Chapter 13
Chemical Equilibrium

Topics

- What is meant by equilibrium?
- Equilibrium conditions
- Equilibrium constant and law of mass action
- Equilibrium expressions involving pressures
- Heterogeneous equilibria
- Applications of equilibrium constant and solving equilibria problems
- Le Chatelier’s Principle

Introduction Chemical Equilibrium

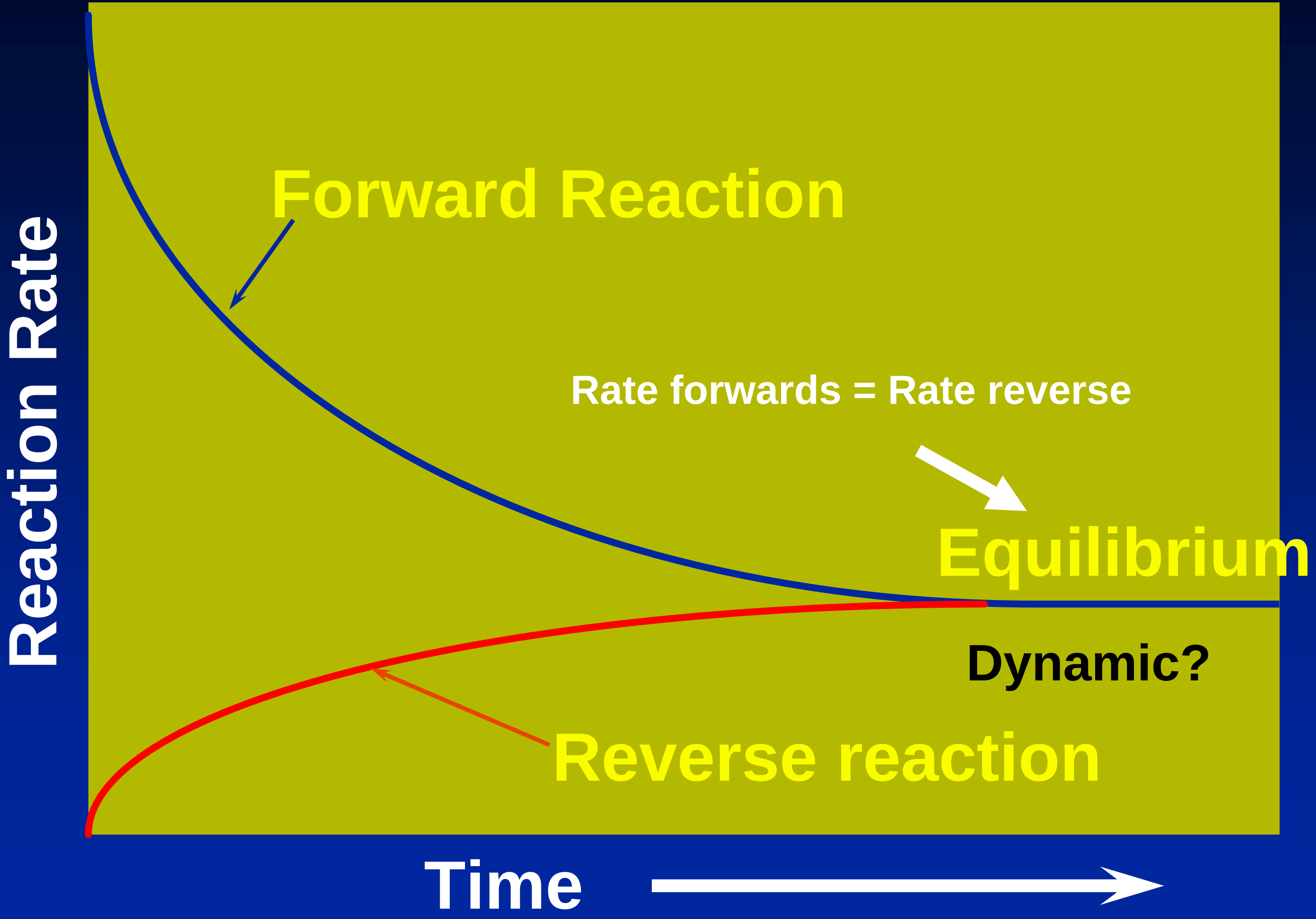
- The state where the concentrations of all reactants and products **remain constant** with time.

- Equilibrium is **not static**, but is a highly dynamic situation.

13.1 The Equilibrium Conditions

Reactions are reversible

- $A + B \longrightarrow C + D$ (forward)
- $C + D \longrightarrow A + B$ (reverse)
- Initially there is only A and B so only the forward reaction is possible
- As C and D build up, the reverse reaction speeds up while the forward reaction slows down.
- Eventually the rates are equal



Forward Reaction

Rate forwards = Rate reverse

Equilibrium

Dynamic?

Reverse reaction

Reaction Rate

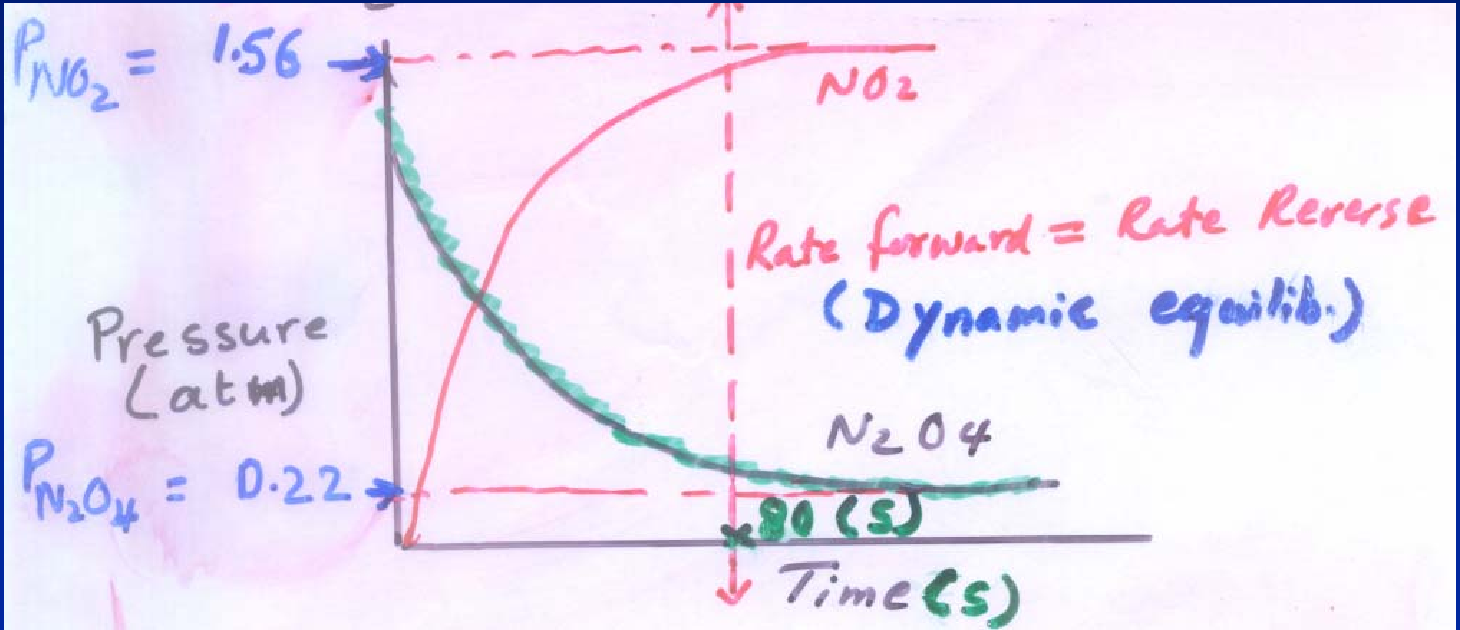
Time

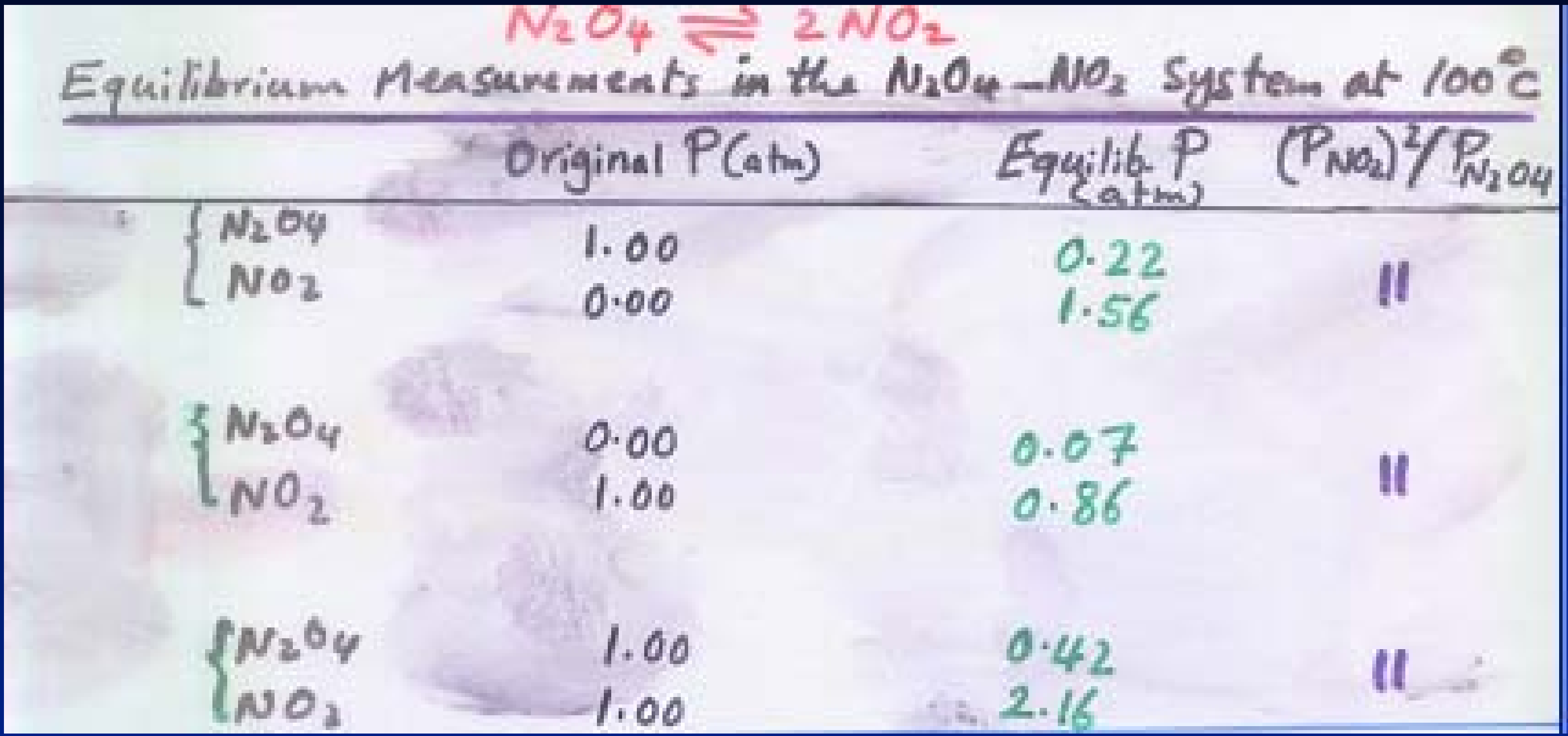
The N_2O_4 - NO_2 Equilibrium System

$$N_2O_4\ (g) \xrightarrow{\text{Forward}} 2NO_2\ (g)$$

$$2NO_2\ (g) \xrightarrow{\text{Reverse}} N_2O_4\ (g)$$

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

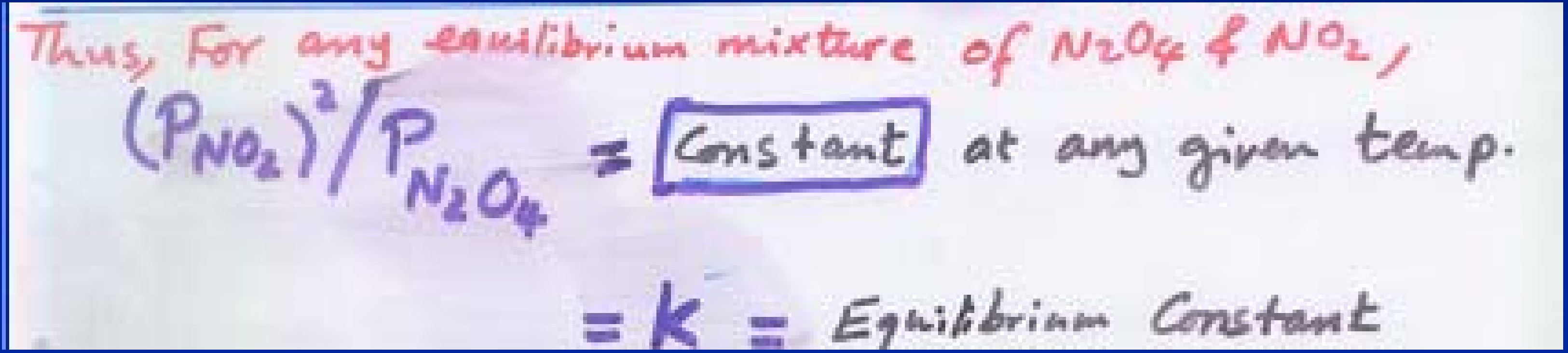




$N_2O_4 \rightleftharpoons 2NO_2$

Equilibrium Measurements in the N_2O_4–NO_2 System at 100°C

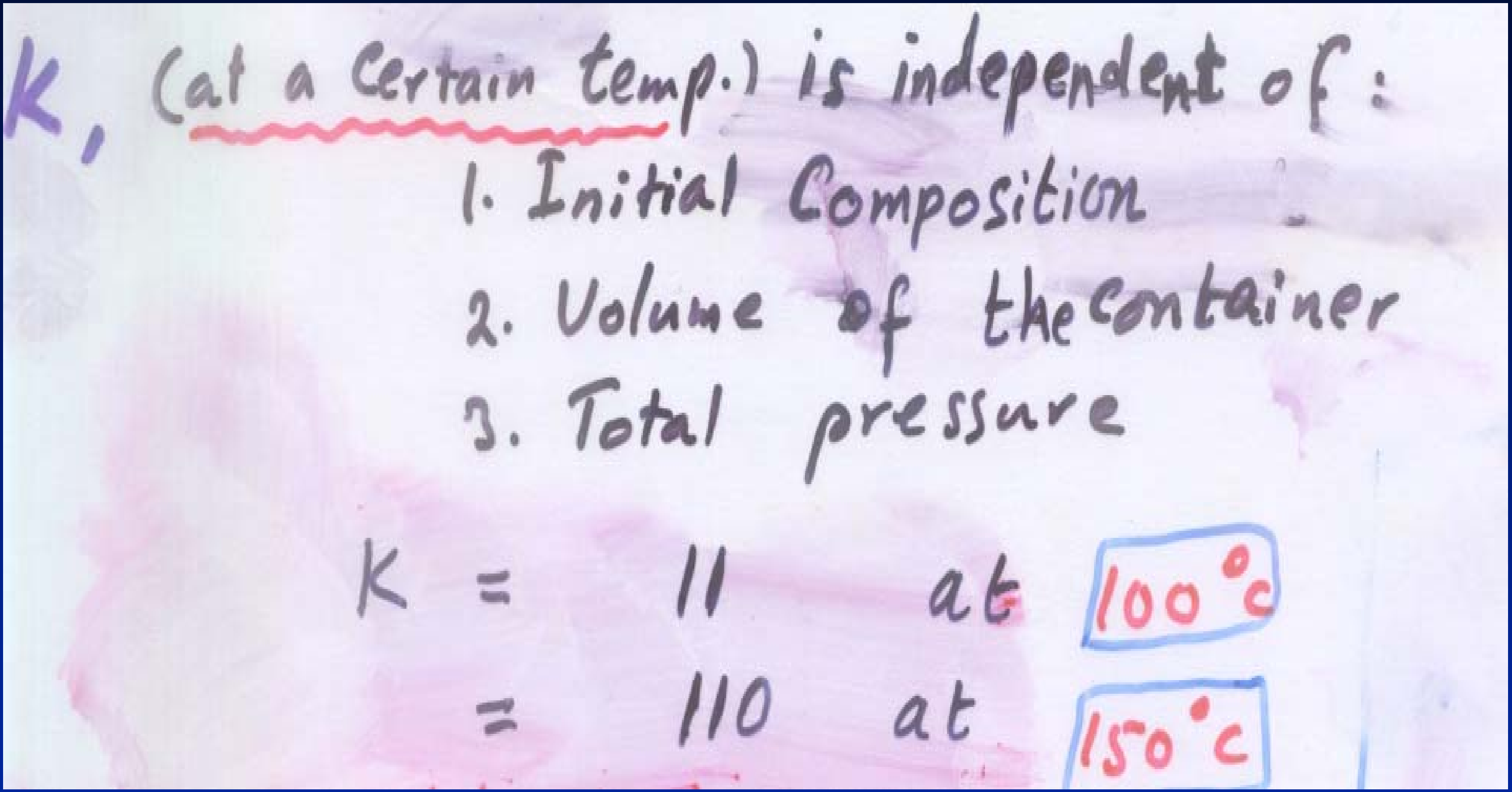
	Original P(atm)	Equilib. P (atm)	$(P_{NO_2})^2/P_{N_2O_4}$
N_2O_4	1.00	0.22	11
NO_2	0.00	1.56	
N_2O_4	0.00	0.07	11
NO_2	1.00	0.86	
N_2O_4	1.00	0.42	11
NO_2	1.00	2.16	



Thus, for any equilibrium mixture of N_2O_4 & NO_2,

$$(P_{NO_2})^2/P_{N_2O_4} = \boxed{\text{Constant}} \text{ at any given temp.}$$

$$= K = \text{Equilibrium Constant}$$



K, (at a certain temp.) is independent of :

1. Initial Composition
2. Volume of the container
3. Total pressure

$K = 11$ at $\boxed{100^\circ c}$

$= 110$ at $\boxed{150^\circ c}$

Equilibrium conditions

- Rates of forward and reverse reactions are equal if temperature remains constant
- Concentrations are not equal.
- Factors affecting the equilibrium position of a reaction:
  - initial concentrations;
  - relative energies of reactants and products;
  - Relative degree of organization of reactants and products
  - (Nature tends to achieve minimum energy and maximum disorder
- The concentrations of reactants or products do not change at equilibrium.

13.2 The equilibrium constant
Law of Mass Action

- For any reaction
- $jA + kB \rightleftharpoons lC + mD$
- $$K = \frac{[C]^{l}[D]^{m}}{[A]^{j}[B]^{k}} \qquad \frac{\text{PRODUCTS}^{\text{power}}}{\text{REACTANTS}^{\text{power}}}$$
- K is called the equilibrium constant.
- $\rightleftharpoons$ is how a reversible reaction is identified

Comments on Law of mass action

- K is constant regardless of the amounts of materials mixed initially
- Equilibrium concentrations will not always be the same but K is the same
- Each set of equilibrium concentrations in an equilibrium system is called equilibrium position
- There is only one K value for a given system but infinite number of equilibrium positions
- The law of mass action applies to solution and gaseous equilibria

Changing the chemical equation of an equilibrium system: Reciprocal rule

- **If we write the reaction in reverse.**
- $lC + mD \rightleftharpoons jA + kB$
- **Then the new equilibrium constant is**
- **K' =** $$\boxed{\frac{[A]^j[B]^k}{[C]^l[D]^m} = \frac{1}{K}} \longleftarrow$$

Reciprocal rule

Multiplying the equation by a coefficient: Coefficient Rule

- If we multiply the equation by a constant
- $njA + nkB \rightleftharpoons nlC + nmD$
- Then the equilibrium constant is
- $$K' = \frac{[C]^{nl}[D]^{nm}}{[A]^{nj}[B]^{nk}} = \frac{([C]^{l}[D]^{m})^{n}}{([A]^{j}[B]^{k})^{n}} = K^{n}$$

Rules of Multiple Equlibria

- Reaction 3 = Reaction 1 + Reaction 2

$SO_2(g) + 1/2O_2 \rightleftharpoons SO_3(g);$ $K_1 = 2.2$

$NO_2(g) \rightleftharpoons NO(g) + 1/2O_2(g);$ $K_2 = 4.0$

$$K_1 = \frac{p_{SO3}}{P_{SO2} X P_{O2}^{1/2}}$$

$$K_2 = \frac{P_{NO} X P_{O2}^{1/2}}{P_{NO2}}$$

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO\ (g);$$

$$K_3 = \boxed{\frac{P_{SO3} X P_{NO}}{P_{SO_2} P_{NO_2}}} = K_1 X K_2$$

$$\boxed{K_3 = K_1 X K_2}$$

$K_3 = 2.2\ x 4.0 = 8.8$

- K (Reaction 3) =K $_{(reaction\ 1)}$ X K $_{(reaction\ 2)}$

Notes on Equilibrium Expressions

- The Equilibrium Expression for a reaction is the **reciprocal** of that for the reaction written in **reverse**.
- When the equation for a reaction is multiplied by *n*, the equilib expression changes as follows:
- $(\text{Equilib Expression})_{\text{final}} = (\text{Equilib Expression}_{\text{initial}})^{n}$
- Usually *K* is written without units

Calculation of K

- $N_2 + 3H_2 \rightleftharpoons 3NH_3$
- **Initial** **At Equilibrium**
- $[N_2]_0 = 1.000\ M$ $[N_2] = 0.921M$
- $[H_2]_0 = 1.000\ M$ $[H_2] = 0.763M$
- $[NH_3]_0 = 0\ M$ $[NH_3] = 0.157M$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 9.47\mathrm{X}10^{-3}$$

Calculation of K

- $N_2 + 3H_2 \rightleftharpoons 3NH_3$
- Initial At Equilibrium
- $[N_2]_0 = 0\ M$ $[N_2] = 0.399\ M$
- $[H_2]_0 = 0\ M$ $[H_2] = 1.197\ M$
- $[NH_3]_0 = 1.000\ M$ $[NH_3] = 0.157M$
- K is the same no matter what the amount of starting materials

Symbols used for equilibrium constant

- K = used when the quantities of reactants and products are expressed as concentrations. That is mol/L
- The symbol K_c is used in some books to express same value.
- K_p is used when the equilibrium involves gases and their quantities are expressed in partial pressures.

13.3 Equilibrium Expressions Involving Pressures

- Some reactions are involve gaseous materials
- For the sake of equilibria, the amounts of gases may be expressed as concentrations (mol/L) or pressures.
- Relationships between P & conc.:
- $PV = nRT$
- $P = (n/V)RT$
- $P = CRT$
- C is a concentration in moles/Liter
- $C = P/RT$

Equilibrium and Pressure

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

$$K_p = \frac{(P_{SO3})^2}{(P_{SO2})^2\ (P_{O2})}$$

$$K = K_c = \frac{[SO_3]^2}{[SO_2]^2\ [O_2]}$$

Relationship between K and K_p

$$K = \frac{[SO_3]^2}{[SO_2]^2[(O_2]}$$

$$K = \frac{(P_{SO3}/RT)^2}{(P_{SO2}/RT)^2(P_{O2}/RT)}$$

$$K = \frac{(P_{SO3})^2 \ (1/RT)^2}{(P_{SO2})^2(P_{O2}) \ (1/RT)^3}$$

$$K = Kp \ X \frac{(1/RT)^2}{(1/RT)^3} = Kp \ RT$$

General Equation for the relationship between K and K_p

$$jA + kB \rightleftharpoons lC + mD$$

$$K_p = \frac{(P_C)^l\,(P_D)^m}{(P_A)^j\,(P_B)^k} = \frac{(C_C x RT)^l\,(C_D x RT)^m}{(C_A x RT)^j (C_B x RT)^k}$$

$$K_p = \frac{(C_C)^l\,(C_D)^m x (RT)^{l+m}}{(C_A)^j (C_B)^k x (RT)^{j+k}}$$

$$K_p = K\,(RT)^{(l+m)-(j+k)} = K\,(RT)^{\Delta n}$$

$\Delta n = (l+m)-(j+k)$ = Change in moles of gas

#moles of Products - #moles of reactants

Homogeneous Equilibria

- All reactants and products are in one phase, gases for example
- K can be used in terms of either concentration or pressure.

13.4 Heterogeneous Equilibria

- If the reaction involves pure solids or pure liquids as well as gases, the concentration of the solid or the liquid doesn’t change.
- As long as they are not used up they are left out of the equilibrium expression.
- Thus, there is no term for L or S in “K” expression.
- However, the presence of L or S is a must for equilibrium to occur.

Example: Equilibrium expression for heterogeneous equilibria

- $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$
- $$K' = \frac{[HI]^2}{[H_2][I_2]}$$
- But the concentration of I_2 does not change.
- $$K'[I_2] = \frac{[HI]^2}{[H_2]} = K$$

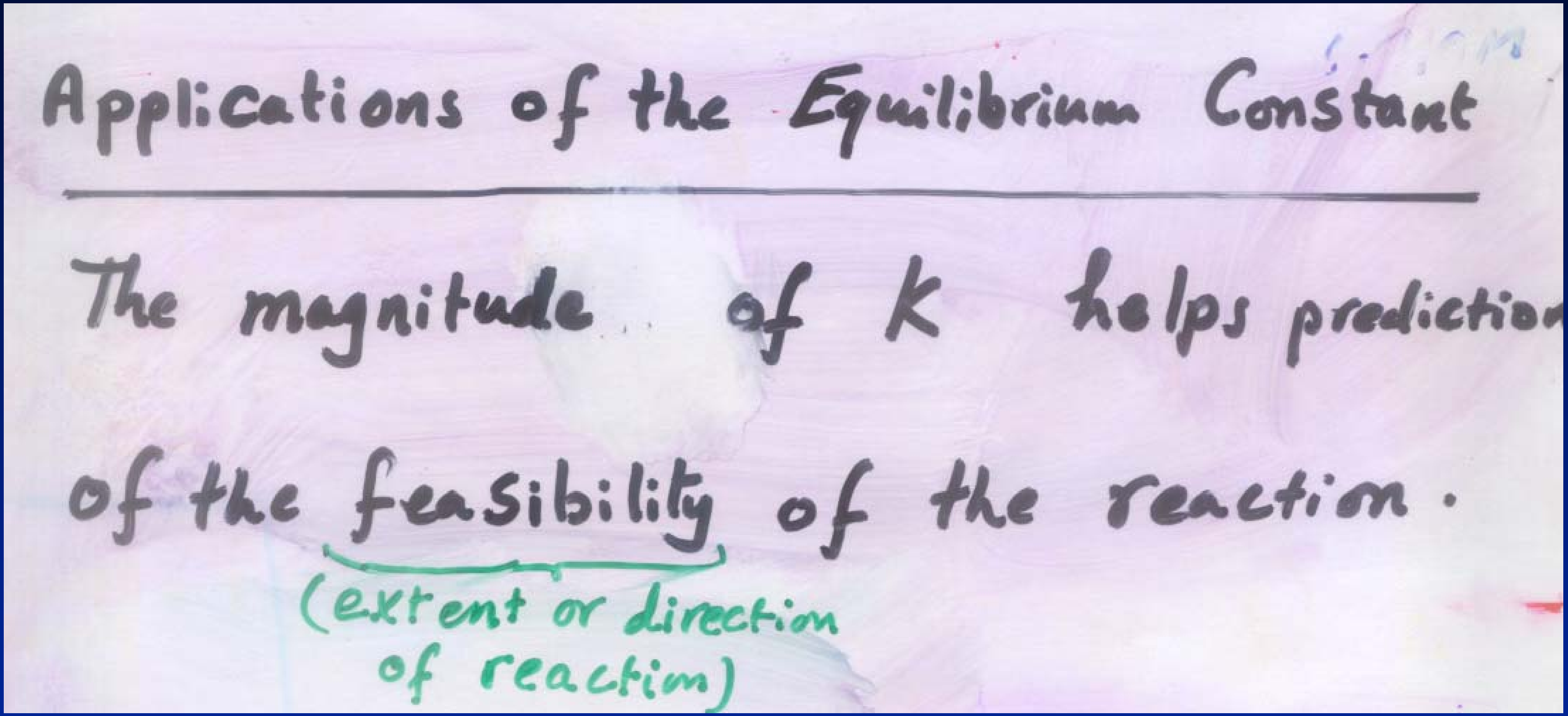
Comments on heterogeneous Equilibrium

- Position of equilibrium is independent of the amount of L or solid as long as some is present
- L and S should be pure otherwise they cannot be neglected because their concentrations change
- Gases enter K expression as their partial pressure
- Solvents do not enter the K expressions
- Species (ions or molecules) in water solution should enter the K expression as their molar concentrations
- Example: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$Kp = P_{CO2} \qquad K = [CO_2]$$

13.5 Applications of the equilibrium Constant

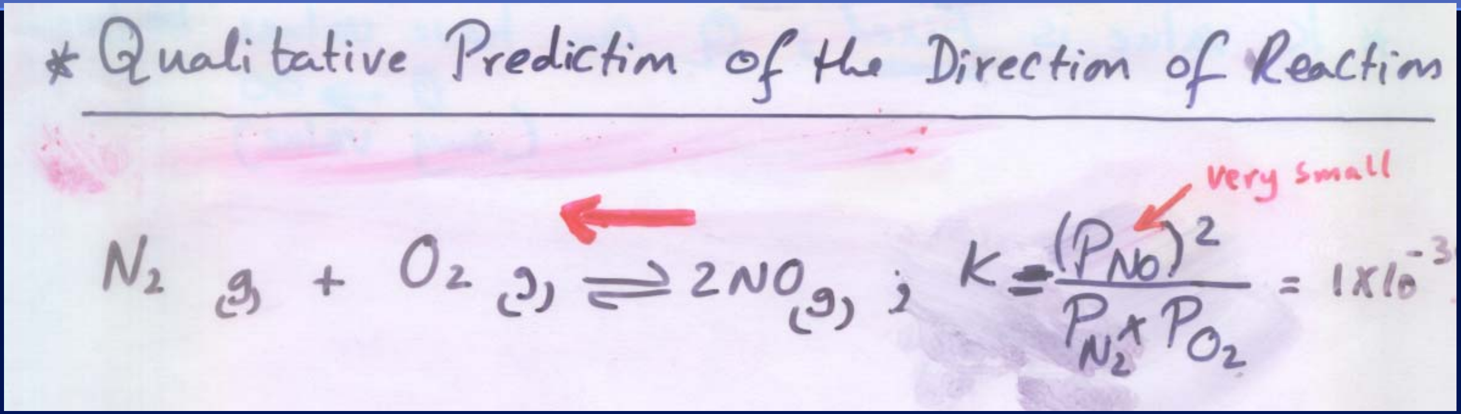
- The magnitude of K helps prediction of the feasibility (extent or direction but not the speed) of the reaction
- K> 1; the reaction system consists mostly products (equilibrium mostly lies to the right)
  - Systems with very large K go mostly to completion
  - Systems with very small values of K do not occur to any significant extent
- There is no relation between the value of K and the time to reach equilibrium (the rate of reaction)
  - Time to reach equilibrium depends on E_a for reactants and products



Applications of the Equilibrium Constant

The magnitude of K helps prediction of the feasibility of the reaction.

(extent or direction of reaction)

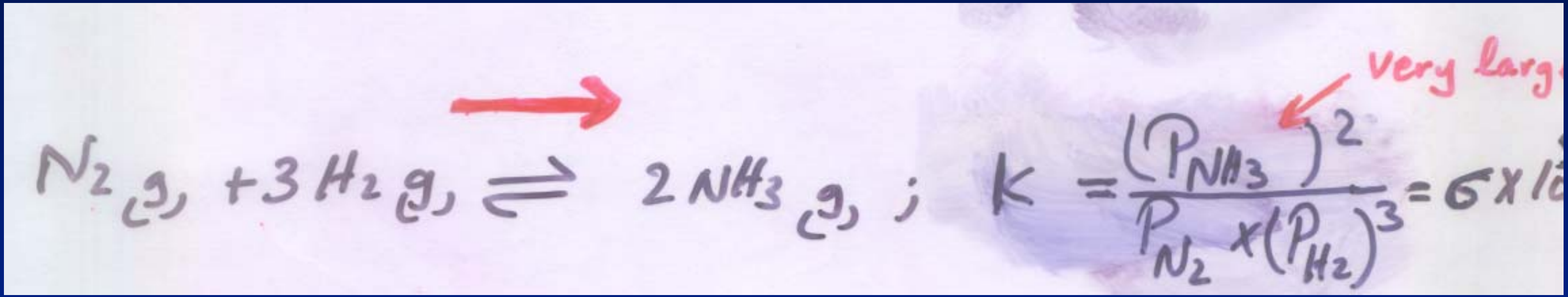


* Qualitative Prediction of the Direction of Reactions

←

very small

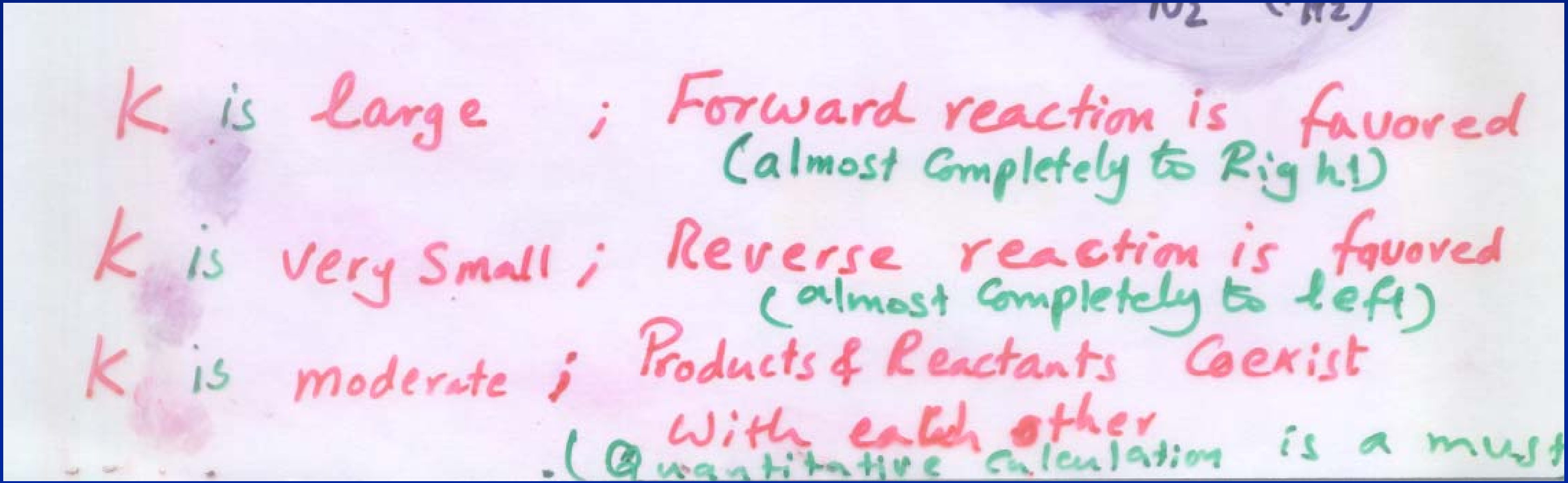
$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \;;\quad K = \frac{(P_{NO})^2}{P_{N_2} \times P_{O_2}} = 1\times10^{-3}$$



→

very larg

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \;;\quad K = \frac{(P_{NH_3})^2}{P_{N_2} \times (P_{H_2})^3} = 6\times10$$



K is large ; Forward reaction is favored (almost Completely to Right)

K is very Small ; Reverse reaction is favored (almost Completely to left)

K is moderate ; Products & Reactants Coexist with each other

(Quantitative Calculation is a must

The Reaction Quotient, Q
(Quantitative prediction of direction of reaction)

- Q Tells how the direction of a reaction will go to reach equilibrium
- Q's are calculated the same as K's, but for a system not at equilibrium
- $$Q = \frac{[\text{Products}]^{\text{coefficient}}}{[\text{Reactants}]^{\text{coefficient}}}$$

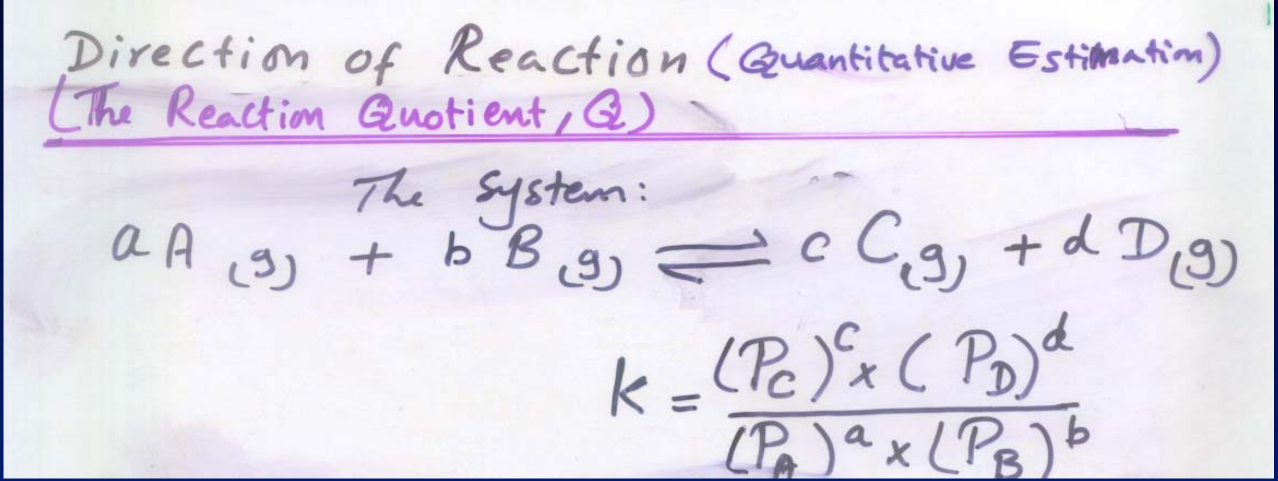
$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$\boxed{Q = \frac{(P_C)^c X (P_D)^d}{(P_A)^a X (P_B)^b}}$$

- Compare value of Q to that of K

What Q tells us?

- If Q<K
  - Not enough products
  - Equilibrium shifts to right; **forward reaction is predominant**
- If Q>K
  - Too many products
  - Equilibrium shifts to left; **reverse reaction is predominant**
- If Q=K system is at equilibrium; there is no further change

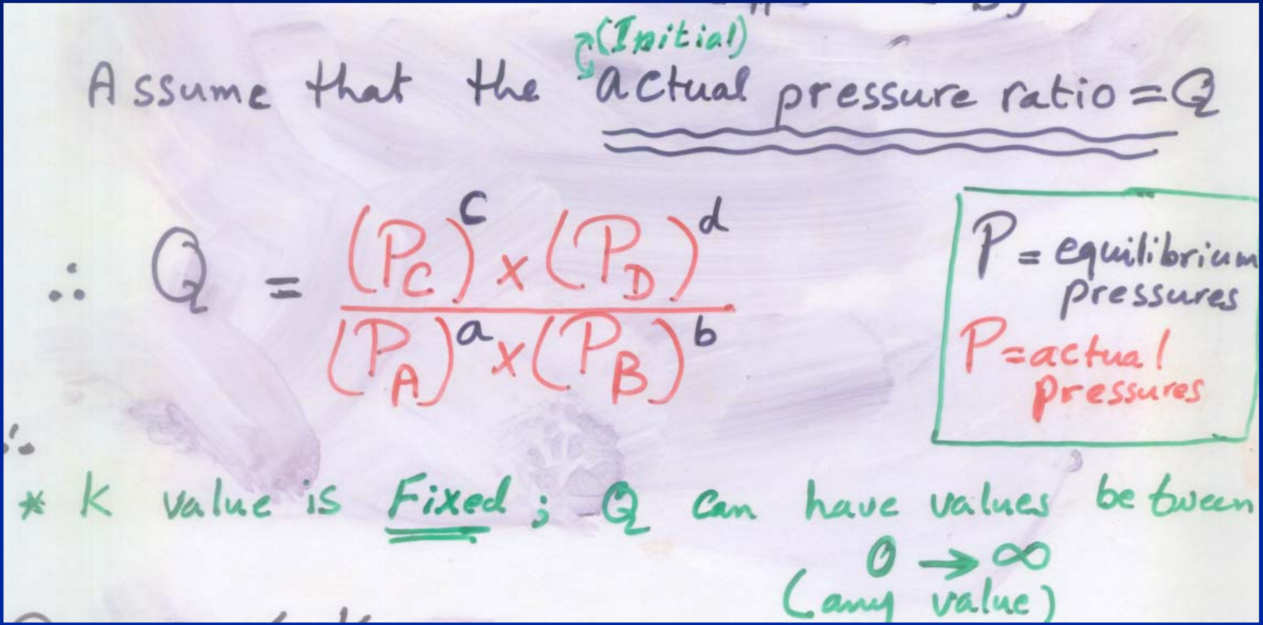


Direction of Reaction (Quantitative Estimation)
(The Reaction Quotient, Q)

The system:

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

$$K = \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b}$$



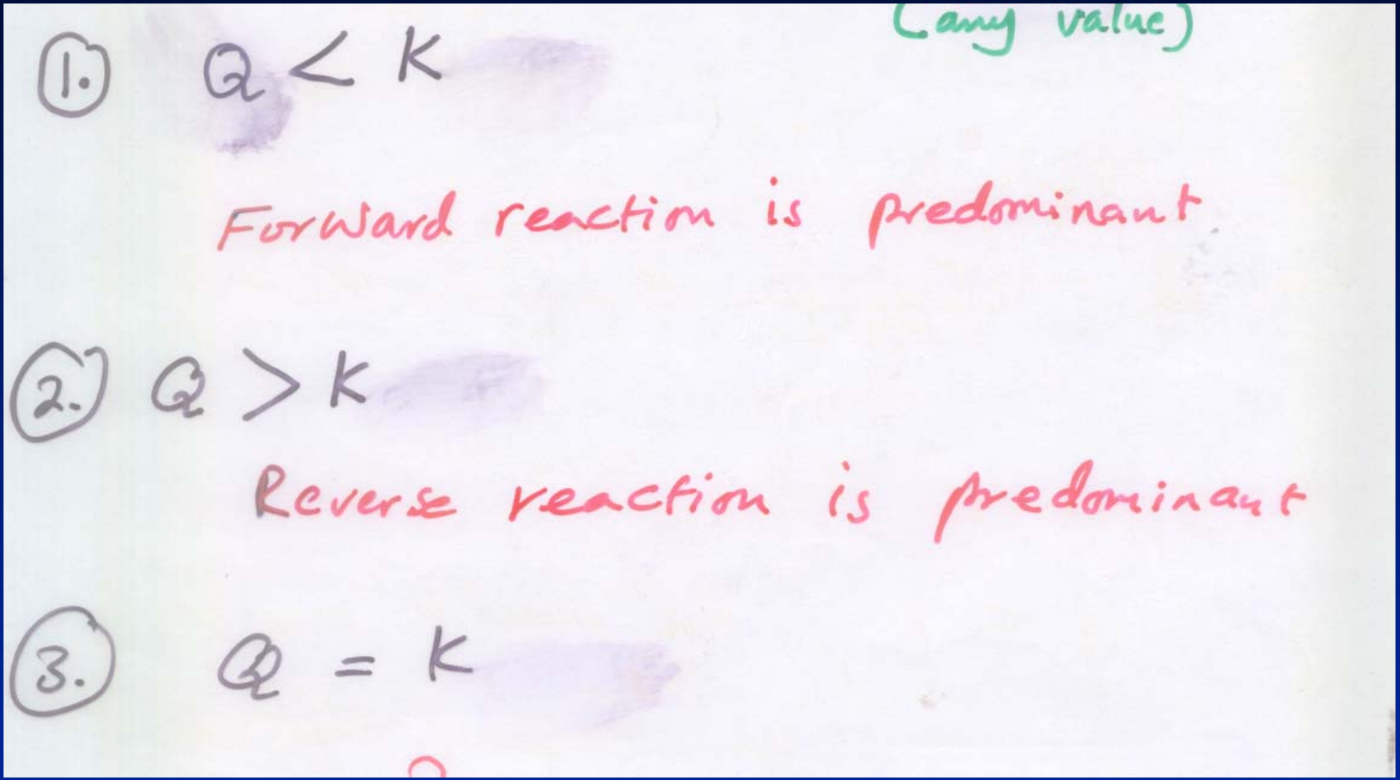
Assume that the (Initial) actual pressure ratio = Q

$$\therefore Q = \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b}$$

P = equilibrium pressures

P = actual pressures

* K value is Fixed; Q can have values between 0 → ∞ (any value)



(any value)

① $Q < K$

Forward reaction is predominant

② $Q > K$

Reverse reaction is predominant

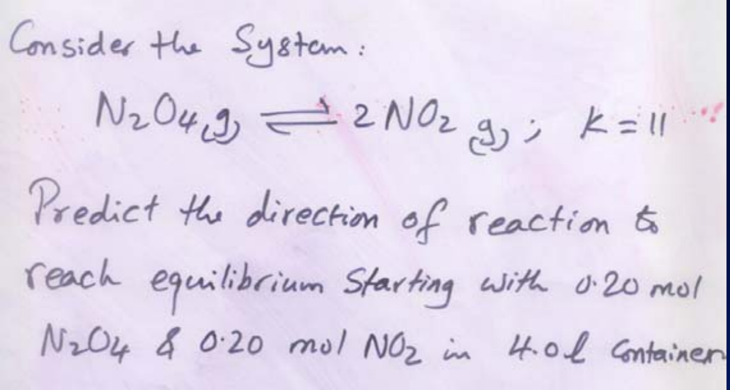
③ $Q = K$

Example

- for the reaction
- $N_2O_4\,(g) \rightleftharpoons 2NO_2(g)$
- K = 11 at 100ºC
- In an experiment 0.20 mol N_2O_4, 0. 20 mol NO_2(g) are mixed in 4.0 L flask.
- Which direction will the reaction proceed to reach equilibrium?

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

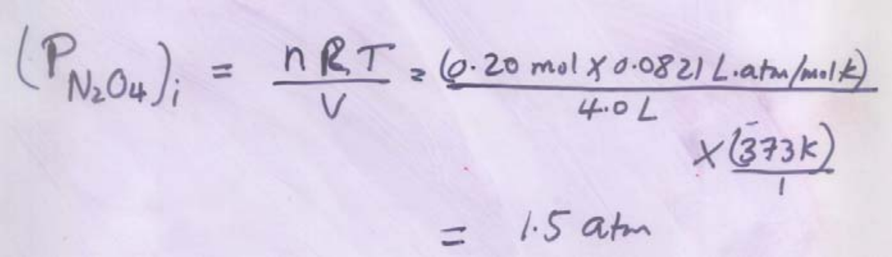
$$= \frac{(0.2/4)^2}{(0.2/4)} = 0.05 \quad < K$$



Consider the System:

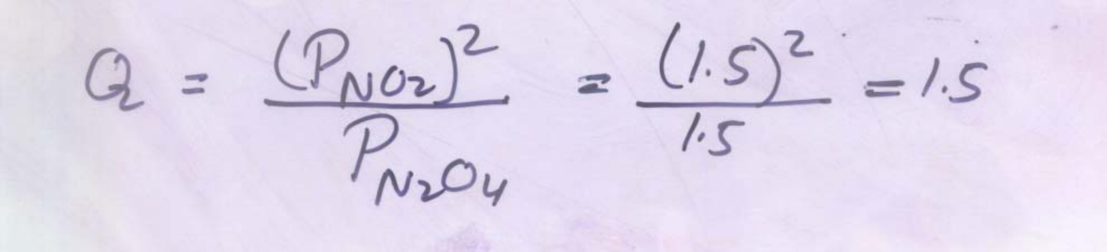
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}; \quad K = 11$$

Predict the direction of reaction to reach equilibrium starting with 0.20 mol N_2O_4 & 0.20 mol NO_2 in 4.0 ℓ container

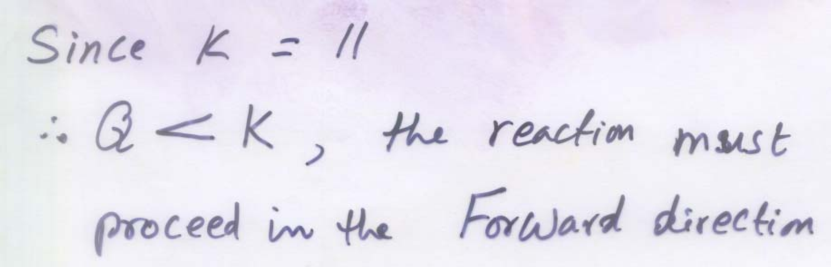


$$(P_{N_2O_4})_i = \frac{nRT}{V} = \frac{(0.20\ \text{mol} \times 0.0821\ \text{L.atm/mol K})}{4.0\ \text{L}} \times \frac{(373\ \text{K})}{1}$$

$$= 1.5\ \text{atm}$$



$$Q = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(1.5)^2}{1.5} = 1.5$$



Since $K = 11$

$\therefore Q < K$, the reaction must proceed in the Forward direction

Calculating equilibrium partial pressures and concentrations

Calculation of Equilibrium Partial Pressures From the Equilibrium Constant K

Example $K_p = 1 \times 10^{-30} = \frac{(P_{NO})^2}{P_{N_2} \times P_{O_2}} = \frac{(P_{NO})^2}{0.78 \times 0.21}$

$N_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\,NO_{(g)}$; $K_p = 1 \times 10^{-30}$

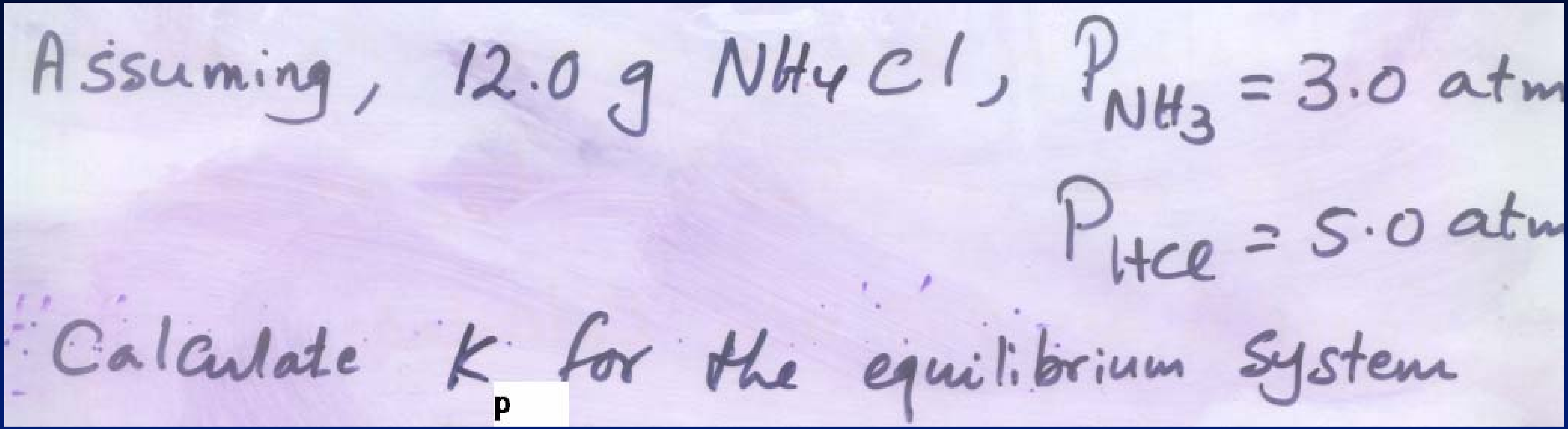
$P_{N_2} = 0.78$, $P_{O_2} = 0.21$ atm, $P_{NO} = ?$

$P_{NO} = \left[(1 \times 10^{-30})(0.78 \times 0.21)\right]^{1/2} = (1.6 \times 10^{-31})^{1/2} = 4 \times 10^{-16}$ atm.

i.e., Essentially, there is no reaction

How about if there is a reaction ?!!

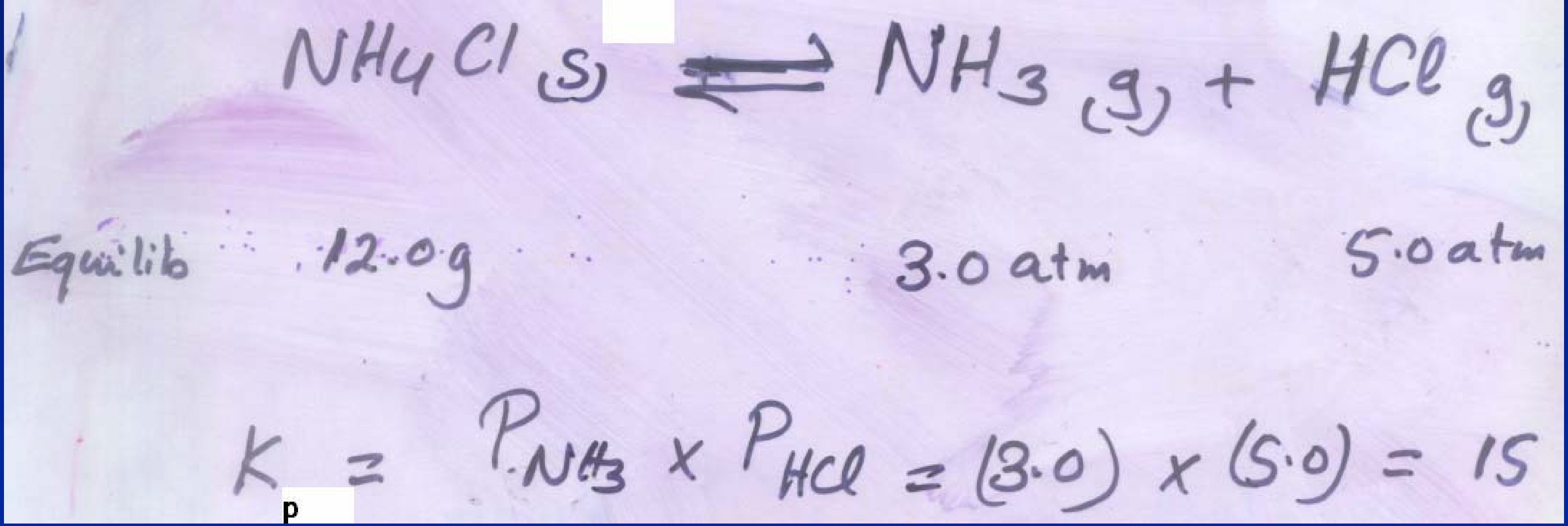
Example



Assuming, 12.0 g NH_4Cl, $P_{NH_3} = 3.0$ atm

$P_{HCl} = 5.0$ atm

Calculate K_p for the equilibrium system

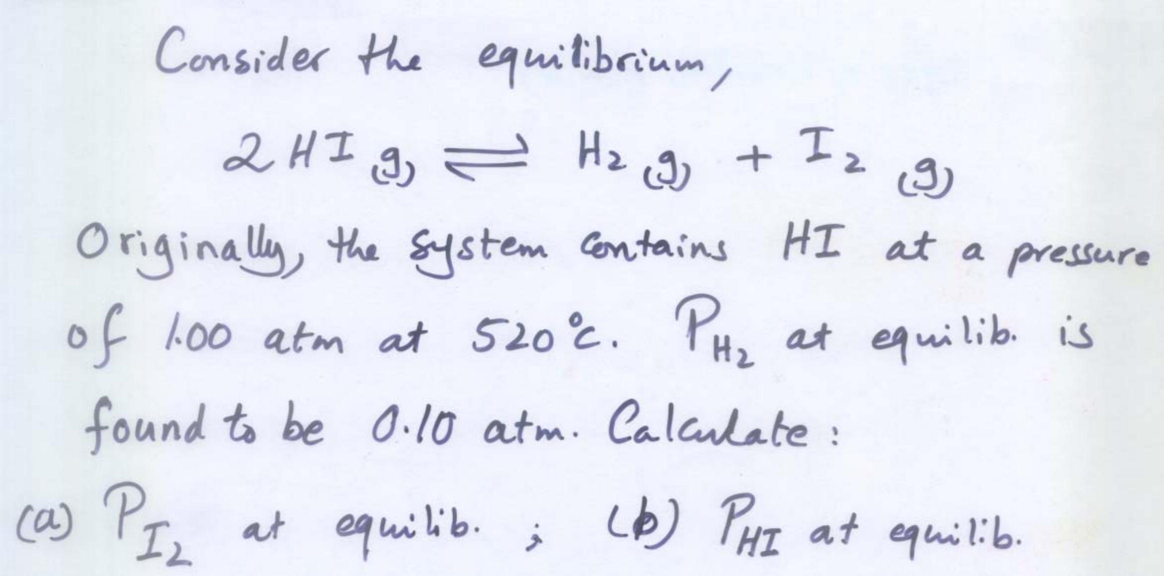


$$NH_4Cl_{(s)} \rightleftharpoons NH_{3\,(g)} + HCl_{(g)}$$

Equilib	12.0g	3.0 atm	5.0 atm

$$K_p = P_{NH_3} \times P_{HCl} = (3.0) \times (5.0) = 15$$

Example

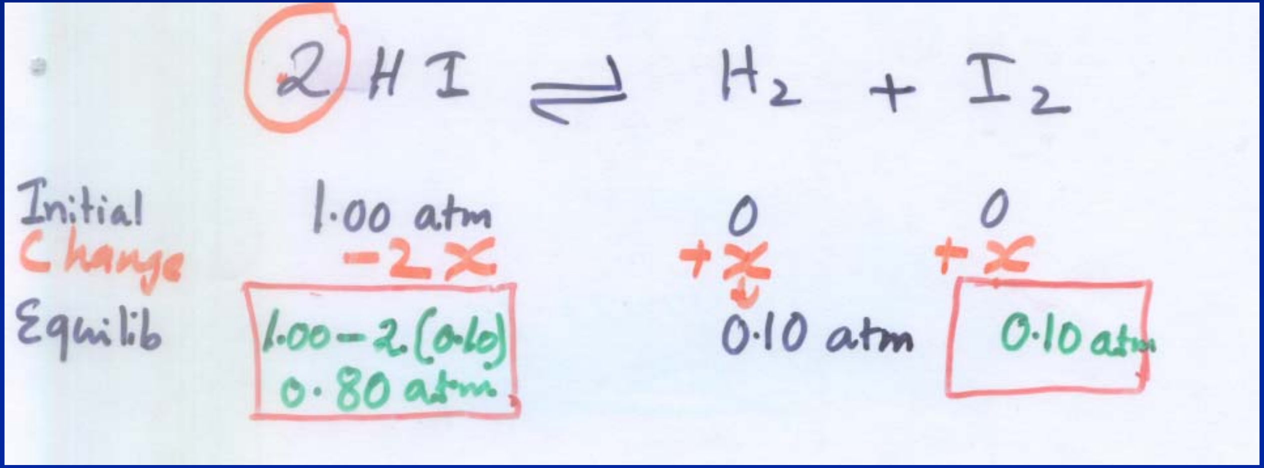


Consider the equilibrium,

$$2HI_{(g)} \rightleftharpoons H_{2\,(g)} + I_{2\,(g)}$$

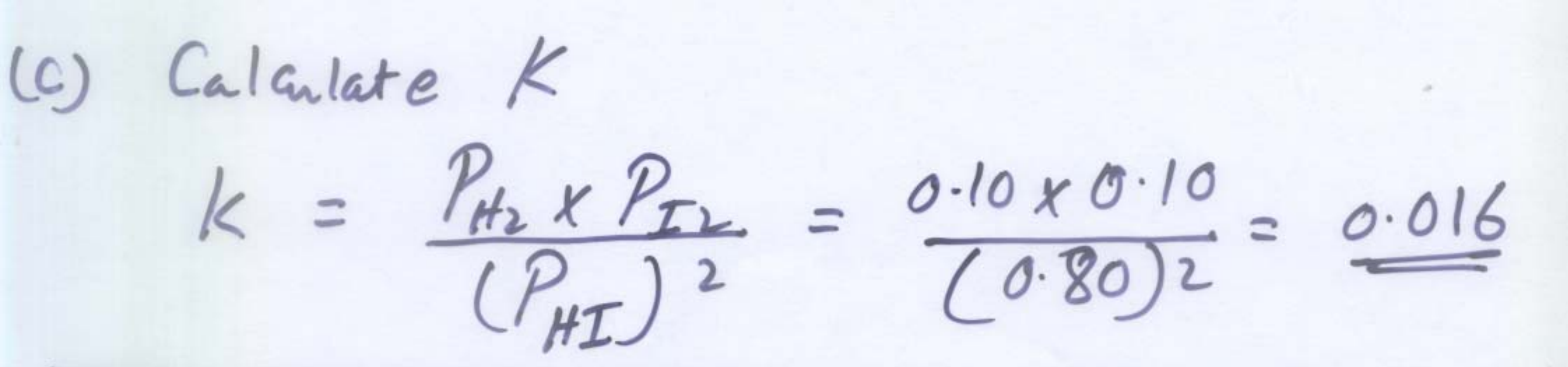
Originally, the system contains HI at a pressure of 1.00 atm at 520 °C. P_{H_2} at equilib. is found to be 0.10 atm. Calculate:

(a) P_{I_2} at equilib. ; (b) P_{HI} at equilib.



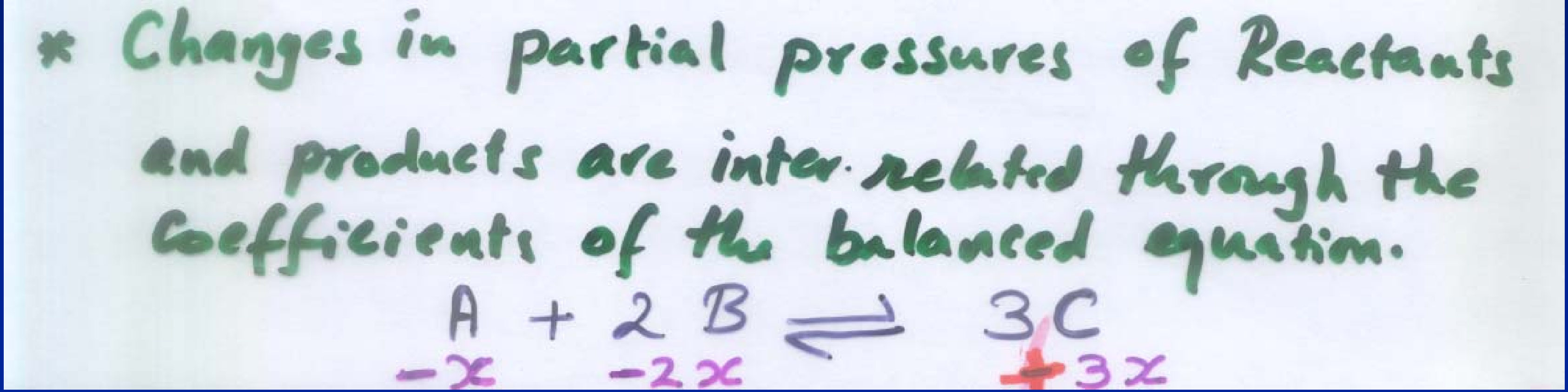
$$②HI \rightleftharpoons H_2 + I_2$$

	② HI	H_2	I_2
Initial	1.00 atm	0	0
Change	$-2x$	$+x$	$+x$
Equilib	$\boxed{1.00-2(0.10)}$ 0.80 atm	0.10 atm	$\boxed{0.10\text{ atm}}$



(c) Calculate K

$$K = \frac{P_{H_2} \times P_{I_2}}{(P_{HI})^2} = \frac{0.10 \times 0.10}{(0.80)^2} = \underline{\underline{0.016}}$$



* Changes in partial pressures of Reactants and products are inter-related through the coefficients of the balanced equation.

$$\underset{-x}{A} + \underset{-2x}{2B} \rightleftharpoons \underset{+3x}{3C}$$

Example 13.9

- At a certain temperature a 1.00-L flask contained 0.298 mol $PCl_3(g)$ and $8.70X10^{-3}$ mol $PCl_5(g)$. After the system had reached equilibrium, $2.00X10^{-3}$ mol $Cl_2(g)$ was found in the flask. Calculate the equilibrium conc. Of all species and the value of K

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

Initial	$8.70X10^{-3}$ mol	0.298 mol	0 mol
[ ] init	$8.70X10^{-3}$ M	0.298 M	0 M
Change	-x	+x	+x
Equilib	?	?	$+2.00X10^{-3}$ M

K = ??

Example 13.10

- Consider:

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

At 700K, K is 5.10. Calculate the equilibrium concentrations of all species if 1.00 mol of each component is mixed in 1.00 L flask

	$CO(g)$	$+\ H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	$+\ H_2(g)$
Initial	1 mol	1 mol		1 mol	1mol
[ ]	1mol/1L	1mol/1L		1mol/1L	1mol/1L
Change	-x	-x		+x	+x
Equilib	**1-x**	**1-x**		**1+x**	**1+x**

$$K = \frac{(1+x)(1+x)}{(1-x)(1-x)} = \frac{(1+x)^2}{(1-x)^2} = 5.10$$

$$\frac{(1+x)}{(1-x)} = \sqrt{5.10}$$

13.6 Solving Equilibrium Problems

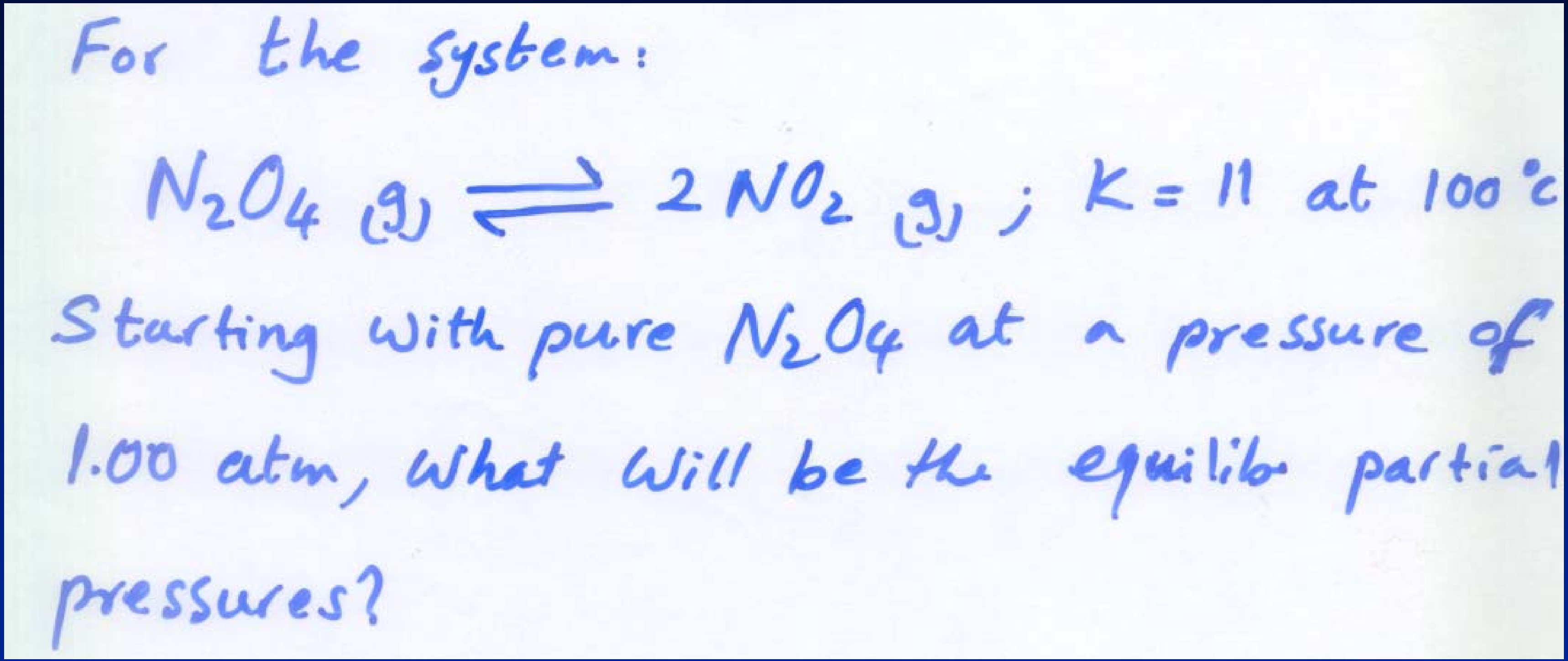
- Given the starting concentrations and one equilibrium concentration.
- Use stoichiometry to figure out other concentrations and K.
- Learn to create a table of initial and final conditions.

- Consider the following reaction at 600ºC
- $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

  In a certain experiment 2.00 mol of SO_2, 1.50 mol of O_2 and 3.00 mol of SO_3 were placed in a 1.00 L flask. At equilibrium 3.50 mol SO_3 were found to be present. Calculate the equilibrium concentrations of O_2 and SO_2, K and K_P

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

Init	2.00 mol/L	1.50 mol/L	3.00 mol/L
Change	-2X	-X	+2X
Equilib			3.50 mol/L



For the system:

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)\ ;\ K = 11 \text{ at } 100\,^{\circ}C$$

Starting with pure N_2O_4 at a pressure of 1.00 atm, what will be the equilib partial pressures?

$N_2O_4 \rightleftharpoons 2\ NO_2$; $k = 11$

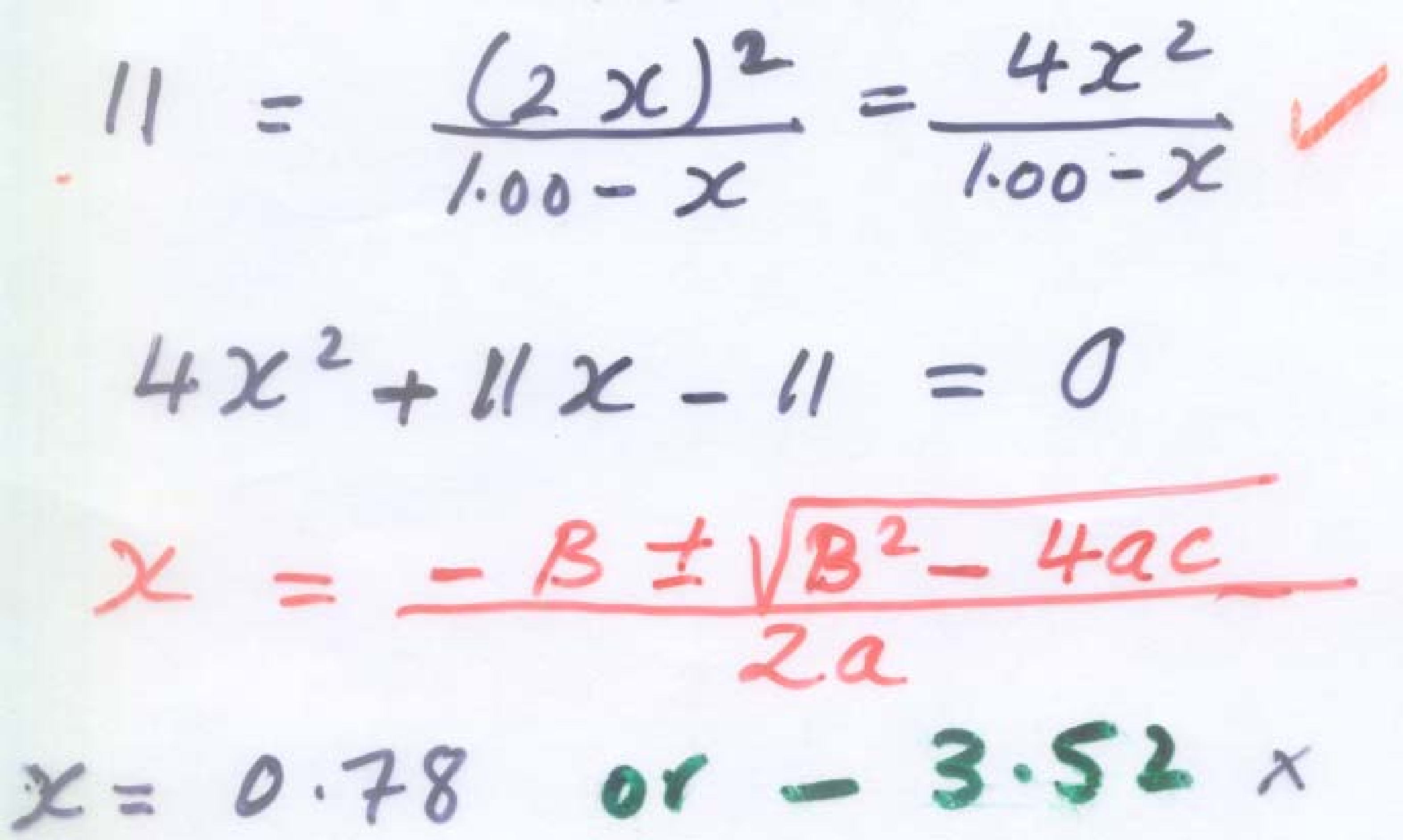
	N_2O_4	$2\ NO_2$
Initial, P_o, atm	1.00	0.00

$N_2O_4 \rightleftharpoons 2\ NO_2$; $k = 11$

	N_2O_4	$2\ NO_2$
Initial, P_o, atm	1.00	0.00
Change, ΔP, atm	$-x$	$+2x$

$N_2O_4 \rightleftharpoons 2\ NO_2$; $k = 11$

	N_2O_4	$2\ NO_2$
Initial, P_o, atm	1.00	0.00
Change, ΔP, atm	$-x$	$+2x$
Equilib., P_{eq}, atm	$1.00 - x$	$2x$

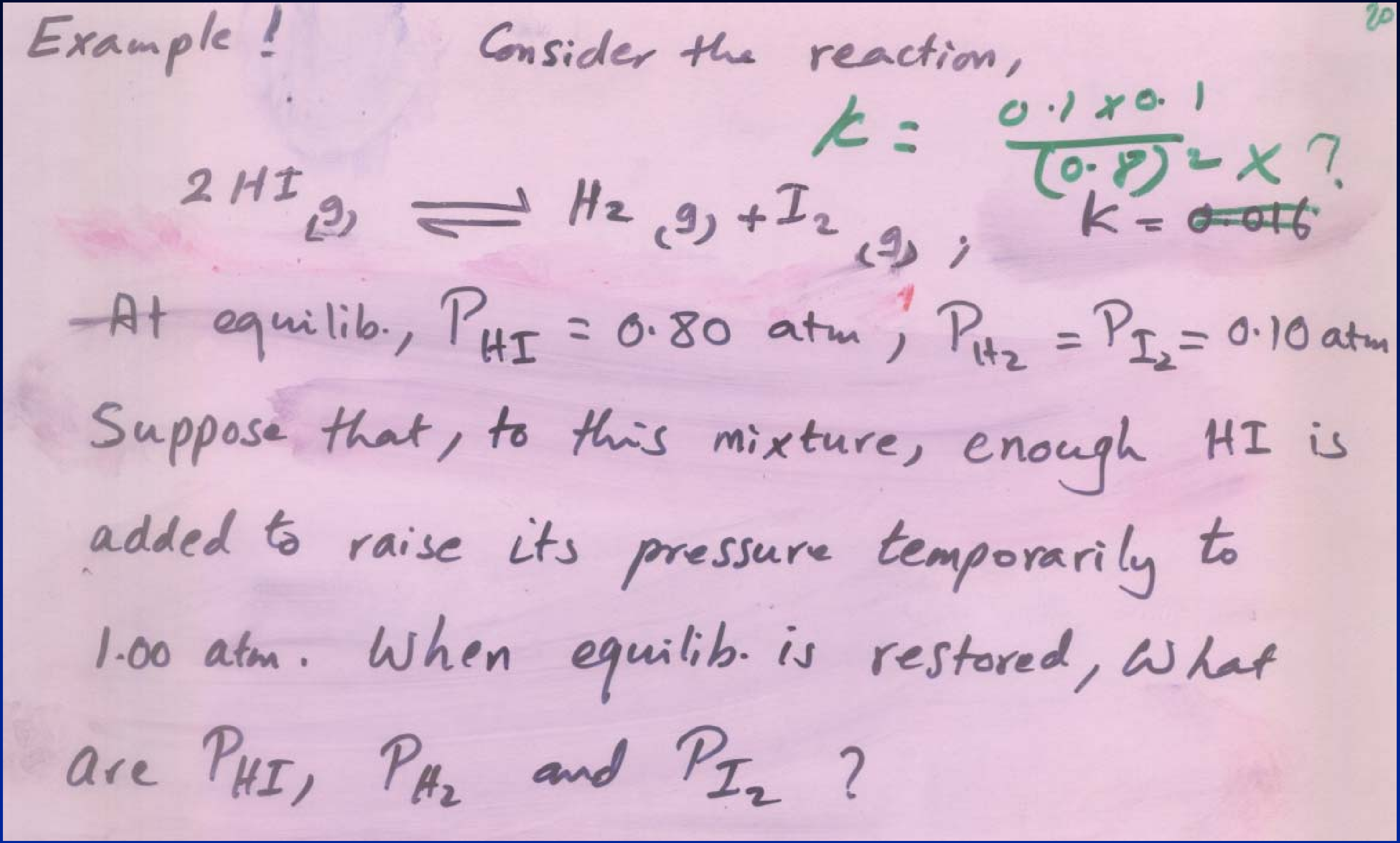


$$11 = \frac{(2x)^2}{1.00 - x} = \frac{4x^2}{1.00 - x}$$ ✓

$$4x^2 + 11x - 11 = 0$$

$$x = \frac{-B \pm \sqrt{B^2 - 4ac}}{2a}$$

$x = 0.78$ or -3.52 ×



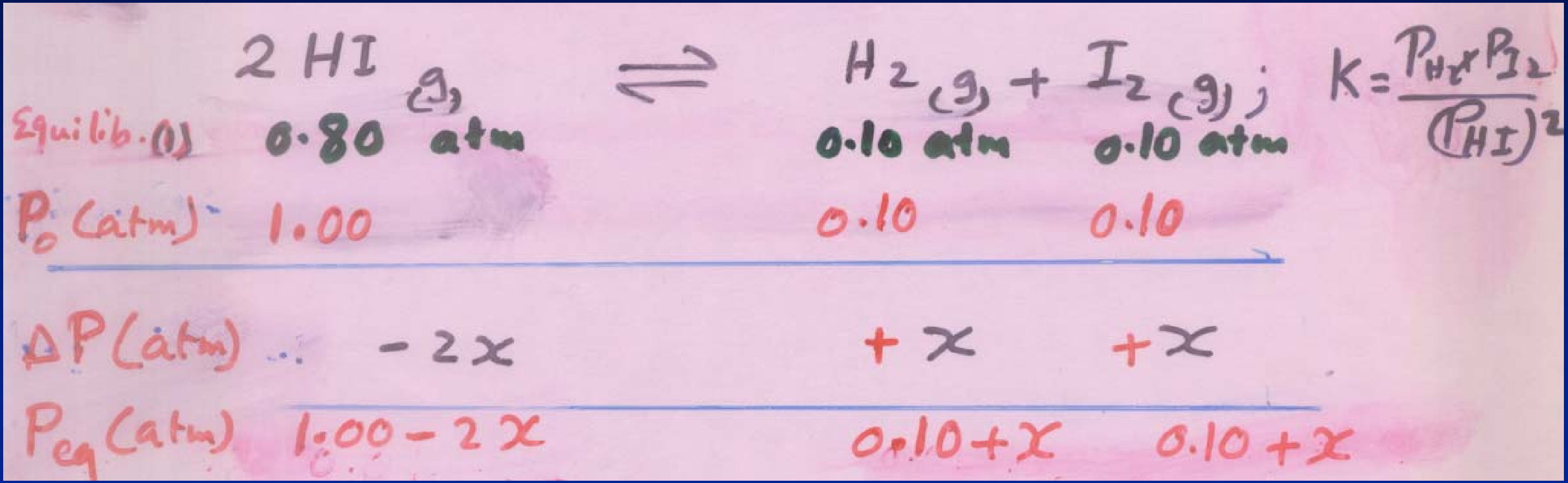
Example! Consider the reaction,

$$k = \frac{0.1 \times 0.1}{(0.8)^2} = x\ ?$$

$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$; k = ~~0.016~~

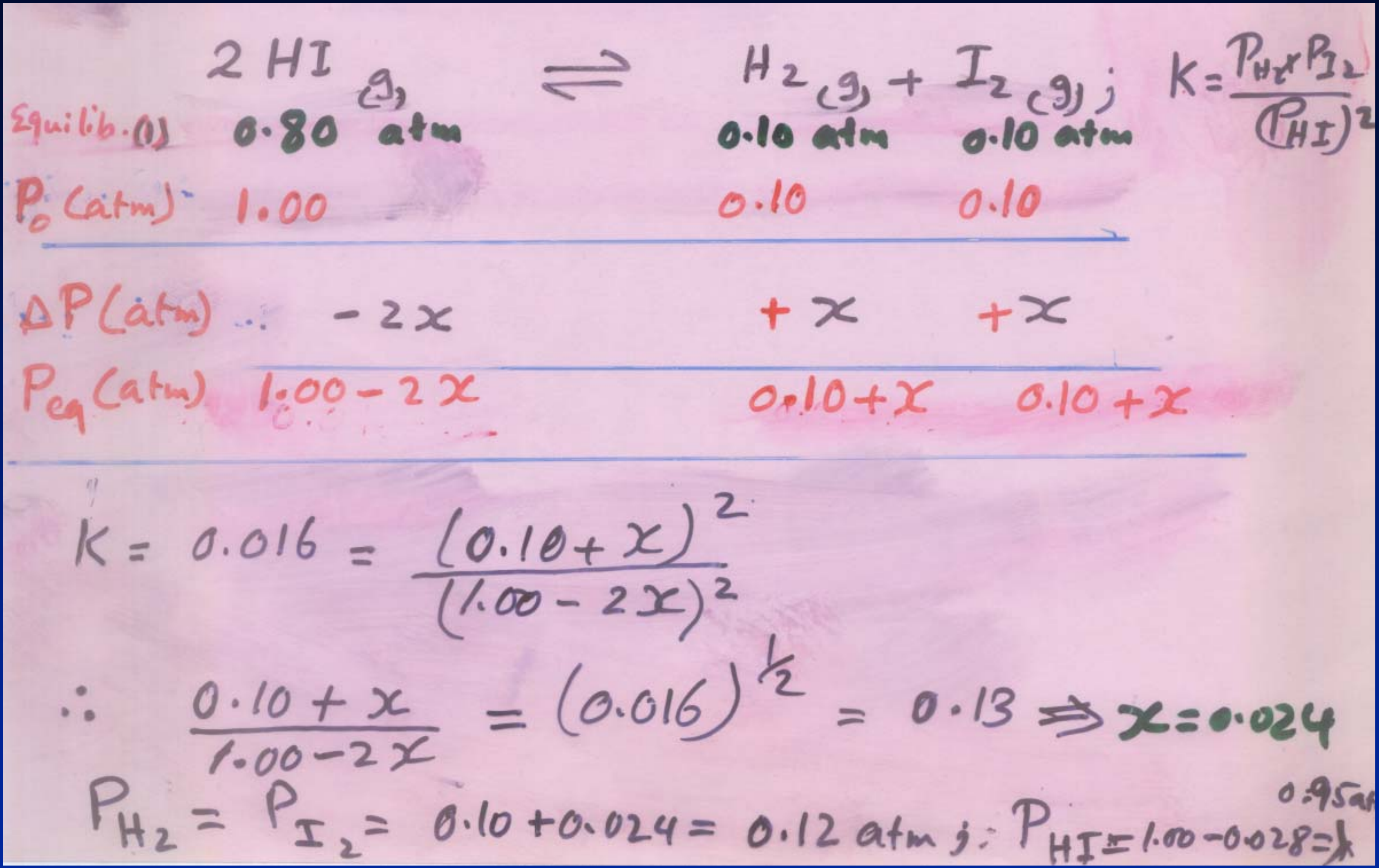
At equilib., $P_{HI} = 0.80$ atm ; $P_{H_2} = P_{I_2} = 0.10$ atm

Suppose that, to this mixture, enough HI is added to raise its pressure temporarily to 1.00 atm. When equilib. is restored, what are P_{HI}, P_{H_2} and P_{I_2} ?



$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}; \quad K = \frac{P_{H_2} \times P_{I_2}}{(P_{HI})^2}$$

Equilib. (1)	0.80 atm	0.10 atm	0.10 atm
P_o (atm)	1.00	0.10	0.10
ΔP (atm)	$-2x$	$+x$	$+x$
P_{eq} (atm)	$1.00 - 2x$	$0.10 + x$	$0.10 + x$



$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}; \quad K = \frac{P_{H_2} \times P_{I_2}}{(P_{HI})^2}$$

	$2HI_{(g)}$	$H_{2(g)}$	$I_{2(g)}$
Equilib. (1)	0.80 atm	0.10 atm	0.10 atm
P_0 (atm)	1.00	0.10	0.10
ΔP (atm) ∴	$-2x$	$+x$	$+x$
P_{eq} (atm)	$1.00 - 2x$	$0.10 + x$	$0.10 + x$

$$K = 0.016 = \frac{(0.10 + x)^2}{(1.00 - 2x)^2}$$

$$\therefore \quad \frac{0.10 + x}{1.00 - 2x} = (0.016)^{\frac{1}{2}} = 0.13 \Rightarrow x = 0.024$$

$P_{H_2} = P_{I_2} = 0.10 + 0.024 = 0.12$ atm ; $P_{HI} = 1.00 - 0.028 = \nearrow$ 0.95 at

What if equilibrium concentration is not given?

- The size of K will determine what approach to take.
- First let's look at the case of a **LARGE** value of K (>100).
- Simplifying assumptions can be made.

Example

- $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
  $K = 7.1 \times 10^2$ at 25ºC
- Calculate the equilibrium conc. if a 5.00 L container initially contains 15.9 g of H_2 and 294 g of I_2.
- $[H_2]_0 = (15.7g/2.02)/5.00\ L = 1.56\ M$
- $[I_2]_0 = (294g/253.8)/5.00L = 0.232\ M$
- $[HI]_0 = 0$

- Q= 0<K so more product will be formed.
- **Assumption:** since K is large reaction will go to completion.
- Stoichiometry tells us I_2 is LR, it will be smallest at equilibrium
- Set up table of initial, change and equilibrium concentrations.

	$H_2(g)$	$I_2(g)$	$HI(g)$
initial	1.56 M	0.232 M	0 M
change	-0.232	-0.232	+0.232X2
Final	1.328	0	+0.464

- (before the reverse reaction takes place)
- When the reverse reaction takes place to achieve an equilibrium a decrease of 2x will take place in HI and an increase of x in each of H_2 and I_2 will take place
- Thus final concentrations will be taken as the initials

	$H_2(g)$	$I_2(g)$	$2HI(g)$
Initial	1.328	0	+0.464
Change	+X	+X	-2X
Equilib	1.328+X	X	0.464-2X

- Now plug these values into the equilibrium expression
- $$K = \frac{(0.464-2X)^2}{(1.328+X)(X)} = 7.1 \times 10^2$$
- When we solve for X we get 2.8×10^{-4}

Can we eliminate X from the equation?

- $K = \frac{(0.464^{-2}-X)2}{(1.328+X)(X)} = 7.1 \times 10^2$
- Since X is going to be small, we can ignore it in relation to 0.464 and 1.328
- So we can rewrite the equation
- $7.1 \times 10^2 = \frac{(0.464)^2}{(1.328)(X)}$
- This makes the algebra easy

- When we solve for X we get

  2.8×10^{-4}
- X was also without approximation 2.8×10^{-4}
- So we can find the other concentrations
- $I_2 = 2.8 \times 10^{-4}$ M
- $H_2 = 1.328$ M
- $HI = 0.464$ M

Problems with small K

$K < .01$

For example

- For the reaction

  $2NOCl \rightleftharpoons 2NO + Cl_2$
- $K = 1.6 \times 10^{-5}$
- If 1.0 mol NOCl, is placed in 2.0L flask What are the equilibrium concentrations?

- Since there are no products exist intially, the system will move to the right to reach equilibrium
- $[NOCl]_0 = 1.0 \text{ mol}/2.0\text{L} = 0.50\text{M}$

	2NOCl	2NO	Cl_2
Initial	0.50M	0	0
Change	-2x	+2x	+ x
Equilib.	0.50-2x	2x	x

- $K = 1.6\mathrm{X}10^{-5} = \dfrac{[NO]^2[Cl_2]}{[NOCl]^2} = \dfrac{(2x)^2(x)}{(0.50-2x)^2}$
- This equation is complicated; an approximation is needed

- K = 1.6X10^{-5} = $\frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(2x)^2(x)}{(0.50-2x)^2}$
- 0.50-2x ≈ 0.50

$$\frac{(2x^2)(x)}{(0.50)^2} = \frac{4x^3}{(0.50)^2}$$

= K = 1.6X10^{-5}

X = 1.0X10^{-2}

13.7 Le Chatelier’s Principle

- if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.
- If a stress is applied to a system at equilibrium, the position of the equilibrium will shift to reduce the stress.
- There are 3 Types of stress

External conditions that cause a disturbance to a chemical equilibrium

- Adding or removing reactants or products
- Changing the volume (or pressure) of the system
- Changing the temperature

The effect of a change in concentration of reactants and/or products

- The system will shift away from the added component

- Adding product makes Q>K ←
- Removing reactant makes Q>K ←
- Adding reactant makes Q<K →
- Removing product makes Q<K →
- knowing the effect on Q, will tell you the direction of the shift
- Adding or removing liquids or solids does not affect the equilibrium

The effect of a Change in Pressure

- The pressure changes as a result of:
  - Adding or removing gaseous reactant or product
  - Adding an inert gas
  - Changing the volume of the container
- Adding inert gas does not affect the equilibrium position; conc. or P will not change.
- By reducing the volume of the container, the system will move in the direction that reduces its volume.

The effect of a Change in Pressure

- The system will respond to the decrease in volume by decreasing the total number of gaseous molecules in the system.

$$PV = nRT$$

$$V = \left(\frac{RT}{P}\right)^{n}$$

Thus V α n

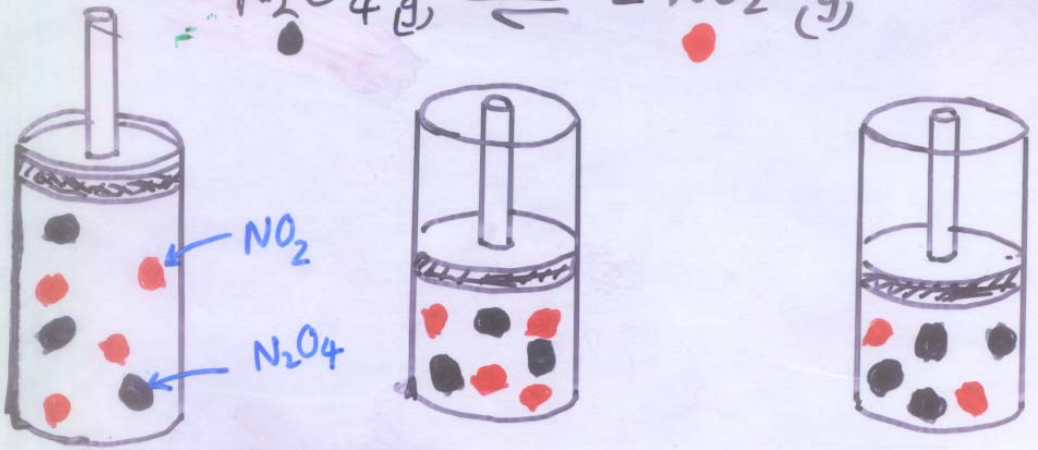
- At constant temp and pressure the volume of a gas is directly proportional to the number of moles of gas present

- Thus V α n

Changes in volume

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

● ●



original equilib.

Equilib. disturbed

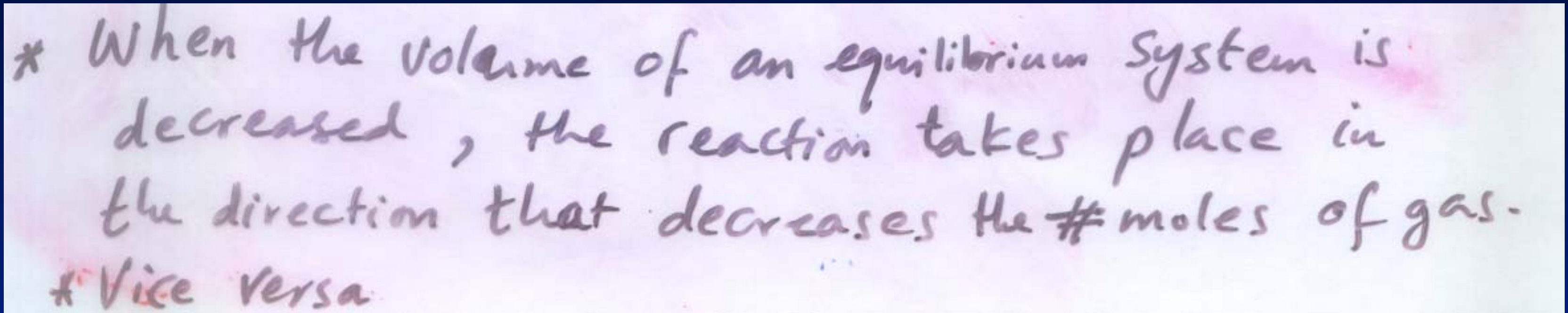
(# molecules/unit volume) increases

Equilib. re-established

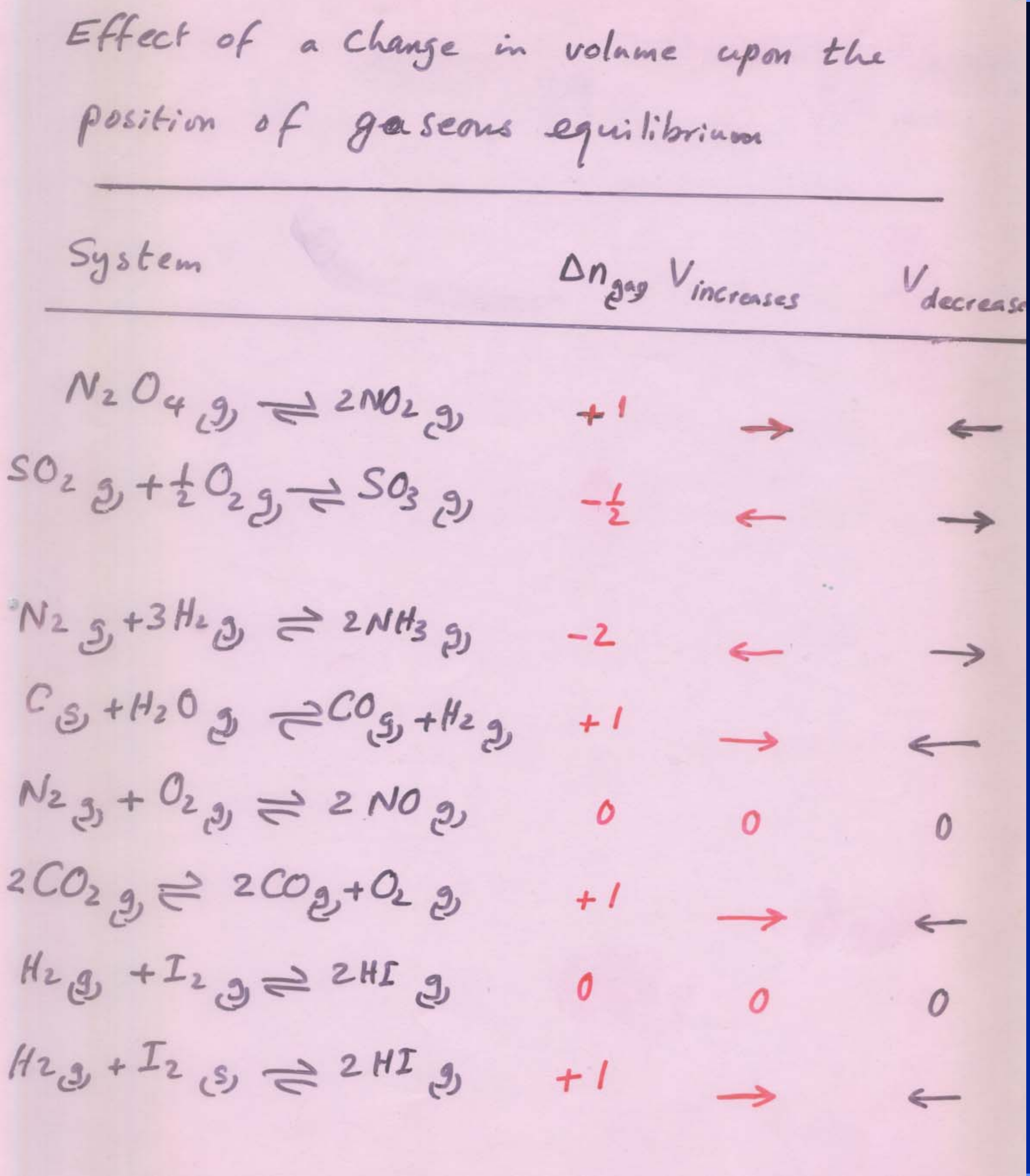
(# molecules/unit vo decreases

When (V) is decreased: The Equilibrium will shift to the direction in which number of molecules decreases

i.e., Reverse reaction is enhanced



* When the volume of an equilibrium system is decreased, the reaction takes place in the direction that decreases the # moles of gas.
* Vice versa



Effect of a change in volume upon the position of gaseous equilibrium

System	Δn_{gas}	$V_{increases}$	$V_{decreas}$
$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$	+1	→	←
$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$	$-\frac{1}{2}$	←	→
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	−2	←	→
$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$	+1	→	←
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	0	0	0
$2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$	+1	→	←
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	0	0	0
$H_{2(g)} + I_{2(s)} \rightleftharpoons 2HI_{(g)}$	+1	→	←

Effect of Changes in Pressure

Same as in Volume effect; on a Condition that a change in volume **must** associate the change in P.

(*) **Addition of an inert gas**:

It affects P **but** does not affect equilib.

as long as the Container Volume is **not Changed**.

Concentrations or partial pressures of reactants or products do not change.

Change in Temperature

- **Affects the rates of both the forward and reverse reactions.**
- **changes the equilibrium constant.**
- **The direction of the shift depends on whether it is exo- or endothermic**

Exothermic

- $\Delta H<0$
- Releases heat
- Think of heat as a product
- Raising temperature push toward reactants.
- Shifts to left.

Endothermic

- $\Delta H>0$
- Heat is added to the system
- Think of heat as a reactant
- Raising temperature push toward products.
- Shifts to right.

Changes in Temperature

(*) Changes in Conc., Volume, or total P cause shift in equilib without changing the value of K

(*) Changes in T: Cause a shift in the position of equilib. in addition to changing the Value of K

(*) Shifting the equilibrium

Endo $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$; $\Delta H^\circ = +58.2$ KJ

*(Increasing T favors the Endothermic reactions)

Exo $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; $\Delta H^\circ = -92.4$

* (Decreasing the T favors the Exothermic reactions)

Learning Outcomes

- Explain how dies a system reach equilibrium.
- Explain how does equilibrium work as a dynamic process.
- Write the equilibrium constant expression according to the law of mass action
- Write K for the reversible reaction; for a reaction whose coefficients are multiplied by any integer; and for a reaction that represents the summation of more than one reaction

- Relating Kp to K (Kc)
- Write equilibrium expression for reactions involving heterogeneous equilibria.
- Explain what is meant by equilibrium position.
- Predict the direction of equilibrium position from the value of the Quotient, Q by comparing Q with K
- Solve equilibria problems
- Apply Le Chaetelier’s principle