reactions, relative to one another

In a container with H_2, Cl_2 and HCl...

1. If $R_f > R_r$, then forward spontaneous: $H_2 + Cl_2 \rightarrow 2HCl$

2. If $R_f < R_r$, then reverse spontaneous: $H_2 + Cl_2 \leftarrow 2HCl$

3. If $R_f = R_r$, then equilibrium: $H_2 + Cl_2 \rightleftharpoons 2HCl$

<u>Chemical equilibrium</u> is the condition when the forward and reverse rates of reaction are equal

Reactions proceed until chemical equilibrium is established!

For a certain temperature,

$$k_f = 1.00 \text{ sec}^{-1} \text{ M}^{-1} \quad \text{and} \quad k_r = 1.36 \text{ sec}^{-1} \text{ M}^{-1}$$

where $R_f = k_f[H_2][Cl_2]$ and $R_r = k_r[HCl]^2$

In which direction is the rxn spontaneous?

$[H_2]$, M	$[Cl_2]$, M	$[HCl]$, M	R_f, M/s	R_r, M/s	Direction
10	10	0	100	0	forward
9	9	2	81	5.4	forward
8	8	4	64	22	forward
7	7	6	49	49	equilibrium

Equilibrium Constant

At equilibrium...

$$R_f = R_r$$

$$k_f [H_2][Cl_2] = k_r [HCl]^2$$

$$\frac{k_f}{k_r} = \frac{[HCl]^2}{[H_2][Cl_2]} \qquad \text{equilibrium constant expression}$$

$k_f / k_r = K_{eq}$, the <u>equilibrium constant</u>

Equilibrium constants (K) are…

  written without units!

  constant only for constant temperature!

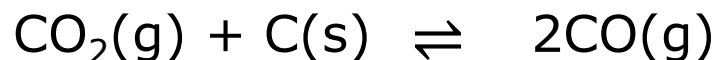Equilibrium constants (K) give measure of how far a reaction goes…

For…   aA + bB $\rightleftharpoons$ cC + dD

We write… $K = \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$ (equilibrium constant expression)

K expression contains substances whose concentrations can change

        gases (g) and dissolved substances (aq) are included
        solids (s) and liquids (l) are not included

Find K_{eq} for

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

in a 2.0-L flask that contains 6.0 mol of CO_2 and 8.0 mol CO at equilibrium

$$K_{eq} = \frac{[CO]^2}{[CO_2]} = \frac{[4.0\,M]^2}{[3.0\,M]} = 5.\underline{3}3\,M = \underline{5.3}$$

What's [CO] if $[CO_2]$ = 2.0 M

$$K_{eq} = \frac{[CO]^2}{[CO_2]} \Rightarrow [CO] = \sqrt{[CO_2]K_{eq}} = \sqrt{(2.0)(5.3)} = 3.\underline{2}5\,M = \underline{3.3\,M}$$

For same temperature, what is K_{eq} for,

$$2CO_2(g) + 2C(s) \rightleftharpoons 4CO(g)$$

$$K'_{eq} = \frac{[CO]^4}{[CO_2]^2} = \left(\frac{[CO]^2}{[CO_2]}\right)^2 = \left(K_{eq}\right)^2 = (5.3)^2 = \underline{28}$$

$$2CO(g) \rightleftharpoons CO_2(g) + C(s)$$

$$K''_{eq} = \frac{[CO_2]}{[CO]^2} = \left(\frac{1}{K_{eq}}\right) = \left(\frac{1}{5.3}\right) = \underline{0.19}$$

There are two types of K_{eq}'s:

1. K_C concentration units (M) are used in the expression

2. K_P pressure units (atm) are used in the expression

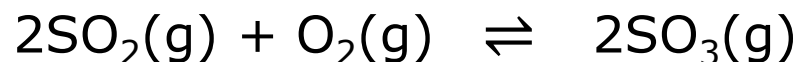$$K_C = \frac{[HCl]^2}{[H_2][Cl_2]} \qquad K_P = \frac{p_{HCl}{}^2}{p_{H_2}\, p_{Cl_2}}$$

Numerical values for K_P and K_C are usually different...

$$K_P = K_C\,(RT)^{\Delta n}$$

R = 0.08206 L atm/mol K
Δn = moles of products minus moles of reactants (for gases)

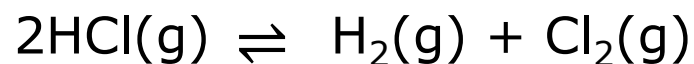The K_C for the following rxn is 100.0 at 27 °C. Find K_P.

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

$K_P = K_C \, (RT)^{\Delta n}$

$\Delta n = 2 - 3 = -1$

$K_P = (100.0)\left[(0.0821 \, \text{L atm} / \text{mol K})(300. \, \text{K})\right]^{-1}$

$= 4.06 \, \text{mol} / \text{L atm}$

$= \underline{4.06}$

K_C = 25 at 20. °C for the reaction

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

Find K_P.

$$K_P = K_C \, (RT)^{\Delta n}$$

$$\Delta n = 2 - 2 = 0$$

$$K_P = (25)\left[(0.0821 \text{ L atm / mol K}) (293 \text{ K})\right]^0$$

$$= \underline{25}$$

Reaction Quotient

Reaction quotient (Q) is used to predict direction to reach equilibrium…
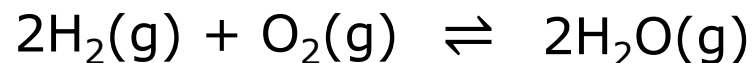
insert concentrations into equilibrium constant expression and compare value to K

if $Q < K_{eq}$, forward reaction is spontaneous

if $Q > K_{eq}$, reverse reaction is spontaneous

if $Q = K_{eq}$, reaction is at equilibrium

For some temperature, the following equilibrium has $K_{eq} = 16$:

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

In which direction is the rxn spontaneous,

if $[H_2] = [O_2] = [H_2O] = 1.0$ M?

$$Q = \frac{[H_2O]^2}{[H_2]^2[O_2]} = \frac{(1.0)^2}{(1.0)^2(1.0)} = 1.0 < 16 = K_{eq} \implies \underline{forward}$$

if $[H_2] = 1.0$ M, $[O_2] = 2.0$ M, $[H_2O] = 6.0$ M?

$$Q = \frac{[H_2O]^2}{[H_2]^2[O_2]} = \frac{(6.0)^2}{(1.0)^2(2.0)} = 18 > 16 = K_{eq} \implies \underline{reverse}$$
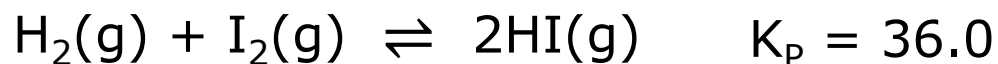
Equilibrium Problems

General types:

      1. equilibrium conc's → K_{eq}
      2. K_{eq} → equilibrium conc's
      3. initial conc's, change → K_{eq}

General steps:

      1. initial conc's
      2. changes (from coefficients)   ICE Table!
      3. equilibrium conc's
      4. write K_{eq} expression
      5. solve for "x"

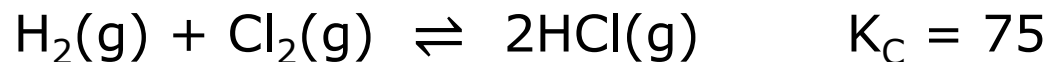A tank is filled with 0.20 atm of H_2 and 0.20 atm of I_2. Find the equilibrium pressure of HI given

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_P = 36.0$$

I	0.20	0.20	0
C	– x	– x	2x
E	0.20 – x	0.20 – x	2x

$$K_P = \frac{p_{HI}^2}{p_{H_2}p_{I_2}} = \frac{[2x]^2}{[0.20 - x]^2} = 36.0 \implies \frac{2x}{0.20 - x} = 6.00 \implies \underline{x = 0.15}$$

$$p_{HI(eq)} = 2(0.15 \text{ atm}) = \underline{0.30 \text{ atm}}$$

0.10 mol of HCl gas is placed in a 2.0 L flask. What is the concentration of HCl at equilibrium?

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) \qquad K_C = 75$$

I	0	0	0.050
C	x	x	− 2x
E	x	x	0.050 − 2x

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{[0.050 - 2x]^2}{[x]^2} = 75 \Rightarrow \frac{0.050 - 2x}{x} = 8.7 \Rightarrow x = 0.0047\,M$$

$[HCl]_{eq}$ = 0.050 M − 2(0.0047 M) = <u>0.041 M</u>

Percent dissociation measures extent of reaction

$$\% \text{ diss.} = \frac{\text{amount dissociated}}{\text{original amount}} (100\ \%)$$

What is the percent dissociation of HCl?

$$\% \text{ diss.} = \frac{2x}{0.050} (100\ \%) = \frac{2(0.0047)}{0.050} (100\ \%) = \underline{19\ \%}$$

2.0 mol NH_3 gas are placed in a 1.0 L container and at equilibrium 1.0 mol remains. Find K_C.

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

	2NH₃	N₂	3H₂
I	2.0	0	0
C	– 2x	x	3x
E	2.0 – 2x	x	3x

$[NH_3]_{eq}$ = 1.0 M = 2.0 – 2x $\Rightarrow$ x = 0.50 M

$[N_2]_{eq}$ = x = 0.50 M

$[H_2]_{eq}$ = 3x = 1.5 M

$$K_C = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{(0.50)(1.5)^3}{(1.0)^2} = \underline{1.7}$$

0.84 mol PCl_5 and 0.18 mol PCl_3 are placed in a 1.0 L flask. At equilibrium 0.72 mol PCl_5 remains. Find K_C for

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

	PCl_5		PCl_3	Cl_2
I	0.84		0.18	0
C	– x		x	x
E	0.84 – x		0.18 + x	x
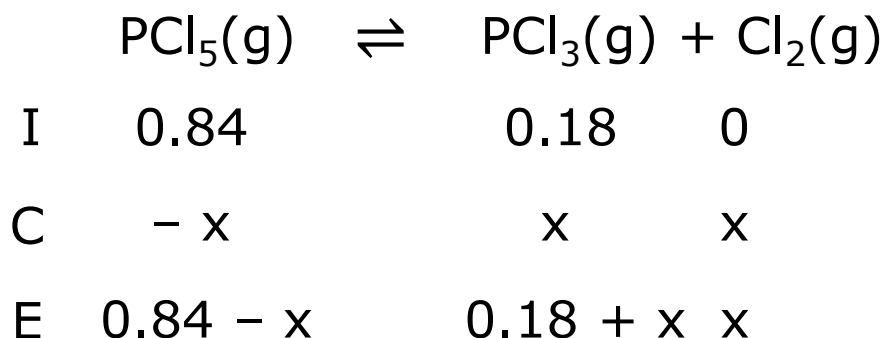
$[PCl_5]_{eq} = 0.72\ M = 0.84 - x \implies x = 0.12\ M$

$[PCl_3]_{eq} = 0.18 + x = 0.30\ M$

$[Cl_2]_{eq} = x = 0.12\ M$

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.30)(0.12)}{(0.72)} = \underline{0.050}$$

Le Chatelier's Principle

Le Chatelier's Principle

If an external stress is applied to a system at equilibrium, the equilibrium position will change to counteract the stress

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
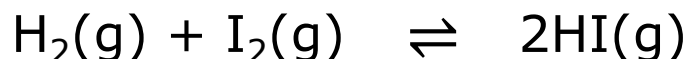
If H_2 is added…

equilibrium shifts right (more products are formed)

K_{eq} stays the same

Change in Enthalpy (ΔH): The energy change during a chemical reaction
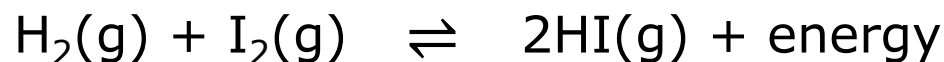
ΔH positive…   E absorbed   endothermic

ΔH negative…   E released   exothermic

When this reaction occurs, energy is released…

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + energy$$

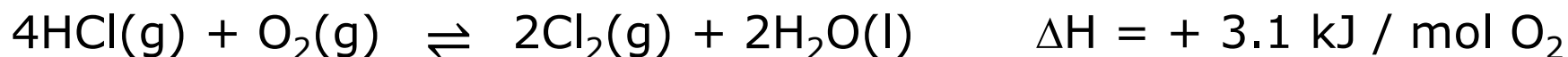ΔH_{298} for reaction = -10.2 kJ (exothermic!)

If T increases…
  equilibrium shifts left (more reactants are formed)
  K_{eq} decreases

If T decreases…
  equilibrium shifts right
  K_{eq} increases

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(l) \qquad \Delta H = + 3.1 \text{ kJ / mol } O_2$$

If T increases…
    equilibrium shifts right K_{eq} increases

If Cl_2 removed…
    equilibrium shifts right K_{eq} stays the same

If H_2O added…
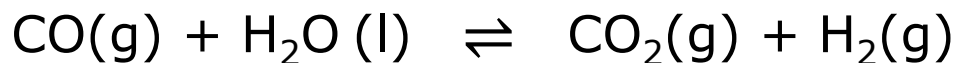   no change; not in K_{eq} expression!

If P increases…
    equilibrium shifts right K_{eq} stays the same
    (pressure affects gases, less gas on right)

$CO(g) + H_2O(l) \rightleftharpoons CO_2(g) + H_2(g)$ $\qquad \Delta H = + 4.1 \text{ kJ}$

Stress	Shift	$\Delta[CO_2]$
add CO	right	incr
add H_2O	none	no
add H_2	left	decr
add CO_2	left	incr
incr T	right	incr
decr T	left	decr
incr P	left	decr
decr P	right	incr

The equilibrium concentrations of 0.30 M HCl, 0.20 M H_2, and 0.10 M Cl_2 are all in a 1.0 L flask. Then 0.10 mol Cl_2 is added. Find the new equilibrium concentration of HCl.

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

E	0.30	0.20	0.10
I	0.30	0.20	0.20
C	+ 2x	− x	− x
E	0.30 + 2x	0.20 − x	0.20 − x

Find K_C from initial eq. conc.'s:

$$K_C = \frac{[H_2][Cl_2]}{[HCl]^2} = \frac{[0.20\,M][0.10\,M]}{[0.30\,M]^2} = 0.22$$

The equilibrium concentrations of 0.30 M HCl, 0.20 M H_2, and 0.10 M Cl_2 are all in a 1.0 L flask. Then 0.10 mol Cl_2 is added. Find the new equilibrium concentration of HCl.

Find new eq. conc.'s:

$$0.22 = \frac{[0.20 - x]^2}{[0.30 + 2x]^2} \implies 0.47 = \frac{0.20 - x}{0.30 + 2x} \implies x = 0.030\,M$$

[HCl] = 0.30 + 2x = <u>0.36 M</u>

A flask is filled with the equilibrium pressures 0.25 atm N_2, 0.25 atm O_2, and 0.40 atm NO. Then 0.10 atm of NO is added. What are the new equilibrium pressures.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

E	0.25	0.25	0.40
I	0.25	0.25	0.50
C	x	x	− 2x
E	0.25 + x	0.25 + x	0.50 − 2x

Find K_P from initial eq. prs.'s:

$$K_P = \frac{p_{NO}^2}{p_{N_2}p_{O_2}} = \frac{[0.40 \text{ atm}]^2}{[0.25 \text{ atm}]^2} = 2.\underline{56}$$

A flask is filled with the equilibrium pressures 0.25 atm N_2, 0.25 atm O_2, and 0.40 atm NO. Then 0.10 atm of NO is added. What are the new equilibrium pressures.

Find new eq. prs.'s:

$$2.56 = \frac{[0.50 - 2x]^2}{[0.25 + x]^2} \implies 1.6 = \frac{0.50 - 2x}{0.25 + x} \implies x = 0.028 \text{ atm}$$

$[N_2] = 0.25 + x = \underline{0.28 \text{ atm}}$

$[O_2] = 0.25 + x = \underline{0.28 \text{ atm}}$

$[NO] = 0.50 - 2x = \underline{0.44 \text{ atm}}$