Chemical Equilibrium

$$A \xrightleftharpoons[k_r]{k_f} B$$
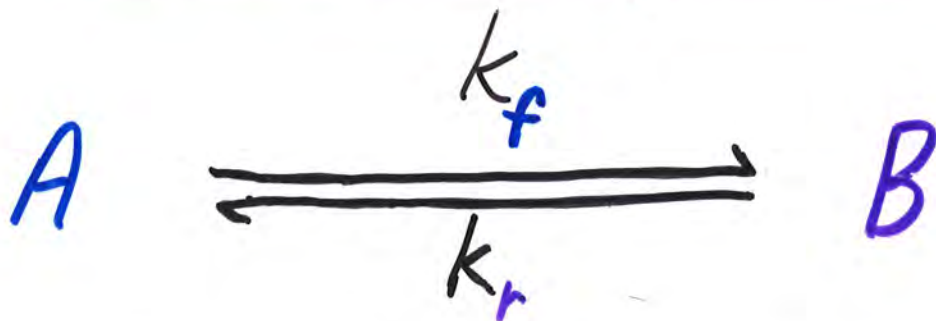
If forward & rev. rx's are **elementary** rx's,
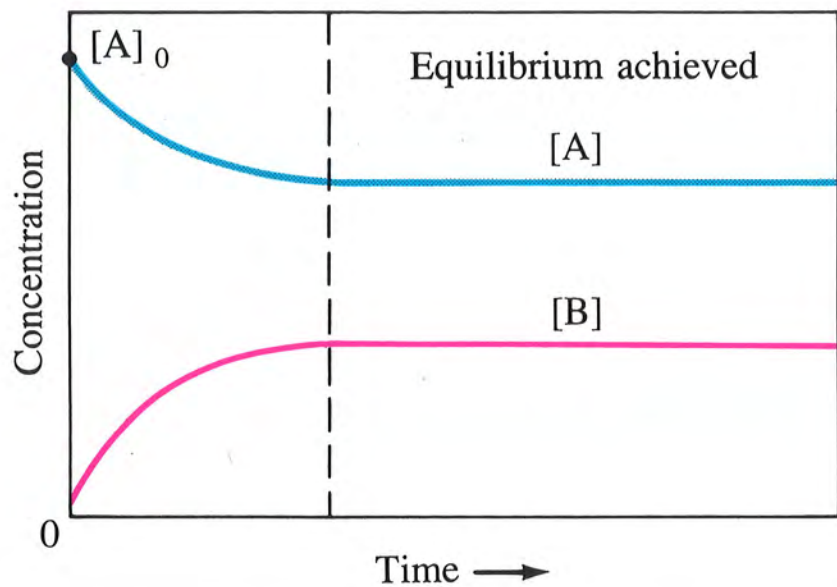
$$r_f = k_f [A]$$

$$r_r = k_r [B]$$

As A gets converted to B,

[A] dec. & [B] inc.

Also, r_f dec.

r_r inc.
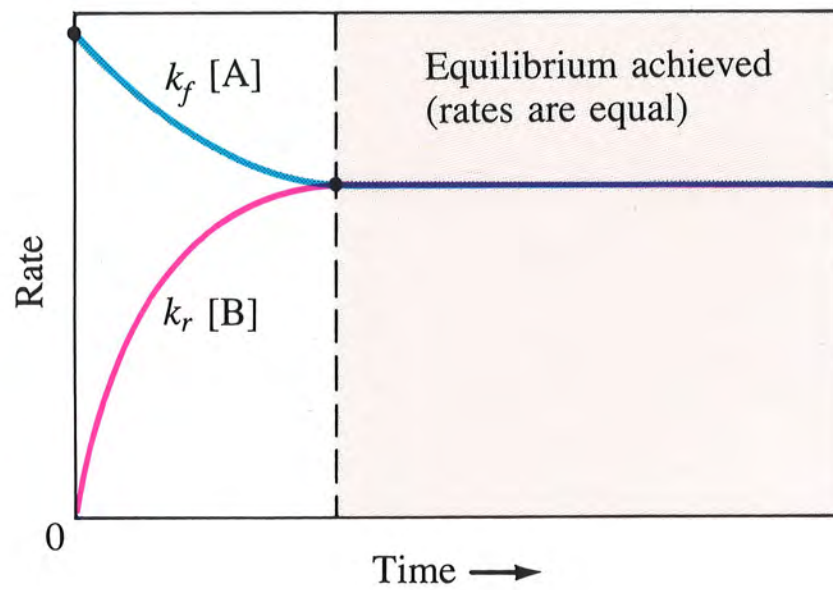
Figure 15.2 Achieving chemical equilibrium for the reaction A$\rightleftharpoons$B

Concentration

[A]$_0$

Equilibrium achieved

[A]

[B]

0

Time ⟶

(a)

Rate

k_f [A]

Equilibrium achieved
(rates are equal)

k_r [B]

0

Time ⟶

(b)

Eventually, $r_f = r_r$ & get

dynamic chemical equilibrium

Also, at equilibrium
$$[A] + [B] \text{ are constant}$$

Since $r_f = r_r$,

$$k_f [A] = k_r [B]$$

$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

$$K_c \equiv \text{Equilibrium Constant}$$

II) Equilibrium Constant

Equilibrium can be reached from **either** direction

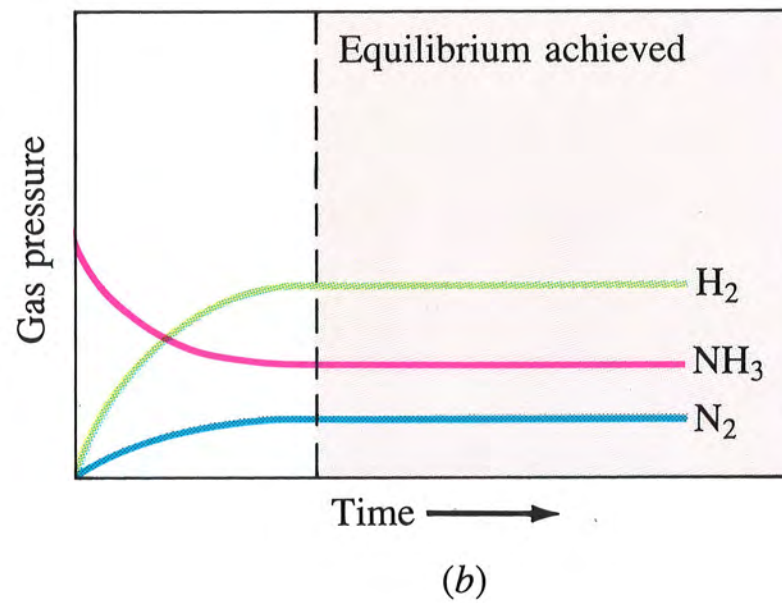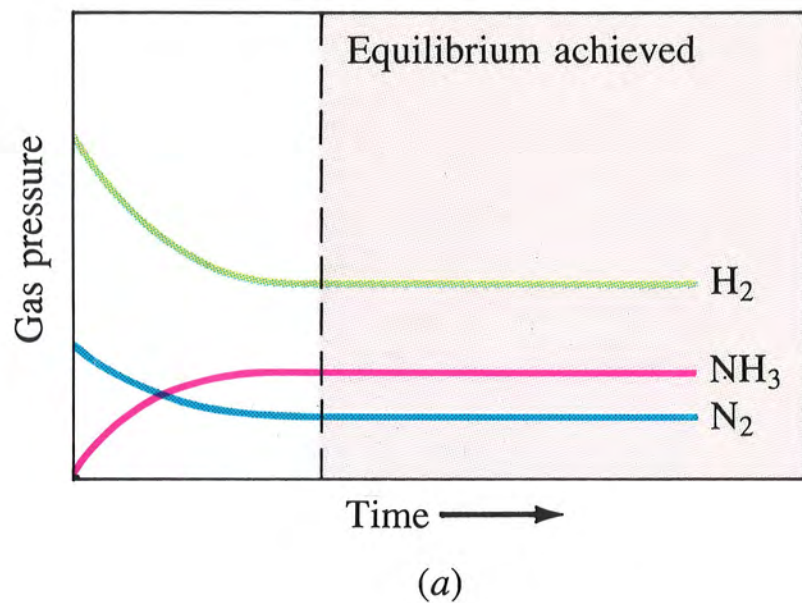For general rx,

$$aA + bB \rightleftharpoons dD + eE$$

A) Law of Mass Action

At equil. the relative conc. of reactants & products can be expressed in terms of a **constant** quantity called the equilibrium constant.

$$K_c = \frac{[D]^d [E]^e}{[A]^a [B]^b}$$

Figure 15.5 Variation in pressures achieving equilibrium for $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(a)

(b)

Remember,

Rate law can only be determined from exp.

Law of mass action, K_c, can be written from balanced chemical equation.

1) coef. in bal. eqn. are used as exponents of conc.'s.

2) Products in numerator
Reactants in denominator

Note:

Condition of equilibrium is,

$$r_f = r_r$$

& $$K_c = constant$$

1) **Ex**

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad (1)$$

$$K_c =$$

Exp. determine K_c
- look at a number of
  equil. systems

At 500°C

$[H_2]$	$[N_2]$	$[NH_3]$	K_c
0.500	1.00	8.66×10^{-2}	
1.35	1.15	4.12×10^{-1}	

2) **Ex** : Variation of K_C w. form of bal. eqn.

a) What is K_C for rx. below in terms of K_{C_1} for previous rx.

$$2\,NH_3 \rightleftharpoons N_2 + 3\,H_2 \qquad (2)$$

b) Give K_C for rx. below in terms of K_{C_1}

$$\tfrac{1}{2}\,N_2 + \tfrac{3}{2}\,H_2 \rightleftharpoons NH_3 \qquad (3)$$
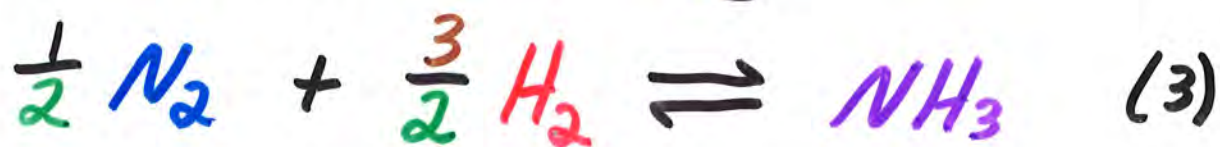
General Rule

If 2 rx's (eqn's) can be *added* to give a 3rd rx. (eqn.) then K_3 is *product* of K_1 & K_2

$$Rx_1 + Rx_2 = Rx_3$$
$$K_1 \times K_2 = K_3$$

(1) $aA + bB \rightleftharpoons xX + yY$

(2) $cC + dD \rightleftharpoons rR + sS$

B) Magnitude of K

Tells us about **position** of **equil.**
  - **extent** to which a rx.
    proceeds toward **completion**

1) Ex

$$H_2 + Cl_2 \rightleftharpoons 2\,HCl, \quad 25°C$$

$$K_c = \frac{[HCl]^2}{[H_2][Cl_2]} = 4.4 \times 10^{32}$$

rx. essentially **complete**
(**equil.** lies to **right**)

2) Ex

$$2\,H_2O \rightleftharpoons 2\,H_2 + O_2, \quad 25°C$$

$$K_c = \frac{[H_2]^2[O_2]}{[H_2O]^2} = 1.1 \times 10^{-81}$$

equil. lies to **left** - **NO** rx.

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3) a) K is very large ($> 10^2$):

    — mostly products

    rx. goes to "completion"

b) K is very small (< 0.01):

    — mostly reactants

    forward rx. does not
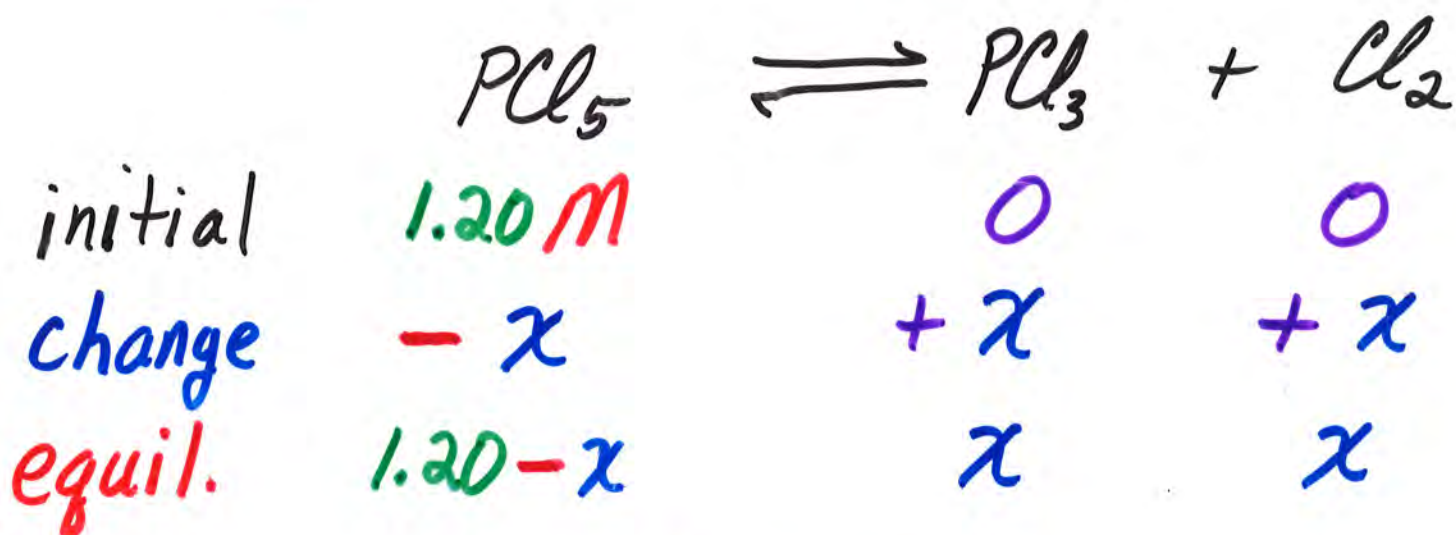
    occur to any great extent

c) K close to 1 ($0.01 - 100$)

    appreciable amt's of

    both reactants & products

III) Evaluating K

A) Determine K_c given equil. conc. if

1.20 mole PCl_5 is put in 1.0 L container at 200°C. At equil. 1.00 mole remains. Calc. K_c.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2
initial	1.20 M	0	0
change	$-x$	$+x$	$+x$
equil.	$1.20 - x$	x	x

$$1.20 - x = 1.00$$

$$x = [PCl_3] = [Cl_2] = 0.20 \text{ M}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{[0.20][0.20]}{[1.00]}$$

$$= 0.040 \text{ (M)}$$

B) Gas Phase Rx's (K_P)

Express equil. constant in terms of conc., K_C, or pressure, K_P.

$$K_P = \frac{P_D^d \cdot P_E^e}{P_A^a \cdot P_B^b}$$

numerically diff. from K_C

Derive relationship of K_P to K_C

Assume ideal gas,
$$PV = nRT$$

Relate partial pressure to conc.

$$P = \frac{n}{V} RT = M RT$$

$$P_A = [A] RT$$

Substitute into K_P,

$$K_P = \frac{[D]^d (RT)^d [E]^e (RT)^e}{[A]^a (RT)^a [B]^b (RT)^b}$$

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

$$\Delta n = (d + e) - (a + b)$$

$$\Delta n = \sum_{prod} n_{prod} - \sum_{react} n_{react}$$

$$K_P = K_C \quad \text{when} \quad \Delta n = 0$$

$$K_P = \frac{[D]^d (RT)^d [E]^e (RT)^e}{[A]^a (RT)^a [B]^b (RT)^b}$$

$$= \frac{[D]^d [E]^e}{[A]^a [B]^b} \cdot \frac{(RT)^d (RT)^e}{(RT)^a (RT)^b}$$

$$= K_C \cdot \frac{(RT)^{d+e}}{(RT)^{a+b}}$$

$$= K_C \cdot (RT)^{(d+e)-(a+b)}$$

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

1) Ex.1 : Evaluate K_p given K_c

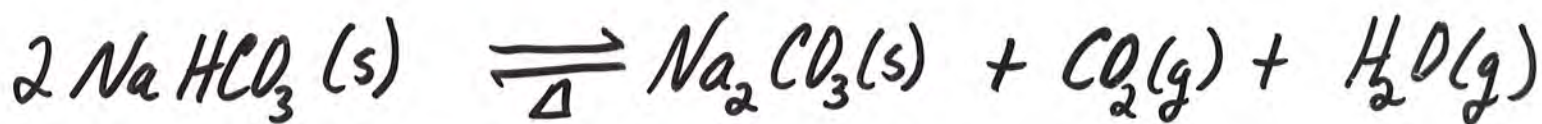Determine K_p for decomp. of PCl_5 at 200°C. $K_c = 0.040$

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

2) Ex.2 : How are K_p & K_c related?

$$X + 2Y \rightleftharpoons 3Z$$

IV) Heterogeneous Equilibria

Substances in equilibrium are in **different** phases.

$$2\,NaHCO_3\,(s) \;\underset{\Delta}{\overset{}{\rightleftharpoons}}\; Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$K_c = \frac{[Na_2CO_3][CO_2][H_2O]}{[NaHCO_3]^2}$$

However, conc. of Na_2CO_3 & $NaHCO_3$ are **constant**

For Na_2CO_3, $D = 2.51\,g/cm^3$

$$\frac{2.51\,g}{cm^3} \times \frac{1\,mol}{106\,g} \times \frac{10^3\,cm^3}{1L} = 23.7\,M$$

Conc. of **solid** does **not** **change** to any appreciable extent.

Incorporate these into K_C

$$K_C \cdot \frac{[NaHCO_3]^2}{[Na_2CO_3]} = [CO_2][H_2O]$$

$$K_c' = [CO_2][H_2O]$$

Same thing applies to liquids

$$[H_2O(\ell)] = 55.\overline{5} \; M$$

Effectively, ignore conc. of pure liquids or solids even though must be physically present in equil. mixture

Ex: Saturated AgCl soln.

$$AgCl(s) + H_2O(\ell) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
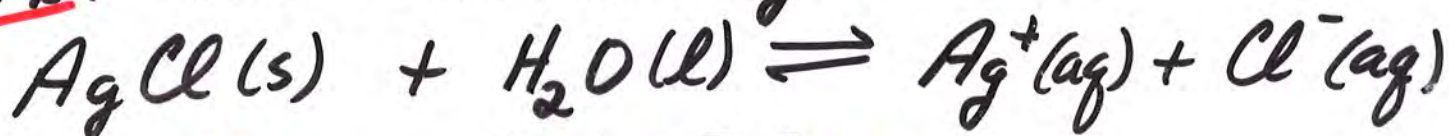
$$K_{sp} = [Ag^+][Cl^-]$$

Solubility Product Constant

A) Ex: What is the expression for K_c for the reaction below?

$$CaCO_3(s) + 2HCl(aq) \rightleftharpoons CaCl_2(aq) + H_2O(l) + CO_2(g)$$

B) Ex: What is the expression for K_p & K_c for the rx. below?

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

V) Applications of Equilibrium Constants

A) Reaction Quotient

If start rx. w. some initial conc., system moves toward equil. in direction req'd. to satisfy the constancy of K expression.

$$Q_c = \frac{[D]_i^d \, [E]_i^e}{[A]_i^a \, [B]_i^b}$$

$[D]_i \equiv$ initial conc

Compare to equil. constant, K_c

1) $\underline{Q_c = K_c}$
rx. at equilibrium

2) $\underline{Q_c > K_c}$

numerator too large

– rx. goes to left –
     [Products] dec.
     [Reactants] inc.
until equil. reached

3) $\underline{Q_c < K_c}$

denominator too large

– rx. goes to right –
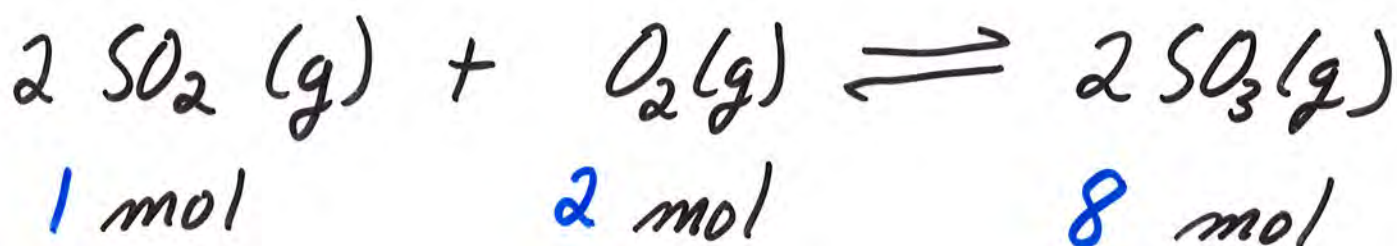   [Products] inc.
     [Reactants] dec.

Ex:

Is the following rx. at equil? If not in which direction will rx. proceed?

$K_c = 100 \quad (m^{-1})$ Vol. = 10L

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

1 mol   2 mol   8 mol

$Q_c =$

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B) Determine Equil. Conc.

Calc. equil. conc. given
initial conc. & K_c

1) Write chem. eqn.

2) Determine equil. conc.
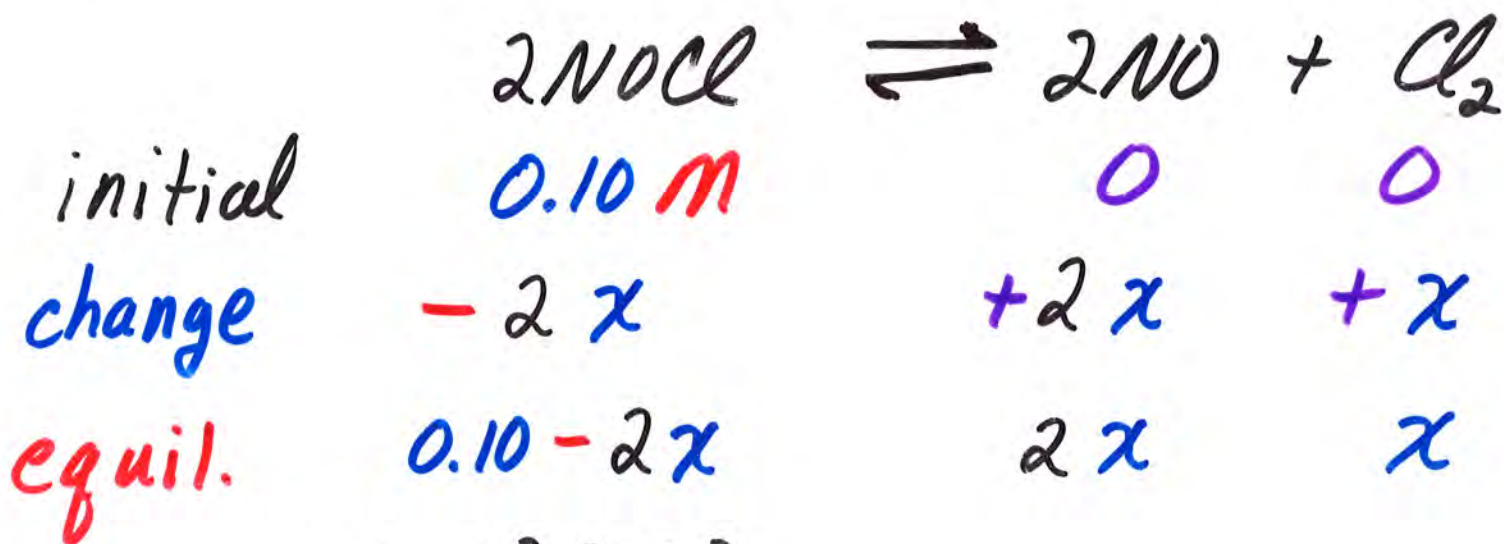using table of initial
conc. and change in conc.

   ICE

3) Write K_c expression

4) substitute & solve
for equil. conc.

Ex:

Gas phase dissociation of $NOCl$ has $K_c = 4.7 \times 10^{-7}$ at a particular temp. Calc. equil. conc's of all species if 0.10 mole $NOCl$ is placed in a 1.0 L container.

$$2NOCl \rightleftharpoons 2NO + Cl_2$$

	$2NOCl$	$2NO$	Cl_2
initial	0.10 M	0	0
change	$-2x$	$+2x$	$+x$
equil.	$0.10 - 2x$	$2x$	x

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

Small K_C - equil. lies to left

  — very little NOCl dissociates

$$2x \ll 0.10$$

$\therefore$ assume, $0.10 - 2x \cong 0.10$

Ex 2: The following gas phase reaction has an equilibrium constant, K_c, of 4.0×10^2 at 20°C. The reaction is started with 1.000 M of each product. What are the equilibrium concentrations of all species?

$$2 \text{ AB} \quad \rightleftharpoons \quad A_2 \quad + \quad B_2$$