CHEMICAL EQUILIBRIUM

6.2 Equilibrium Constants (Part I)

At the end of the lesson, students should be able to:

(a) Define homogeneous and heterogeneous equilibria.

(b) Deduce and write expressions for equilibrium constants in terms of concentration, K_c and partial pressure, K_p for homogeneous and heterogeneous systems.

(c) Derive and use the equation, $K_p = K_c (RT)^{\Delta n}$.

LESSON DURATION: 1 hour

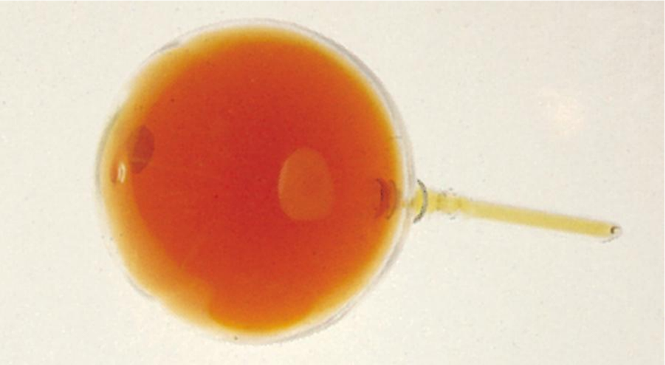
HOMOGENEOUS EQUILIBRIUM

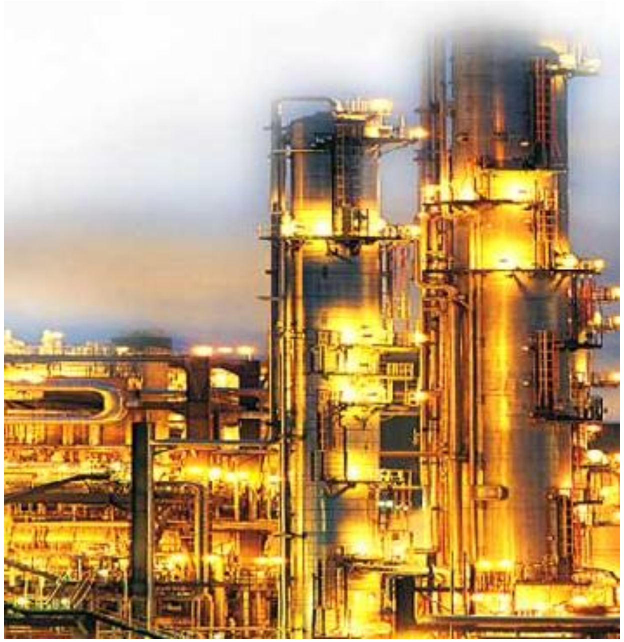
☞ **Products and reactants are in the same phase.**

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

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

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$





WRITING K_P AND K_C EXPRESSIONS

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Subscript C in K_C = concentrations of the reacting species

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$K_C = \frac{[NO_2]^2}{[N_2O_4]}$$

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$$K_C = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Note: Unit of concentration = M (mol L^{-1})

WRITING K_p AND K_c EXPRESSIONS

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_P = \frac{P_C{}^c\,P_D{}^d}{P_A{}^a\,P_B{}^b}$$

P = equilibrium partial pressure of the gas

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$K_P = \frac{P_{NO_2}^{\,2}}{P_{N_2O_4}}$$

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

$$K_P = \frac{P_{NH_3}^{\,2}}{P_{N_2} \times P_{H_2}^{\,3}}$$

Note:
Equilibrium constant expression (K_C or K_P) also called Equilibrium law expression

Note: Unit of pressure = atm.

WRITING K_p AND K_c EXPRESSIONS

$$PV = nRT$$

So

$$P = \frac{n}{V} RT \quad \text{or} \quad \frac{P}{RT} = \frac{n}{V}$$

At constant temperature, pressure is directly proportional to molar concentration (*n*/*V*).

The equilibrium constant for reaction involved gases, can be expressed based on concentrations (K_C) and pressures (K_P).

Keep in mind!

The equilibrium constant (K_C and K_P) is a dimensionless (no unit) quantity.

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

$K_C = 1.67$ (at 500K)

$K_P = 4.07 \times 10^{-2}$ (at 500K)

Keep in mind!

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

$$K_C = 1.67 \text{ (at 500K)}$$

$$K_P = 4.07 \times 10^{-2} \text{ (at 500K)}$$

In quoting a value for the K_P or K_C, you MUST specify the balanced equation (including the phase of each reactant/product) and the temperature.

EXERCISE - 2

Write expressions for K_C, and K_P if applicable, for the following reversible reactions at equilibrium:
Note: balance the equations first.

a) $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

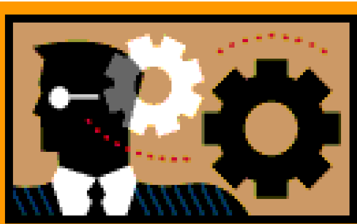
b) $NO(g) + O_2(g) \rightleftharpoons NO_2(g)$

c) $N_2O_5(g) \rightleftharpoons NO_2(g) + O_2(g)$

d) $C_3H_8(g) + O_2(g) \rightleftharpoons CO_2(g) + H_2O(g)$

e) $NH_3(g) + O_2(g) \rightleftharpoons NO(g) + H_2O(g)$

f) $NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$



EXAMPLE - 1

ANS:

The following equilibrium process has been studied at 230°C:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

In one experiment the concentration of the reacting species at equilibrium are found to be [NO] = 0.0542 M, $[O_2]$ = 0.127 M, and $[NO_2]$ = 15.5 M. Calculate the equilibrium constant (K_C) of the reaction at this temperature.

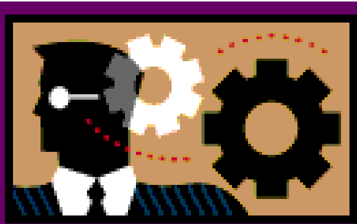
$$K_c = \frac{[NO_2]}{[NO]^2[O_2]} = \frac{(15.5)^2}{(0.0542)^2 \times 0.127} = \boxed{6.44 \times 10^5}$$

EXERCISE - 3

Consider the following equilibrium process at 700°C:

$$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g)$$

Analysis shows that at equilibrium, there are 2.50 mol of H_2, 1.35×10^{-5} mol of S_2, and 8.70 mol of H_2S present in a 12.0–L flask. Calculate the equilibrium constant K_C for the reaction.



EXERCISE - 4

At a certain temperature, $K_C = 1.8 \times 10^4$ for the reaction

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

If the equilibrium concentrations of N_2 and NH_3 are 0.015 M and 2.00 M, respectively, what is the equilibrium concentrations of H_2?

EXERCISE - 5

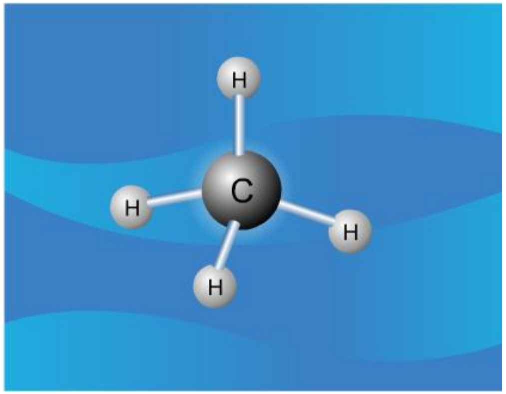
In a study of the conversion of methane to other fuels, a chemical engineer mixes gaseous CH_4 and H_2O in a 0.32–L flask at 1200 K.

At equilibrium, the flask contains 0.26 mol of CO, 0.091 mol of H_2, and 0.041 mol of CH_4.

What is $[H_2O]$ at equilibrium?

K_C = 0.26 for the equation

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

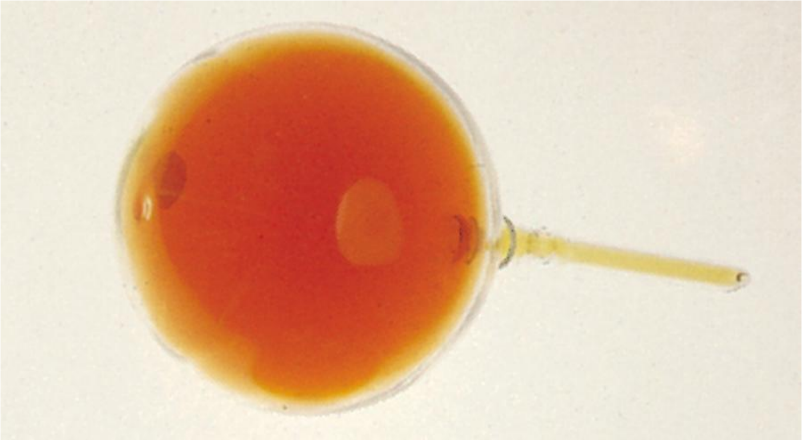


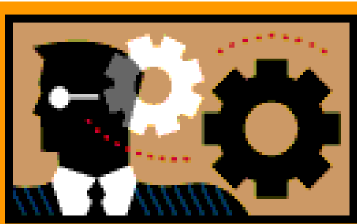
EXERCISE - 6

Equilibrium is established at 25°C in the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_C = 4.61 \times 10^{-3}$$

If $[NO_2] = 0.0236$ M in a 2.26–L flask, how many grams of N_2O_4 are also present?





EXAMPLE - 2

The equilibrium constant K_p for the reaction

$$2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g)$$

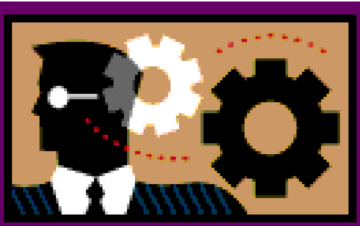
is 158 at 1000K. What is the equilibrium pressure of O_2 if the P_{NO_2} = 0.400 atm and P_{NO} = 0.270 atm?

ANS:

$$K_p = \frac{P_{NO}^2\,P_{O_2}}{P_{NO_2}^2}$$

$$P_{O_2} = K_p\,\frac{P_{NO_2}^2}{P_{NO}^2}$$

P_{O_2} = 158 x $(0.400)^2/(0.270)^2$ = **346.8 atm**

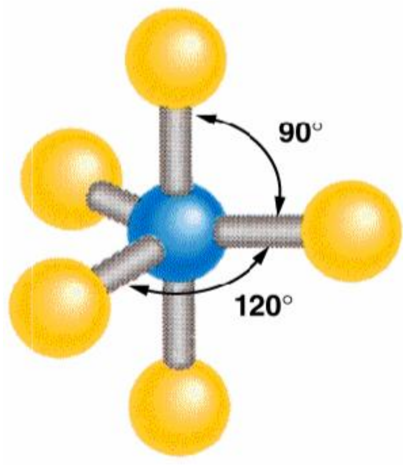


EXERCISE - 7

The equilibrium constant K_P for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecule chlorine

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

is found to be 1.05 at 250°C. If the equilibrium partial pressure of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C.



EXERCISE - 8

For the Haber process,

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

$$K_P = 1.45 \times 10^{-5} \text{ at } 500^oC.$$

In an equilibrium mixture of the three gases at 500°C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm.
What is the partial pressure of NH_3 in this equilibrium?

Keep in mind!

The value of K_C and K_P depend on how the equilibrium equation is written and balanced.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \text{(at 25°C)}$$

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \text{(at 25°C)}$$

$$K_C = \frac{[N_2O_4]}{[NO_2]^2} = 216$$

Keep in mind!

The value of K_C and K_P depend on how the equilibrium equation is written and balanced.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \text{(at 25°C)}$$

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g) \qquad \text{(at 25°C)}$$

$$K_C = \frac{[NO_2]}{[N_2O_4]^{1/2}} = 0.0680$$

EXERCISE - 9

For the ammonia–formation reaction,

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

K_c = 2.4 x 10^{-3} at 1000 K. If we change the coefficients of this equation, what are the values of K_c for the following balanced equations?

a) $\frac{1}{3}N_2(g) + H_2(g) \rightleftharpoons \frac{2}{3}NH_3(g)$

b) $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$

EXERCISE - 10

At 25°C, $K_C = 7.0 \times 10^{25}$ for the reaction:

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

What is the value of K_C for the reaction:

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$

HETEROGENEOUS EQUILIBRIUM

☞ **Reactants and products are in different phases.**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K'_C = \frac{[CaO][CO_2]}{[CaCO_3]}$$

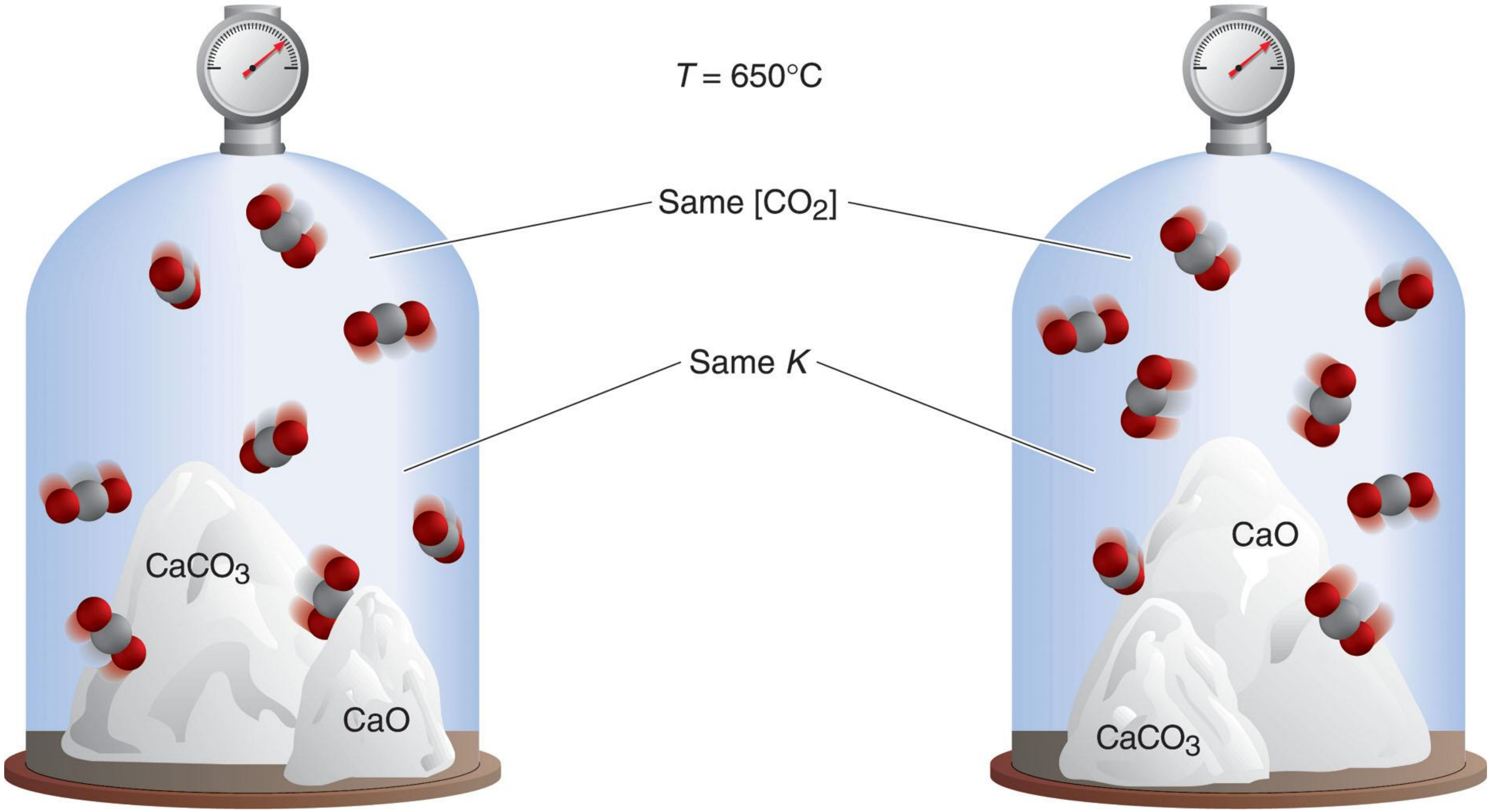
$[CaCO_3]$ = **constant**

$[CaO]$ = **constant**

$$K_C = [CO_2]$$

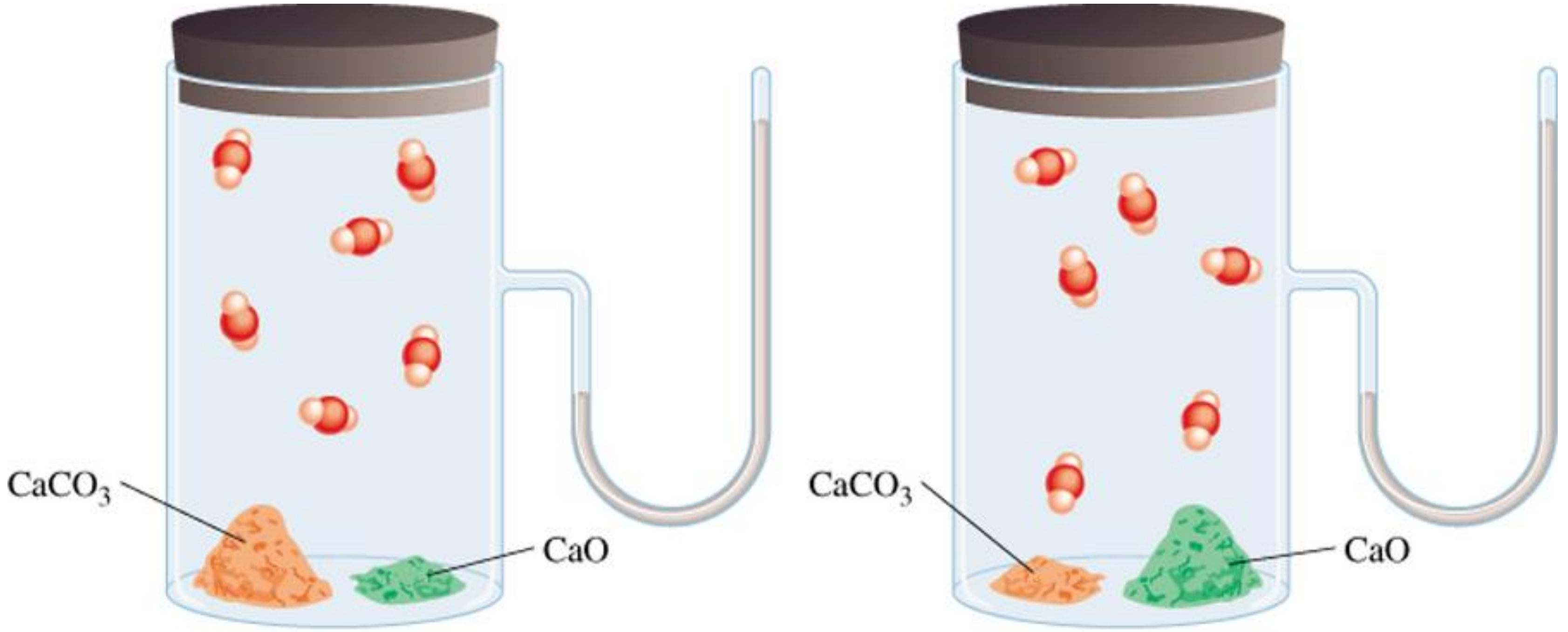
$$K_P = P_{CO_2}$$

The concentration of pure solids, pure liquids and solvents do not appear in the equilibrium constant expression.



- A pure solid always has the same concentration at a given temperature → same number of moles per liter of the solid.
- Just as it has same density at any given temperature.
- Same reason applies to pure liquid.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$



$$P_{CO_2} = K_P$$

P_{CO_2} does not depend on the amount of $CaCO_3$ or CaO.

EXAMPLE - 3

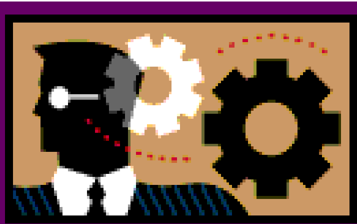
ANS:

Write equilibrium constant expression for K_C and K_P for the formation of nickel tetracarbonyl, which is used to separate nickel from other impurities:

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$$

$$K_C = \frac{[Ni(CO)_4]}{[CO]^4}$$

$$K_P = \frac{P_{Ni(CO)_4}}{P_{CO}^{\,4}}$$



EXERCISE - 11

Balance each of the following equations and write its equilibrium constant expression, K_C and K_P:

a) $Na_2O_2(s) + CO_2(g) \rightleftharpoons Na_2CO_3(s) + O_2(g)$

b) $H_2O(l) \rightleftharpoons H_2O(g)$

c) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

d) $H_2O(l) + SO_3(g) \rightleftharpoons H_2SO_4(aq)$

e) $KNO_3(s) \rightleftharpoons KNO_2(s) + O_2(g)$

f) $S_8(s) + F_2(g) \rightleftharpoons SF_6(g)$

EXERCISE - 12

Balance each of the following equations and write its equilibrium constant expression, K_C and K_P:

a) $NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$

b) $SnO_2(s) + H_2(g) \rightleftharpoons Sn(s) + H_2O(g)$

c) $H_2SO_4(l) + SO_3(g) \rightleftharpoons H_2S_2O_7(l)$

d) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

e) $CO_2(s) \rightleftharpoons CO_2(g)$

c) $N_2O_5(s) \rightleftharpoons NO_2(g) + O_2(g)$

EXAMPLE - 4

ANS:

Consider the following equilibrium at 295 K:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_P for the reaction?

$$K_P = P_{NH_3} P_{H_2S} = 0.265 \times 0.265 = \boxed{0.0702}$$

EXERCISE - 13

At equilibrium in the following reaction at 60^{o}C, the partial pressure of the gases are found to be P_{HI} = 3.65 x 10^{-3} atm and P_{H_2S} = 0.996 atm.

What is the value of K_P for the reaction?

$$H_2S(g) + I_2(s) \rightleftharpoons 2HI(g) + S(s)$$

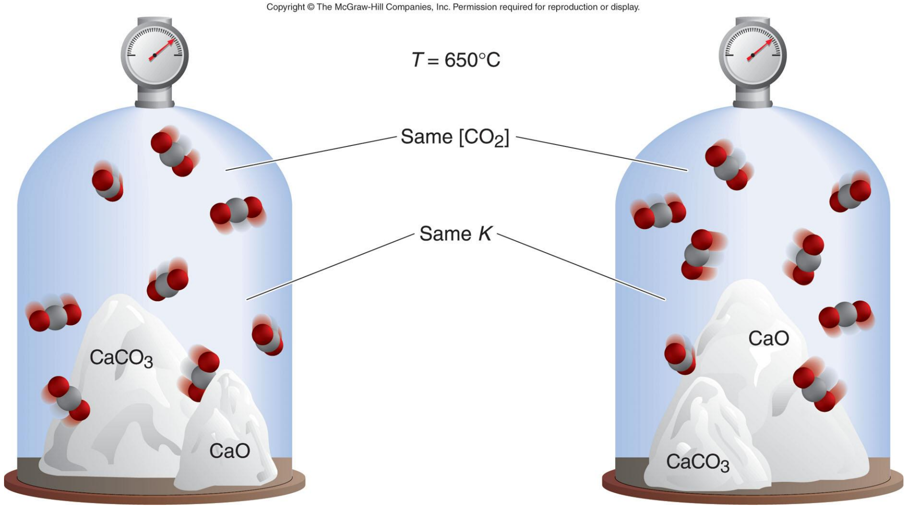
EXERCISE - 14

At equilibrium, the pressure of reacting mixture

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

is 0.105 atm at 350°C.

Calculate K_P for this reaction.



RELATION BETWEEN K_p AND K_c

In most cases

$$K_C \neq K_P$$

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad K_P = \frac{P_C^{\,c} P_D^{\,d}}{P_A^{\,a} P_B^{\,b}}$$

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

But, how do we derive this equation?

Δn = moles of gaseous products – moles of gaseous reactants $= (c + d) - (a + b)$

Derivation of equation: $K_P = K_C(RT)^{\Delta n}$

Let us consider the following equilibrium in gas phase:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

The equilibrium constant K_C:

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The expression for K_P:

$$K_P = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$$

Assuming the gases behave as ideal gases: $PV = nRT$

$$P_A = \frac{n_A}{V} RT = [A]RT \qquad P_B = \frac{n_B}{V} RT = [B]RT \qquad P_C = \frac{n_C}{V} RT = [C]RT \qquad P_D = \frac{n_D}{V} RT = [D]RT$$

Derivation of equation: $K_P = K_C(RT)^{\Delta n}$

$$P_A = \frac{n_A}{V}RT = [A]RT \qquad P_B = \frac{n_B}{V}RT = [B]RT \qquad P_C = \frac{n_C}{V}RT = [C]RT \qquad P_D = \frac{n_D}{V}RT = [D]RT$$

*Notice that, n_A/V, n_B/V, n_C/V and n_D/V have units mol L^{-1} and been replaced by [A], [B], [C] and [D]

By substituting these relations into the expression of K_P:

$$K_P = \frac{P_C^{\,c}\,P_D^{\,d}}{P_A^{\,a}\,P_B^{\,b}}$$

$$= \frac{([C]RT)^c \times ([D]RT^d)}{([A]RT)^a \times ([B]RT^b)}$$

$$= \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \times (RT)^{(c + d)-(a + b)}$$

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

Δn = moles of gaseous products - moles of gaseous reactants

Keep in mind!

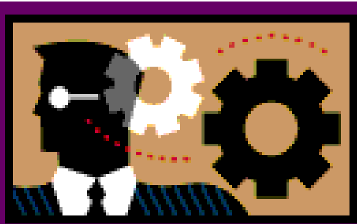
Relationship between K_P and K_C can also be written as $\boldsymbol{K_P = K_C(0.0821T)^{\Delta n}}$

R = 0.0821 L atm mol^{-1} K^{-1}

If Δn = 0: $\boldsymbol{K_P = K_C(0.0821T)^0}$

$\boldsymbol{K_P = K_C}$

Example: $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$



EXERCISE - 15

Show how you can get the following equation:

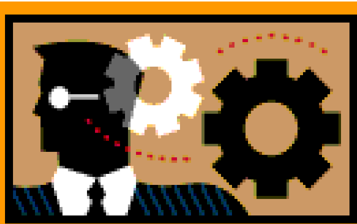
$$K_P = K_C(RT)^{\Delta n}$$

Hints:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_C = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad K_P = \frac{P_C{}^c\,P_D{}^d}{P_A{}^a\,P_B{}^b}$$

$$PV = nRT$$



EXAMPLE - 5

ANS:

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (*g*) at 74^0C are [CO] = 0.012 M, $[Cl_2]$ = 0.054 M, and $[COCl_2]$ = 0.14 M. Calculate the equilibrium constants K_C and K_P.

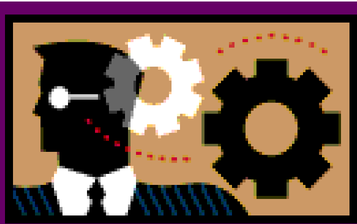
$$CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$$

$$K_C = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \times 0.054} = \boxed{216}$$

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

$$\Delta n = 1 - 2 = -1 \qquad R = 0.0821 \qquad T = 273 + 74 = 347\ K$$

$$K_P = 216 \times (0.0821 \times 347)^{-1} = \boxed{7.58}$$



EXERCISE - 16

Determine Δn_{gas} for each of the following reactions:

a) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$

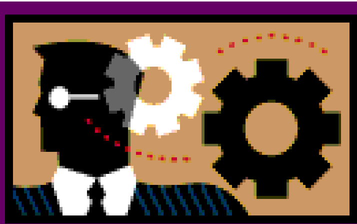
b) $2PbO(s) + O_2(g) \rightleftharpoons 2PbO_2(s)$

c) $I_2(s) + 3XeF_2(s) \rightleftharpoons 2IF_3(s) + 3Xe(g)$

d) $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$

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

f) $HNO_3(l) + ClF(g) \rightleftharpoons ClONO_2(g) + HF(g)$



EXERCISE - 17

Calculate K_C for the following equilibria:

a) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

$K_P = 3.9 \times 10^{-2}$ at 1000K

b) $S_2(g) + C(s) \rightleftharpoons CS_2(g)$

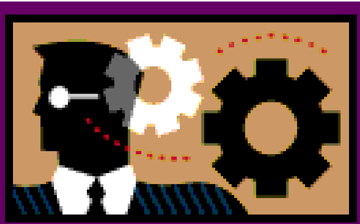
$K_P = 28.5$ at 500K

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

$K_P = 49$ at 730K

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

$K_P = 2.5 \times 10^{10}$ at 500K



EXERCISE - 18

Calculate K_P for the following equilibria:

a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$K_C = 6.1 \times 10^{-3}$ at 298K

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

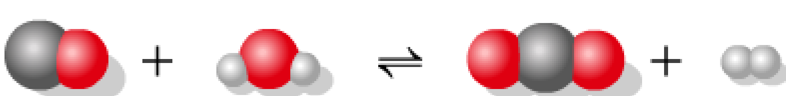
$K_C = 2.4 \times 10^{-3}$ at 1000K

c) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

$K_C = 0.77$ at 1020K

d) $3O_2(g) \rightleftharpoons 2O_3(g)$

$K_C = 1.8 \times 10^{-56}$ at 570K



EXERCISE - 19

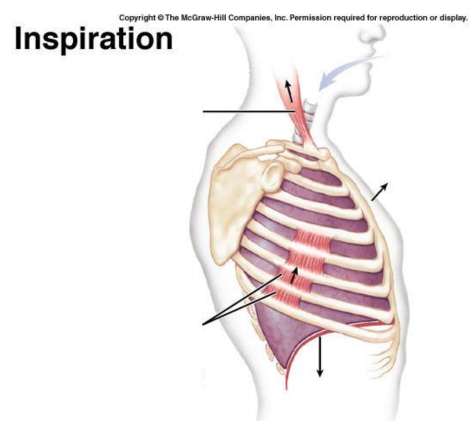
Nitric oxide, oxygen, and nitrogen react by the following equation:

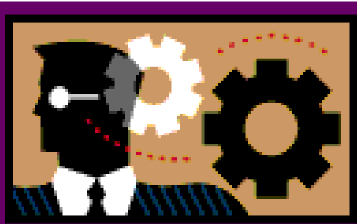
$$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

$$K_C = 2.3 \times 10^{30} \text{ at } 298K.$$

In the atmosphere, P_{O_2} = 0.209 atm and P_{N_2} = 0.781 atm.

What is the partial pressure of NO in the air we breath?





EXERCISE - 20

Consider the following heterogeneous equilibrium:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

At 800°C, the pressure of CO_2 is 0.236 atm. Calculate K_P and K_C for the reaction at this temperature.

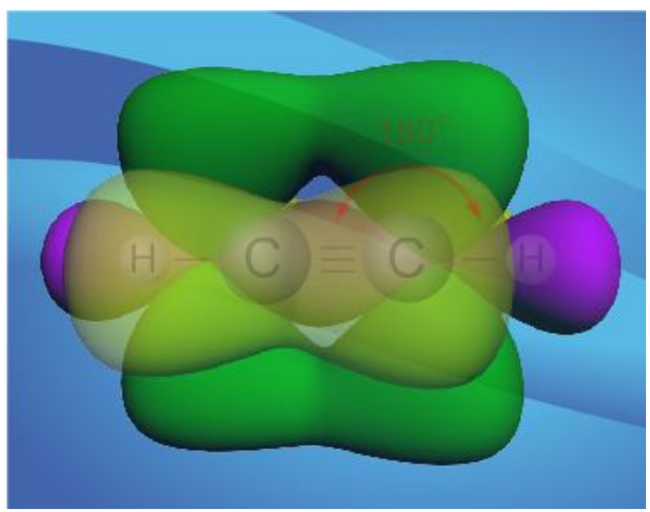
EXERCISE - 21

For which of the following reactions does $K_P = K_C$?

a) $2H_2(g) + C_2H_2(g) \rightleftharpoons C_2H_6(g)$

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

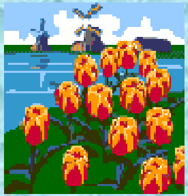
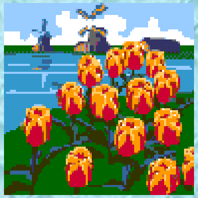
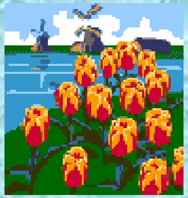
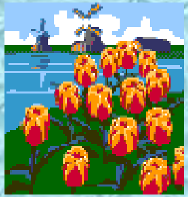
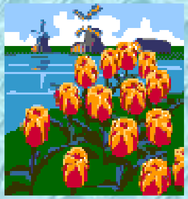
c) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$







END OF SLIDE SHOW

CHEMICAL EQUILIBRIUM

6.2 Equilibrium Constants (Part II)

At the end of the lesson, students should be able to:

(a) Calculate K_c, K_p or the quantities of species present at equilibrium.

(b) Define and determine the degree of dissociation, α.

LESSON DURATION: 2 hours

EQUILIBRIUM PROBLEMS

Two types:

1

☞ **Equilibrium quantities (concentrations , partial pressure) are given**

☞ **Solve for K_C or K_P**

2

☞ **Initial quantities (initial concentrations , initial partial pressure) and K_P or K_C are given**

☞ **Solve for equilibrium quantities (concentrations , partial pressure)**

USING A REACTION (*ICE*) TABLE

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown *x*, which represents the change in concentration.

2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for *x*.

3. Having solved for *x*, calculate the equilibrium concentrations of all species.

EXAMPLE - 6

At a certain temperature, a mixture of H_2 and I_2 was prepared by placing 0.200 mol of H_2 and 0.200 mol of I_2 into a 2.00 L flask. After a period of time the equilibrium

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

was established.

At equilibrium, the concentration of I_2 concentration had dropped to 0.020 M. What is the value of K_c for this reaction at this temperature?

EXAMPLE - 6

ANS:

	$H_2(g)$ +	$I_2(g) \rightleftharpoons$	$2HI(g)$
Initial (M)	$\frac{0.200 \text{ mol}}{2.00 \text{ L}}$ = 0.100	$\frac{0.200 \text{ mol}}{2.00 \text{ L}}$ = 0.100	0.000
Change (M)	$-x$	$-x$	$+2x$
Equilibrium (M)	$0.100 - x$	$0.100 - x$ = 0.020	$0.000 + 2x$ = $2x$

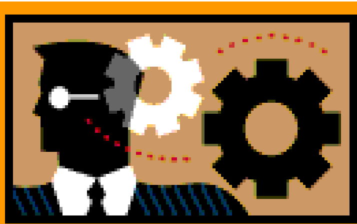
ICE

So, $x = 0.100 - 0.020$
$= 0.080$

$[I_2] = 0.020$ M

$[H_2] = (0.100 - 0.080)$ M
$= 0.020$ M

$[HI] = 2 \times 0.080$ M
$= 0.160$ M



EXAMPLE - 6

ANS:

$$H_2(g) \quad + \quad I_2(g) \rightleftharpoons \quad HI(g)$$

$[H_2] = 0.020$ M $\quad [I_2] = 0.020$ M $\quad [I_2] = 0.160$ M

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

$$= \frac{(0.160)^2}{0.020 \text{ x } 0.020}$$

$$= \boxed{64.0}$$

EXAMPLE - 7

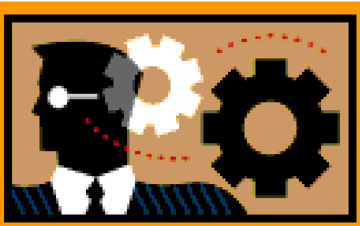
The atmospheric oxidation of nitric oxide,

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

was studied at 184°C with pressure of 1.000 atm of NO and 1.000 atm of O_2.

At equilibrium, P_{O_2} = 0.506 atm.

Calculate K_P.



EXAMPLE - 7

ANS:

	$2NO(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2NO_2(g)$
Initial (atm)	1.000	1.000	0.000
Change (atm)	$-\ 2x$	$-\ x$	$+\ 2x$
Equilibrium (atm)	$1.000 - 2x$	$1.000 - x$ $= 0.506$	$0.000 + 2x$ $= 2x$

So, $x = 1.000 - 0.506$

$= 0.494$

P_{NO} = (1.000 – 2x0.494) atm
= 0.012 atm

P_{NO_2} = 2x0.494 atm
= 0.988 atm

P_{O_2} = 0.506 atm

EXAMPLE - 7

ANS:

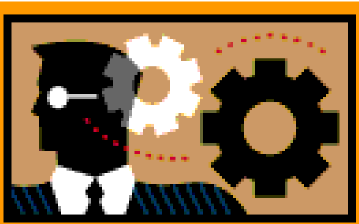
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

$P_{NO} = 0.012$ atm $\quad P_{O_2} = 0.506$ atm $\quad P_{NO_2} = 0.988$ atm

$$K_p = \frac{P^2_{NO_2}}{P^2_{NO}\,P_{O_2}}$$

$$= \frac{(0.988)^2}{(0.012)^2 \times 0.506}$$

$$= \boxed{1.34 \times 10^4}$$



EXAMPLE - 8

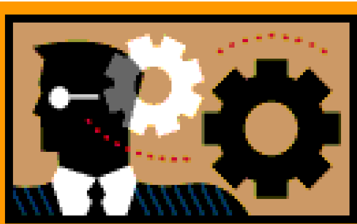
At 1280°C the equilibrium constant (K_c) for the reaction

$$Br_2(g) \rightleftharpoons 2Br(g)$$

is 1.1 x 10^{-3}. If the initial concentrations are $[Br_2]$ = 0.063 M and [Br] = 0.012 M, calculate the concentrations of these species at equilibrium.

ANS: **Let *x* be the change in concentration of Br_2**

	$Br_2(g)$ $\rightleftharpoons$	$2Br(g)$
Initial (M)	0.063	0.012
Change (M)	$-x$	$+2x$
Equilibrium (M)	$0.063 - x$	$0.012 + 2x$



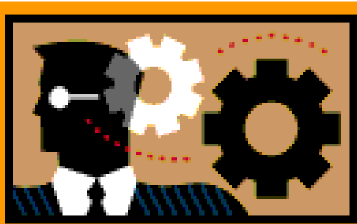
EXAMPLE - 8

ANS:

	$Br_2(g) \rightleftharpoons$	$2Br(g)$
Initial (M)	**0.063**	**0.012**
Change (M)	$-x$	$+2x$
Equilibrium (M)	$0.063 - x$	$0.012 + 2x$

$$K_c = \frac{[Br]^2}{[Br_2]} \qquad K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3}$$

☞ **Solve for *x***



EXAMPLE - 8

ANS:

$$Br_2(g) \rightleftharpoons 2Br(g)$$

	$Br_2(g)$	$2Br(g)$
Initial (M)	0.063	0.012
Change (M)	$-x$	$+2x$
Equilibrium (M)	$0.063 - x$	$0.012 + 2x$

$$K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3}$$

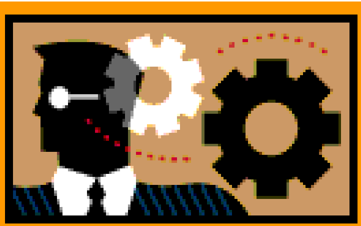
given

$$4x^2 + 0.048x + 0.000144 = 0.0000693 - 0.0011x$$

$$4x^2 + 0.0491x + 0.0000747 = 0$$

$$ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x = -0.0105$ $\qquad$ $x = -0.00178$



EXAMPLE - 8

ANS:

☞ **Determine chemically meaningful x value**

	$Br_2(g) \rightleftharpoons 2Br(g)$	
Initial (M)	**0.063**	**0.012**
Change (M)	**– x**	**+ 2x**
Equilibrium (M)	**0.063 – x**	**0.012 + 2x**
$(x = \cancel{-0.0105})$	$= \cancel{0.0705}$	$= \cancel{-0.009}$
(x = – 0.00178)	= 0.0648	= 0.00844

☑ correct

Note: Only one x value makes sense chemically!

At equilibrium, $[Br] = 0.00844$ M

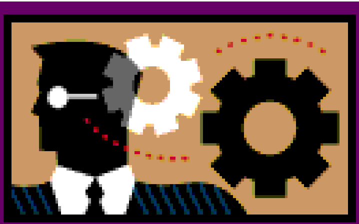
$[Br_2] = 0.0648$ M

EXERCISE - 22

At particular temperature, suppose that the initial temperatures of H_2, I_2, and HI are 0.00623 M, 0.00414 M and 0.0224 M.

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

Calculate the concentrations of these species ($[H_2]$, $[I_2]$, $[HI]$) at equilibrium.



EXERCISE - 23

At 1280^{o}C the equilibrium constant (K_C) for the reaction

$$Br_2(g) \rightleftharpoons 2Br(g)$$

is 1.1 x 10^{-3}. If the initial concentrations are $[Br_2]$ = 6.3 x 10^{-2} M and [Br] = 1.2 x 10^{-2} M. Calculate the concentrations of these species at equilibrium.

EXERCISE - 24

Consider the following equilibrium process at 686°C:

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

The equilibrium concentrations of the reacting species are [CO] = 0.050 M, [H_2] = 0.045 M, [CO_2] = 0.086 M, and [H_2O] = 0.040 M.

a) Calculate K_C for the reaction at 686°C.

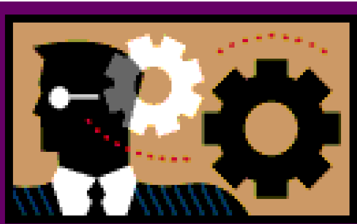
b) If we add CO_2 to increase its concentration to 0.50 M, what will be the concentrations of all gases be when equilibrium is reestablished?

EXERCISE - 25

In a particular experiment, it was found that when $O_2(g)$ and $CO(g)$ were mixed and reacted according to the equation

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

The O_2 concentration decreased by 0.030 M when the reaction reached equilibrium.
How had the concentrations of CO and CO_2 changed?



EXERCISE - 26

The reaction

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

has K_c = 4.06 at 500°C. If 0.100 mol of CO and 0.100 mol of H_2O(g) are placed in a 1.00 liter reaction vessel at this temperature, what are the concentration of the reactants and products when the system reaches equilibrium?

EXERCISE - 27

The reaction

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

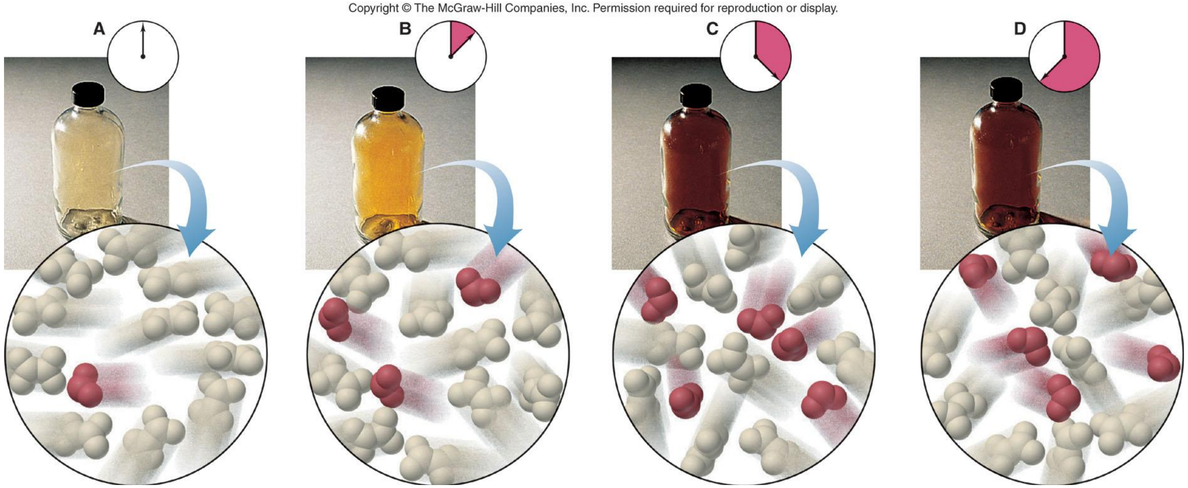
has K_c = 4.06 at 500°C.
Suppose 0.0600 mol each of CO and H_2O are mixed with 0.100 mol each of CO_2 and H_2 in a 1.00 L reaction vessel.
What will the concentrations of all the substances be when the mixture reaches equilibrium at this temperature?

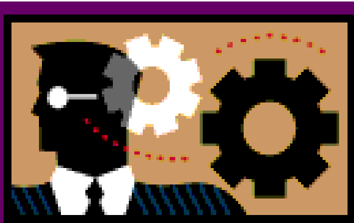
EXERCISE - 28

At a certain temperature K_C = 4.50 for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If 0.300 mol of N_2O_4 is placed into a 2.00 L container at this temperature, what will be the equilibrium concentrations of both gases?





EXERCISE - 29

Phosgene ($COCl_2$) is toxic substance that forms readily from carbon monoxide and chlorine at elevated temperatures:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

If 0.350 mol of each reactant is placed a 0.500–L flask at 600 K, what are the concentrations of each substance at equilibrium?
(K_C = 4.95 at this temperature)

Vocabulary: ***elevated***
increasing, high

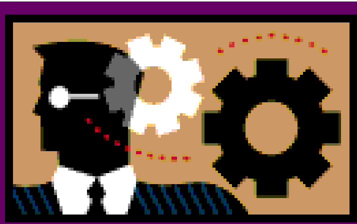
EXERCISE - 30

Fuel engineers use the extent of the change from CO and H_2O to CO_2 and H_2 to regulate the proportions of synthetic fuel mixture.

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

If 0.250 mol of CO and 0.250 mol of H_2O are placed in a 125–mL flask at 900 K, what is the equilibrium concentrations of each gas in the mixture?

At 900 K, K_c = 1.56.



EXERCISE - 31

A 1.000–L flask is filled with 1.000 mol of H_2 and 2.000 mol of I_2 at 448°C.

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

$$K_C = 50.5 \text{ at } 448^{o}C.$$

What is the partial pressure of H_2, I_2 and HI at equilibrium?

EXERCISE - 32

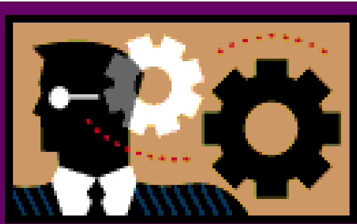
Hydrogen iodide decomposes according to the reaction

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

A sealed 1.50–L container initially holds 0.00623 mol of H_2, 0.00414 mol of I_2, and 0.0244 mol of HI at 703 K.

When equilibrium is reached, the concentration of $H_2(g)$ is 0.00467 M.

What are the equilibrium concentrations of HI(g) and $I_2(g)$?



EXERCISE - 33

Compound A decomposes according to the equation

$$A(g) \rightleftharpoons 2B(g) + C(g)$$

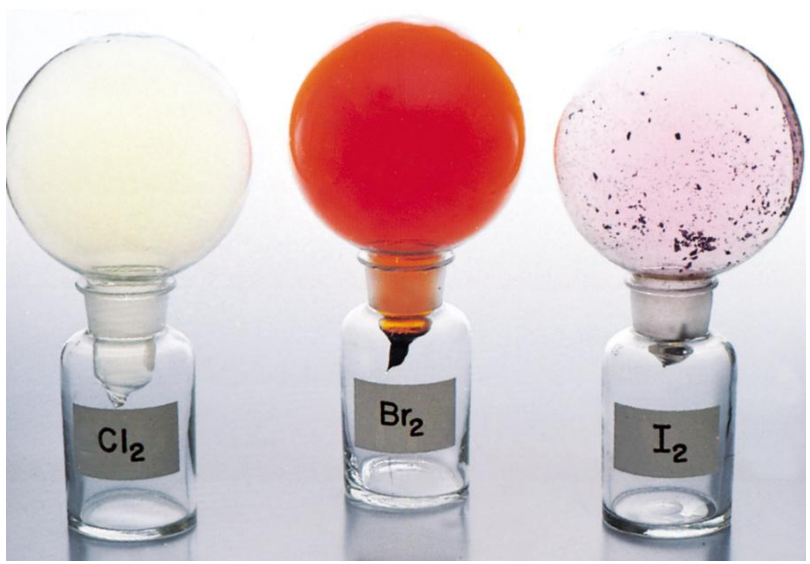
A sealed 1.50–L reaction vessel initially contains 1.75×10^{-3} mol of A(g), 1.25×10^{-3} mol of B(g), and 6.50×10^{-4} mol of C(g) at 100°C.
When equilibrium is reached, the concentration of A(g) is 2.15×10^{-3} M.
What are the equilibrium concentrations of B(g) and C(g) ?

EXERCISE - 34

0.500 mol of ICl was placed in a 5.00–L flask and allowed to decompose at a high temperature:

$$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$$

Calculate the equilibrium concentrations of I_2, Cl_2, and ICl. (K_C = 0.110 at this temperature)

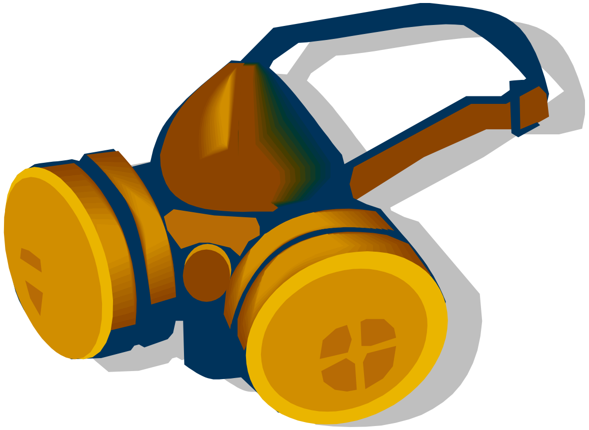


EXERCISE - 35

A United Nations toxicologist studying the properties of mustard gas, $S(CH_2CH_2Cl)_2$, a blistering agent used in warfare, prepares a mixture of 0.675 M SCl_2 and 0.973 M C_2H_4 and allows to react at room temperature (20.0°C):

$$SCl_2(g) + 2C_2H_4(g) \rightleftharpoons S(CH_2CH_2Cl)_2(g)$$

At equilibrium, $[S(CH_2CH_2Cl)_2]$ = 0.350 M. Calculate K_P.



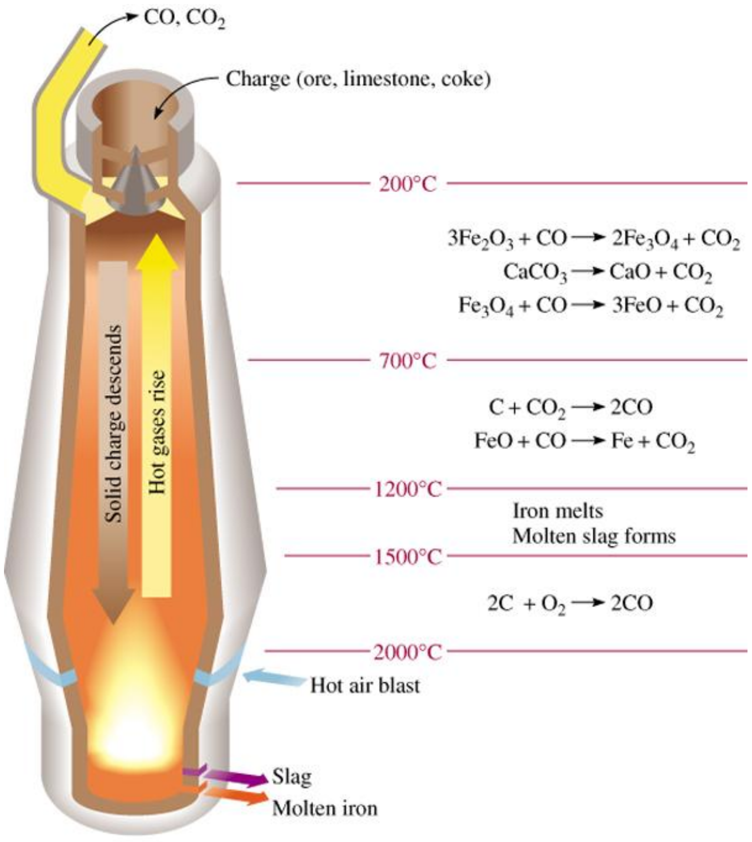
EXERCISE - 36

A key step in extraction of iron from its ore is

$$\mathbf{FeO(}\boldsymbol{s}\mathbf{)\ +\ CO(}\boldsymbol{g}\mathbf{)\ \rightleftharpoons\ Fe(}\boldsymbol{s}\mathbf{)\ +\ CO_2(}\boldsymbol{g}\mathbf{)}$$

K_P = 0.403 at 1000°C

What are the equilibrium partial pressure of CO(*g*) and CO_2(*g*) when 1.00 atm of CO(*g*) and excess FeO(*s*) react in a sealed container at 1000°C?



EXERCISE - 37

An industrial chemist introduces 2.0 atm of H_2 and 2.0 atm of CO_2 into a 1.00–L container at 25°C and then raises the temperature to 700°C, at which K_C = 0.534:

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

How many grams of H_2 are present after equilibrium is established?

EXERCISE - 38

A quality control engineer examining the conversion of SO_2 to SO_3 in the manufacture of sulfuric acid determines that $K_C = 1.7 \times 10^8$ at 600K for the reaction

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

a) At equilibrium $P_{SO_3} = 300$ atm and $P_{O_2} = 100$ atm. Calculate P_{SO_2}.

b) The engineer places a mixture of 0.0040 mol of $SO_2(g)$ and 0.0028 mol of $O_2(g)$ in a 1.0–L container and raises the temperature to 1000K. At equilibrium, 0.0020 mol of $SO_3(g)$ is present. Calculate K_C and P_{SO_2} for this reaction at 1000K.

EQULIBRIUM CALCULATIONS WHEN K_c IS VERY SMALL

☞ The **concentration change** (x) can often be **neglected**.

$$[A]_{initial} - x = [A]_{equilibrium} \approx [A]_{initial}$$

Note: You must check that the assumption is justified or not.

CHECK: 5% rule

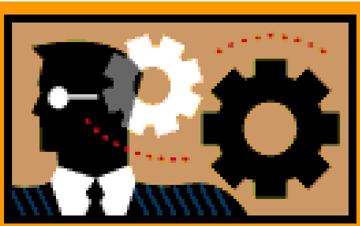
$$\frac{x}{[A]_{initial}} \times 100 < 5\%$$

☞ Assumption is OK

$$\frac{x}{[A]_{initial}} \times 100 > 5\%$$

☞ Assumption is NOT OK

☞ Use quadratic formula



EXAMPLE - 9

ANS:

Phosgene is a potent chemical warfare agent that is now outlawed by international agreement. It decomposes by the reaction

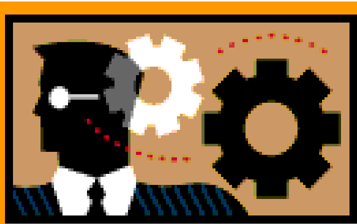
$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

$$K_c = 8.3 \times 10^{-4} \text{ (at 360}^{o}\text{C)}$$

Calculate [CO], [Cl_2], and [$COCl_2$], when the following amounts of phosgene decompose and reach equilibrium in a 10–L flask:

a) 5.000 mol of $COCl_2$

b) 0.100 mol of $COCl_2$



EXAMPLE - 9

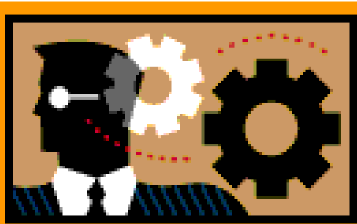
ANS:

a)

	$COCl_2(g) \rightleftharpoons$	$CO(g)$ +	$Cl_2(g)$
Initial (M)	$\frac{5.000 \text{ mol}}{10.0 \text{ L}}$ = 0.500	0.000	0.000
Change (M)	$- x$	$+ x$	$+ x$
Equilibrium (M)	$0.500 - x$	x	x

$$K_C = \frac{[CO][Cl_2]}{[COCl_2]} \qquad K_C = \frac{x^2}{(0.500 - x)} = 8.3 \times 10^{-4}$$

☞ Solve for x



EXAMPLE - 9

ANS:

$$K_C = \frac{[CO][Cl_2]}{[COCl_2]}$$

$$K_C = \frac{x^2}{(0.500 - x)} = 8.3 \times 10^{-4}$$

☞ **Solve for *x***

K_C is very small
Assume x very small, 0.500 – x ≈ 0.500

$$K_C = \frac{x^2}{0.500} = 8.3 \times 10^{-4}$$

$$x^2 = 8.3 \times 10^{-4} \times 0.500$$

$$x = 2.0 \times 10^{-2}$$

Checking the assumption:

$$\frac{2.0 \times 10^{-2}}{0.500} \times 100 = 4\ \% \quad (< 5\%)$$

OK!

EXAMPLE - 9

ANS:

	$COCl_2(g)$ $\rightleftharpoons$	$CO(g)$ +	$Cl_2(g)$
Initial (M)	= 0.500	0.000	0.000
Change (M)	– x	+ x	+ x
Equilibrium (M)	0.500 – x	x	x

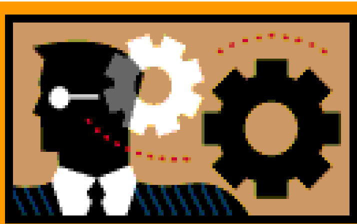
($x = 2.0 \times 10^{-2}$)

$[CO] = \boxed{2.0 \times 10^{-2}\ M}$

$[Cl_2] = \boxed{2.0 \times 10^{-2}\ M}$

$[COCl_2] = (0.500 - 2.0 \times 10^{-2})\ M$

$= \boxed{0.480\ M}$



EXAMPLE - 9

ANS:

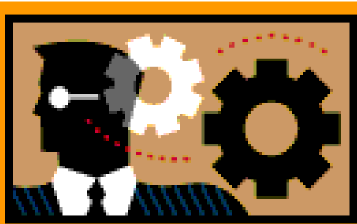
b)

	$COCl_2(g)$ $\rightleftharpoons$	$CO(g)$ +	$Cl_2(g)$
Initial (M)	$\frac{0.100\ \text{mol}}{10.0\ \text{L}}$ = 0.010	0.000	0.000
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.010 - x$	x	x

$$K_C = \frac{[CO][Cl_2]}{[COCl_2]}$$

$$K_C = \frac{x^2}{(0.010 - x)} = 8.3 \times 10^{-4}$$

☞ **Solve for x**



EXAMPLE - 9

ANS:

$$K_C = \frac{[CO][Cl_2]}{[COCl_2]}$$

$$K_C = \frac{x^2}{(0.010 - x)} = 8.3 \times 10^{-4}$$

☞ **Solve for *x***

K_c is very small

Assume x very small, 0.010 – x ≈ 0.010

$$K_C = \frac{x^2}{0.010} = 8.3 \times 10^{-4}$$

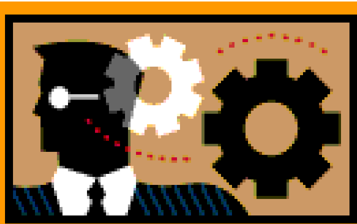
$$x^2 = 8.3 \times 10^{-4} \times 0.010$$

$$x = 2.9 \times 10^{-3}$$

Checking the assumption:

$$\frac{2.9 \times 10^{-3}}{0.010} \times 100 = 29\ \% \quad (> 5\%)$$

NOT OK!



EXAMPLE - 9

ANS:

$$K_C = \frac{[CO][Cl_2]}{[COCl_2]}$$

$$K_C = \frac{x^2}{(0.010 - x)} = 8.3 \times 10^{-4}$$

☞ **Solve for *x* using quadratic formula**

$$x^2 + (8.3 \times 10^{-4})x - 8.3 \times 10^{-6} = 0$$

Do it yourself

$x = 2.5 \times 10^{-3}$ **(the only meaningful value of *x*)**

$[CO] = 2.5 \times 10^{-3}$ M

$[Cl_2] = 2.5 \times 10^{-3}$ M

$[COCl_2] = (0.010 - 2.5 \times 10^{-3})$ M

$= 7.5 \times 10^{-3}$ M

DEGREE OF DISSOCIATION, α

Dissociation reaction: a molecule is broken down into smaller molecules, atoms or ions

EXAMPLE:

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

Fraction or the percentage of molecules that dissociate is called **degree of dissociation, α**

α = 1 or 100% if complete dissociation occurs

If incomplete dissociation occurs:

$$\alpha = \frac{[\ ]_{changes}}{[\ ]_{initial}} \times 100\%$$

THERMAL DISSOCIATION

- A **reversible reaction** brought about by the **application of heat**
- When **cool**, the **products bond again to give the original compound**
- Example: PCl_5, N_2O_4 and NH_4Cl

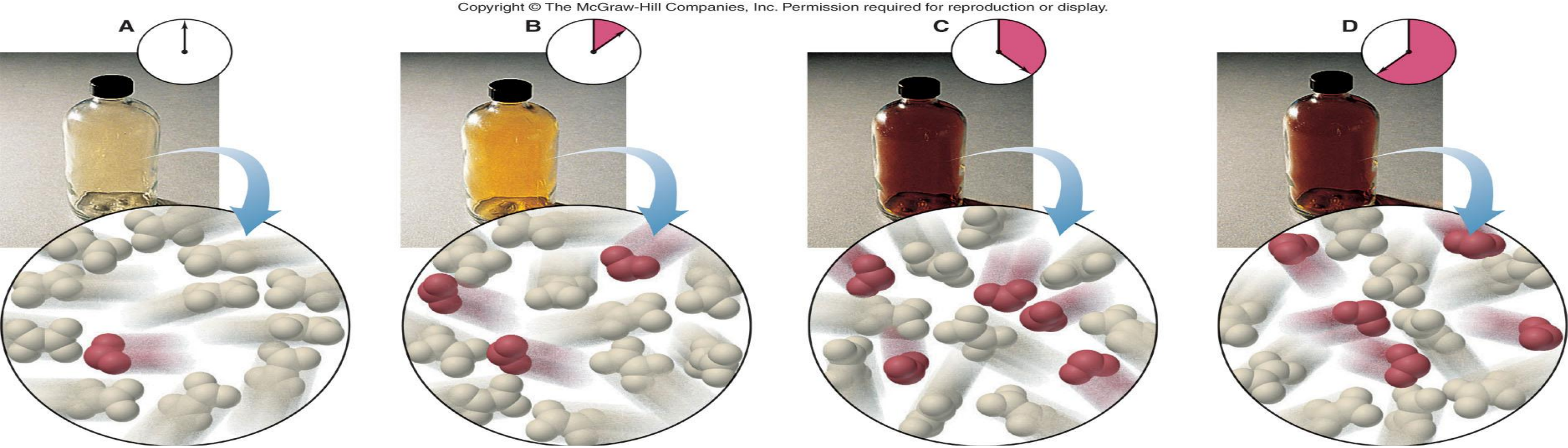
$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

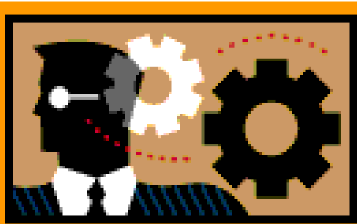
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$NH_4Cl(g) \rightleftharpoons NH_3\,(g) + HCl\,(g)$$

EXAMPLE - 10

The degree of dissociation of dinitrogen tetroxide at 250°C and 1 atm is 0.15. Calculate the degree of dissociation at 250°C and 5 atm.





EXAMPLE - 10

ANS:

According to Dalton's law of partial pressure:

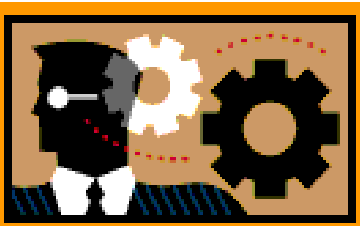
Partial pressure of NO_2 = 0.3/1.15 x 1atm = 0.261 atm

Partial pressure of N_2O_4 = 0.85/1.15 x 1atm = 0.739 atm

$$K_P = \frac{P_{NO2}^{\,2}}{P_{N2O4}}$$

$$K_P = \frac{0.261^2}{0.739}$$

$$= 9.21 \times 10^{-2} \text{ atm}$$



EXAMPLE - 10

ANS:

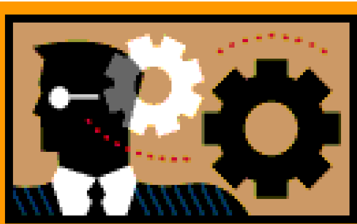
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

	$N_2O_4(g)$	$2NO_2(g)$
Initial (mol)	1	0
Changes	-0.15	+0.15
Equilibrium (mol)	1-0.15 = 0.85	2(0.15) = 0.30

Total number of moles after dissociation

= 0.85 + 0.30

= 1.15 mol



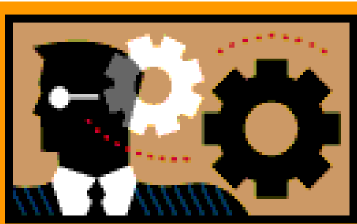
EXAMPLE - 10

ANS:

Let the degree of dissociation, α at 5 atm = x

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

	$N_2O_4(g)$	$2NO_2(g)$
Initial (mol)	1	0
Changes	-x	+x
Equilibrium (mol)	1- x	2x



EXAMPLE - 10

ANS:

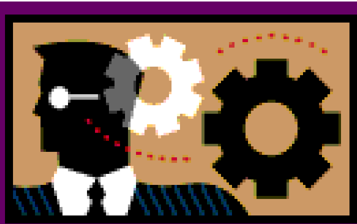
$$P_{NO2} = \frac{2x}{1 - x + 2x} \quad (5 \text{ atm})$$

$$P_{N2O4} = \frac{1\ x}{1 - x + 2x} \quad (5 \text{ atm})$$

$$K_P = \frac{(\ 2x / 1 + x\ )^2\ (5^2)}{(\ 1 - x / 1 + x\ )\ (5)} = 9.21 \text{ X } 10^{-2}$$

x = 0.068

Only 6.8% of dinitrogen tetroxide dissociates at 250°C and 5 atm



EXERCISE - 39

6.2

At a pressure of 4.4 x 10^5 Pa and a temperature of 150 °C, phosphorus pentachloride is 25% dissociated. Calculate the partial pressure equilibrium constant for this reaction.

EXERCISE - 40

6.2

Hydrogen, a potential fuel, is found in great abundance in water. Before hydrogen can be used as a fuel, however, it must be separated from oxygen; the water must be split into H_2 and O_2. one possibility is thermal decomposition, but this requires very high temperatures. Even at 1000°C, K_C = 7.3 x 10^{-18} for the reaction

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

If at 1000°C the H_2O concentration in a reaction vessel is set initially at 0.100 *M*, what will be the equilibrium concentration of H_2?

EXERCISE - 41

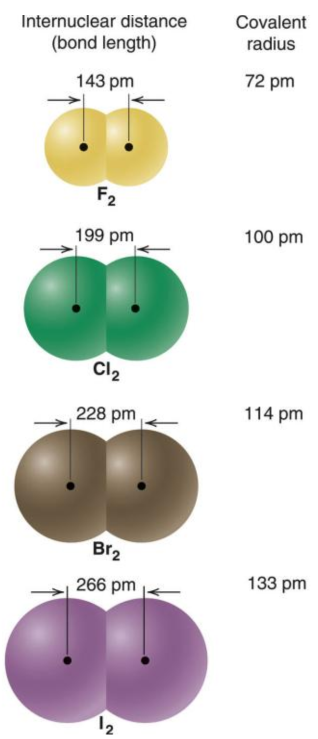
6.2

In a study of halogen bond strengths, 0.50 mol of I_2 was heated in a 2.5–L vessel, and the following reaction occurred:

$$I_2(g) \rightleftharpoons 2I(g)$$

a) Calculate $[I_2]$ and $[I]$ at equilibrium at 600K; $K_C = 2.94 \times 10^{-10}$

b) Calculate $[I_2]$ and $[I]$ at equilibrium at 2000K; $K_C = 0.209$



EXERCISE - 42

6.2

Even at high temperature, the formation of nitric oxide is not favored:

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

$$K_C = 4.10 \times 10^{-4} \text{ at } 2000^{o}C$$

What is the equilibrium concentration of NO(*g*) when a mixture of 0.20 mol of N_2(*g*) and 0.15 mol of O_2(*g*) is allowed to come to equilibrium in a 1.0–L container at this temperature?

EXERCISE - 43

6.2

Nitrogen dioxide decomposes according to the reaction:

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

where $K_P = 4.48 \times 10^{-13}$ at a certain temperature. A pressure of 0.75 atm of NO_2 is introduced into a container and allowed to come to equilibrium.

What are the equilibrium partial pressures of $NO(g)$ and $O_2(g)$?

EXERCISE - 44

6.2

The dissociation of molecular iodine into iodine atoms represented as

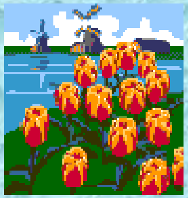
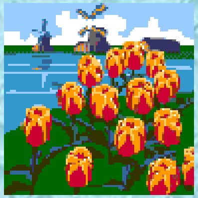
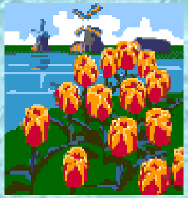
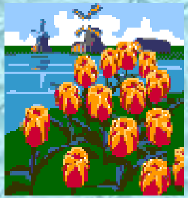
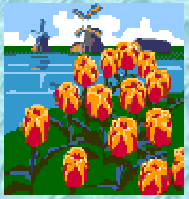
$$I_2(g) \rightleftharpoons 2I(g)$$

At 1000K, K_C for the reaction is 3.80×10^{-5}.
Suppose you start with 0.0456 mol of I_2 in a 2.30–L flask at 1000K.
What are the concentrations of the gases at equilibrium?





END OF SLIDE SHOW

CHEMICAL EQUILIBRIUM

6.2 Equilibrium Constants (Part III)

At the end of the lesson, students should be able to:

Deduce the expression for reaction quotient, *Q* and predict the direction of net reaction by comparing the values of *Q* and K_{eq}.

LESSON DURATION: 1 hour

REACTION QUOTIENT (Q)

- Calculated by substituting the **initial concentrations** (or **pressures**) of the reactants and products into K_C or K_P **expression**.

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

[A], [B], [C], [D] : equilibrium concentrations

$$Q_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

[A], [B], [C], [D] : any (initial) concentrations

COMPARING *Q* AND *K*

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

Suppose you know the value of K_c at any given temperature of the reaction.

How do you know if the reaction has reached equilibrium?

If it hasn't, how do you know in which direction it is progressing to reach equilibrium?

☞ **Compare the value of K_c and Q_c.**

COMPARING *Q* AND *K*

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g) \qquad Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

▪ $Q < K$

☞ **Denominator (reactants) is large relative to numerator (products)**

☞ **To reach equilibrium, $Q = K$:**
the products must increase, reactants decrease.

If $Q < K$, reactants $\longrightarrow$ products

The reaction will progress to the right (more product forms) until equilibrium is reached.

COMPARING *Q* AND *K*

$$aA(g) \quad + \quad bB(g) \rightleftharpoons cC(g) \quad + \quad dD(g) \qquad Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

■ $Q > K$

☞ **Denominator (reactants) is small relative to numerator (products)**

☞ **To reach equilibrium, $Q = K$:**
the products must decrease, reactants increase.

If $Q > K$, reactants $\longleftarrow$ products

The reaction will progress to the left (more reactant forms) until equilibrium is reached.

COMPARING *Q* AND *K*

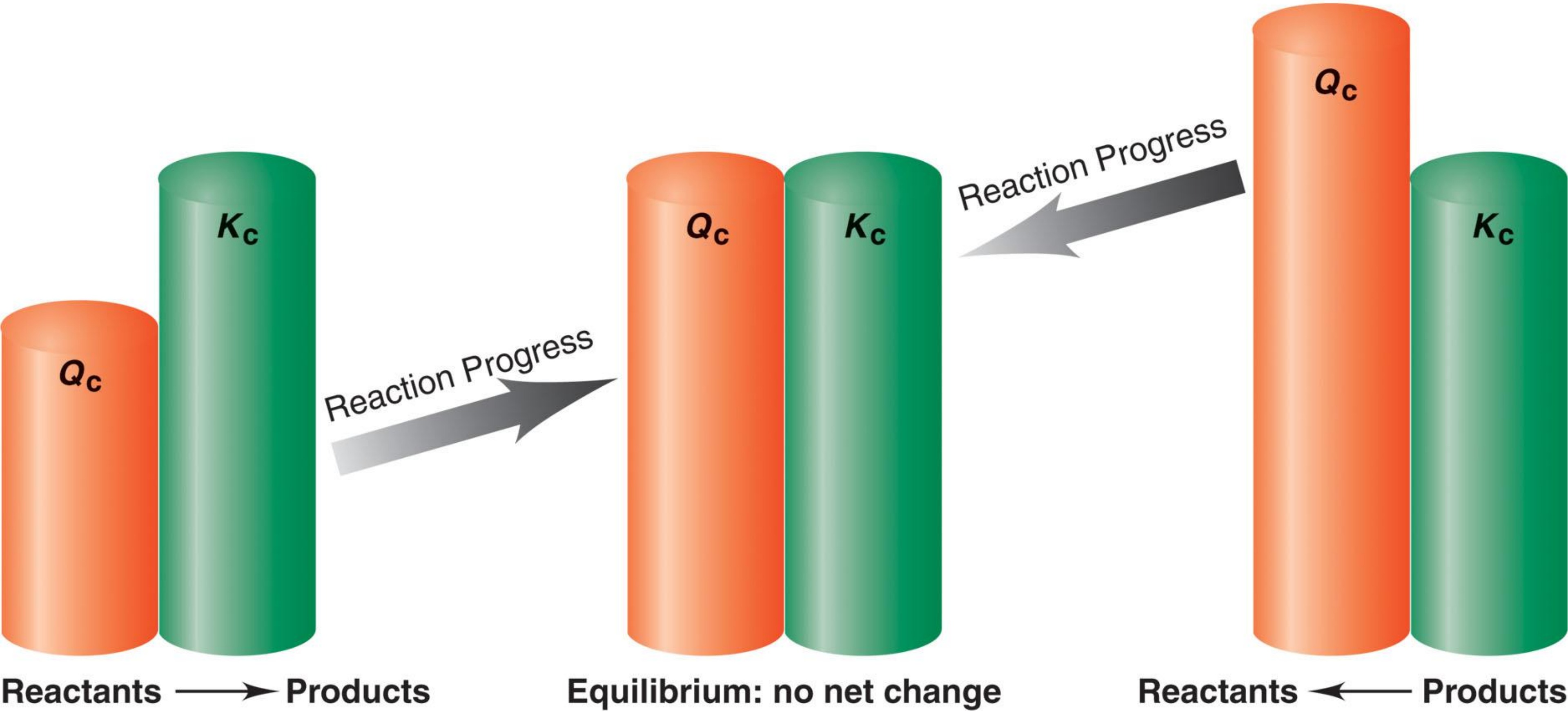
$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g) \qquad Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- **$Q = K$**

☞ **When the reactant and product concentrations (or pressures) has attained their equilibrium values.**

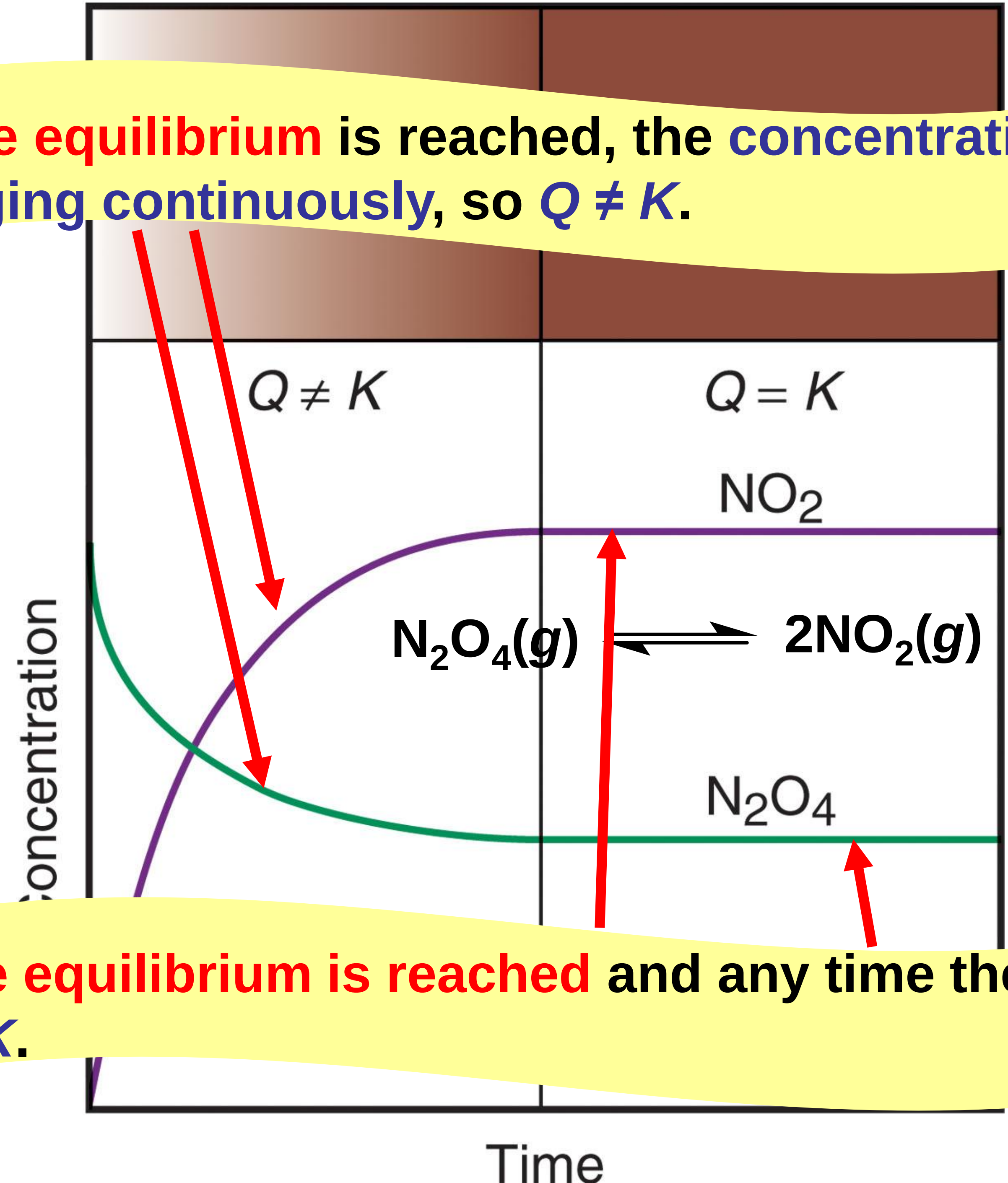
If $Q = K$, reactants $\rightleftharpoons$ products

No further net change.

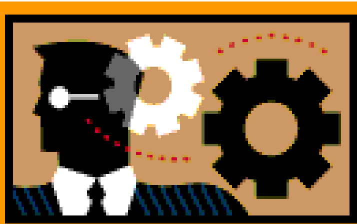

Q_c
K_c
Reaction Progress
Q_c
K_c
Reaction Progress
Q_c
K_c
Reactants ⟶ Products
Equilibrium: no net change
Reactants ⟵ Products

- ***Q* < *K***
- ***Q* = *K***
- ***Q* > *K***

Before equilibrium is reached, the **concentration are changing continuously**, so $Q \neq K$.



Once equilibrium is reached and any time thereafter, $Q = K$.



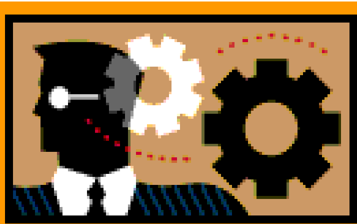
EXAMPLE - 11

K_C for the formation of nitrosyl chloride, an orange–yellow compound, from nitric oxide and molecular chlorine

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

is 6.5×10^4 at 35°C. In certain experiment, 2.0×10^{-2} mole of NO, 8.3×10^{-3} mole of Cl_2, and 6.8 moles of NOCl are mixed in a 2.0–L flask.

In which direction will the system proceed to reach equilibrium?



EXAMPLE - 11

ANS:

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

$$K_C = 6.5 \times 10^4$$

$$Q_C = \frac{[NOCl]^2}{[NO]^2\,[Cl_2]}$$

Initial concentrations:

$$[NOCl_2] = \frac{6.8 \text{ mol}}{2.0 \text{ L}}$$

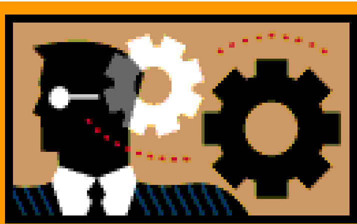
$$= 3.4 \text{ M}$$

$$[NO] = \frac{2.0 \times 10^{-2} \text{ mol}}{2.0 \text{ L}}$$

$$= 0.01 \text{ M}$$

$$[Cl_2] = \frac{8.3 \times 10^{-3} \text{ mol}}{2.0 \text{ L}}$$

$$= 0.0042 \text{ M}$$



EXAMPLE - 11

ANS:

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

$K_C = 6.5 \times 10^4$

Initial concentrations:

$[NOCl_2] = 3.4\ M$

$[NO] = 0.01\ M$

$[Cl_2] = 0.0042\ M$

$$Q_C = \frac{[NOCl]^2}{[NO]^2 [Cl_2]}$$

$$= \frac{3.4^2}{0.01^2 \times 0.0042}$$

$$= 2.75 \times 10^7$$

$Q_C > K_C$

(2.75×10^7) (6.5×10^4)

Numerator (products) is larger than denominator (reactants)

The reaction is not at equilibrium and will proceed to the left until $Q_C = K_C$.

Summary of the steps involved in solving equilibrium problems

PRELIMINARY SETTING UP

1. Write the balanced equation
2. Write the reaction quotient, Q
3. Convert all amounts into the correct units (M or atm)

WORKING ON THE REACTION TABLE

4. When reaction direction is not known, compare Q with K
5. Construct a reaction table

✓Check the sign of x, the change in the quantity

SOLVING FOR x AND EQUILIBRIUM QUANTITIES

6. Substitute the quantities into Q
7. To simplify the math, assume that x is negligible ($[A]_{init} - x = [A]_{eq} \approx [A]_{init}$)
8. Solve for x

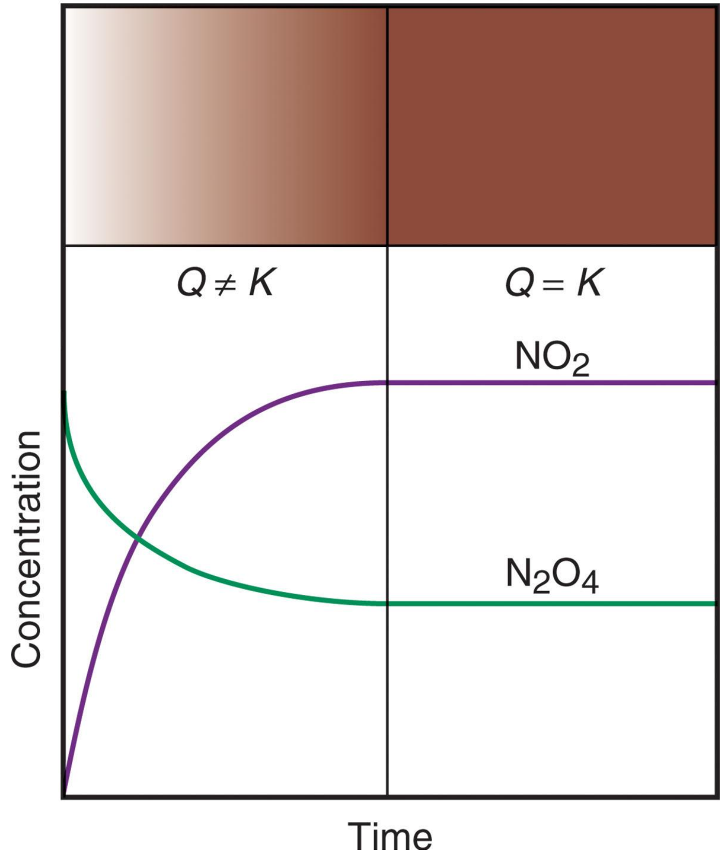
✓Check that assumption is justified (< 5% error). If not, solve quadratic equation for x.

9. Find the equilibrium quantities

✓Check to see that calculated values give the known K

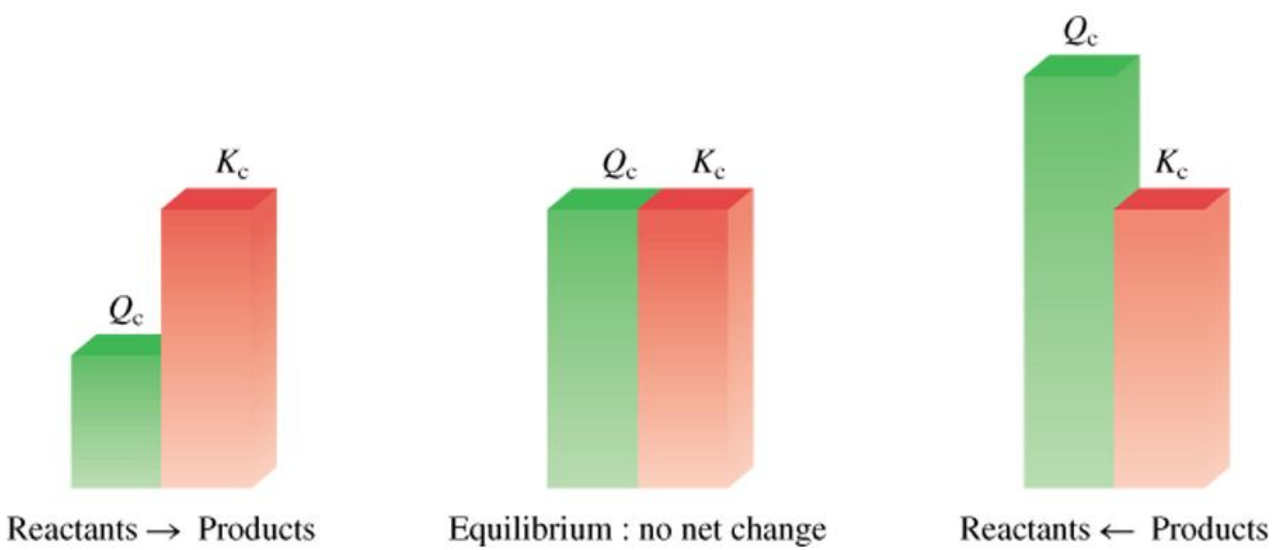
EXERCISE - 45

State three criteria that characterize a chemical system that characterize a chemical system at equilibrium.



EXERCISE - 46

State the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$,
K_C = 0.21 at 100°C. At a point during the reaction,
$[N_2O_4]$ = 0.12 M and $[NO_2]$ = 0.55 M.
Is the reaction at equilibrium?
If not, in which direction is it progressing?



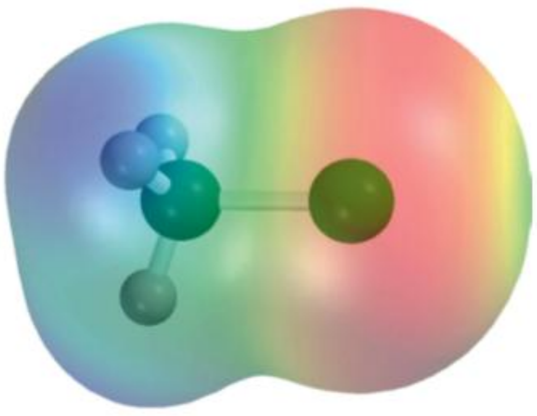
EXERCISE - 47

Chloromethane forms by the reaction

$$CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g),$$

At 1500 K, $K_P = 1.6 \times 10^4$. In the reaction mixture,
$P_{CH_4} = 0.13$ atm, $P_{Cl_2} = 0.035$ atm
$P_{CH_3Cl} = 0.24$ atm, and $P_{HCl} = 0.47$ atm.

Is CH_3Cl or CH_4 forming?



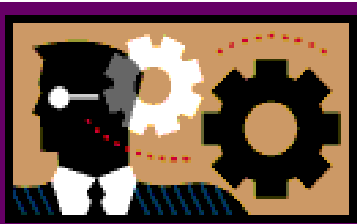
Chloromethane (CH_3Cl)

EXERCISE - 48

At the start of a reaction, there are 0.249 mol N_2, 3.21×10^{-2} mol H_2, and 6.42×10^{-4} mol NH_3 in a 3.50–L reaction vessel at 375°C.
If K_C for the reaction

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

is 1.2 at this temperature, decide whether the system is at equilibrium.
If not, predict which way the net reaction will proceed.

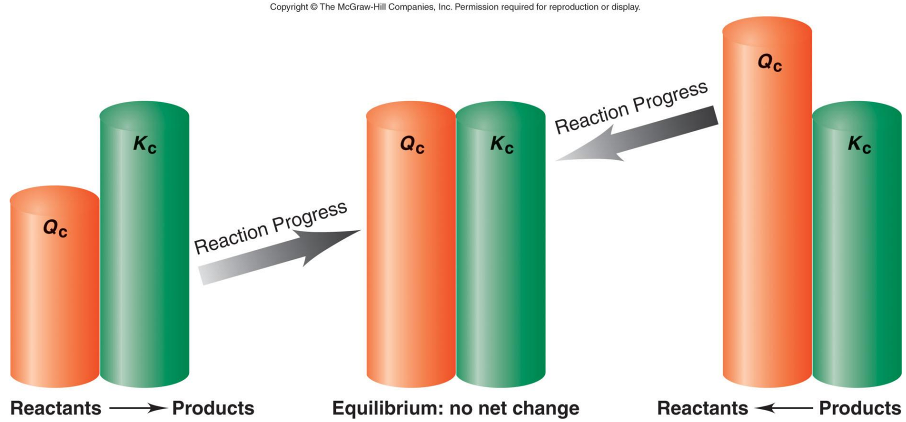


EXERCISE - 49

For the synthesis of ammonia

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

K_c at 375°C is 1.2. Starting with $[H_2]$ = 0.76 M, $[N_2]$ = 0.60 M, $[NH_3]$ = 0.48 M, which gases will increased in concentration and which will have decreased in concentration when the mixture comes to equilibrium?



EXERCISE - 50

At 425°C, K_P = 4.18 x 10^{-9} for the reaction

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$$

In one experiment, 0.20 atm of HBr(g), 0.010 atm of $H_2(g)$, and 0.010 atm of $Br_2(g)$ are introduced into a container.

Is the system at equilibrium?

If not, in which direction will it proceed?

EXERCISE - 51

At 100°C, K_P = 60.6 for the reaction

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

In a given temperature, 0.10 atm of each component is placed in a container.

Is the reaction at equilibrium?

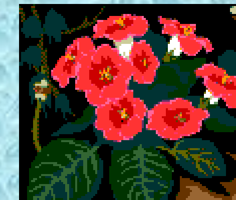
If not, in which direction will it proceed?

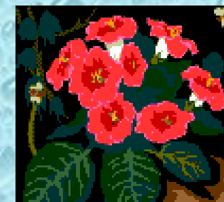
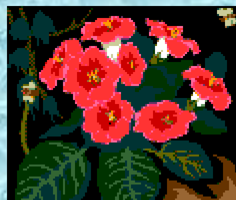
EXERCISE - 52

The water–gas shift reaction plays a central role in the chemical methods for obtaining cleaner fuels from coal:

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

In a given temperature, $K_P = 2.7$.
If 0.13 mol of CO, 0.56 mol of H_2O, 0.62 mol of CO_2, and 0.43 mol of H_2 are introduced into a 2.0–L flask, in which direction must the reaction proceed to reach equilibrium?




END OF SLIDE SHOW