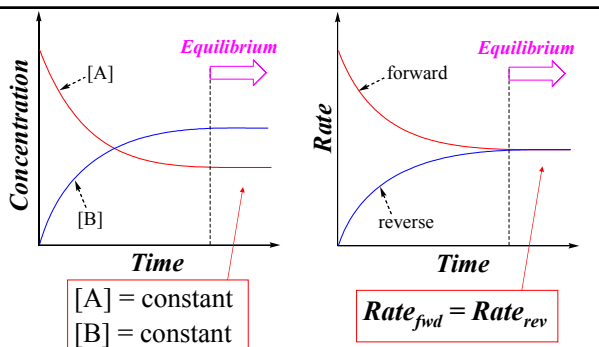


## Equilibrium: The Extent of Reactions

- Chemical equilibrium – studies the extent of reactions and the ways it can be altered
- Kinetics and equilibrium are two *different* aspects of chemical reactions (fast reactions may proceed to a great, lesser or a limited extent; same is true for slow reactions)

### 16.1 The Dynamic Nature of the Equilibrium State

- Chemical equilibrium** – a state in which the concentrations of reactants and products no longer change



- At a given  $T$ , the same equilibrium state is reached even if the process is started from different starting points

➤ Equilibrium is **not** a stationary state or a unidirectional process

**Example:**  $A \rightarrow B \rightarrow C$

If the rates of step 1 and step 2 are equal,  $[B]$  remains constant  $\rightarrow$  not an equilibrium state

➤ **Equilibrium is a dynamic state** achieved by the equalization of the forward and reverse rates of a **reversible** (bidirectional) **process**

**Example:**  $A \leftrightarrow B$

If the rates of the forward and reverse reactions are equal,  $[A]$  and  $[B]$  remain constant  $\rightarrow$  an equilibrium state

$\Rightarrow$  At equilibrium  $\rightarrow$   $\boxed{\text{Rate}_{\text{fwd}} = \text{Rate}_{\text{rev}}}$

**Example:**  $\text{N}_2\text{O}_4(\text{g}; \text{colorless}) \leftrightarrow 2\text{NO}_2(\text{g}; \text{brown})$

- The reaction can be started from pure  $\text{N}_2\text{O}_4(\text{g}; \text{colorless})$  or from pure  $\text{NO}_2(\text{g}; \text{brown})$ .
- In both cases at equilibrium, the same light-brown color is reached (the same proportion of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  is produced)
- The reaction has a single step mechanism (the forward and reverse reactions are elementary), so at equilibrium:

$$\text{Rate}_1 = \text{Rate}_{-1} \rightarrow k_1[\text{N}_2\text{O}_4] = k_{-1}[\text{NO}_2]^2$$

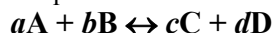
$\Rightarrow \frac{k_1}{k_{-1}} = K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$   $\rightarrow K$  is a constant which depends on  $T$  ( $K = 0.211$  at  $100^\circ\text{C}$ )  
 $\rightarrow K$  determines the proportion of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at equilibrium

## 17.2 The Equilibrium Constant and the Reaction Quotient

### The Law of Mass-Action

- Equilibrium constant ( $K$ )**

– For a general reaction at equilibrium:

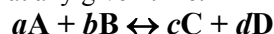


$$K_c = \frac{[\text{C}]_e^c [\text{D}]_e^d}{[\text{A}]_e^a [\text{B}]_e^b}$$

- $\rightarrow K_c$  is the **equilibrium constant** in terms of concentration (depends on  $T$  and the specific reaction)
- $\rightarrow [A]_e, [B]_e, [C]_e,$  and  $[D]_e$  are the **equilibrium concentrations** of the reactants and products
- $\rightarrow a, b, c,$  and  $d$  are the **stoichiometric coefficients** of the reactants and products

- Reaction quotient ( $Q$ )** – has the same mass-action expression as  $K$

– For a general reaction at any given time:



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

- $\rightarrow Q_c$  is the **reaction quotient** in terms of concentration ( $Q_c$  varies during the reaction)
- $\rightarrow [A], [B], [C],$  and  $[D]$  are the **current concentrations** of the reactants and products at any given time during the reaction
- $\rightarrow$  When the current concentrations become equal to the equilibrium concentrations,  $Q_c = K_c$

$\Rightarrow$  **At equilibrium**  $\rightarrow Q = K$

**Example:** Write the mass action expression for the reaction:  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{H}_2\text{O}(\text{g})$

$$Q_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]} \quad \text{At equilibrium} \rightarrow Q_c = K_c$$

- The mass-action expressions for  $Q$  and  $K$  depend on the form of the chemical equation



or



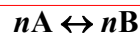
$$Q_c^{\rightarrow} = \frac{[\text{B}]}{[\text{A}]}$$

$$Q_c^{\leftarrow} = \frac{[\text{A}]}{[\text{B}]} = \frac{1}{Q_c^{\rightarrow}}$$

$\Rightarrow Q$  (or  $K$ ) of the reverse reaction is the reciprocal of  $Q$  (or  $K$ ) of the forward reaction



or



$$Q_c = \frac{[\text{B}]}{[\text{A}]}$$

$$Q_c' = \frac{[\text{B}]^n}{[\text{A}]^n} = (Q_c)^n$$

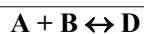
$\Rightarrow$  Multiplying a reaction by a factor,  $n$ , raises  $Q$  (or  $K$ ) to  $n^{\text{th}}$  power



$$Q_1 = \frac{[\text{C}]}{[\text{A}][\text{B}]}$$



$$Q_2 = \frac{[\text{D}]}{[\text{C}]}$$

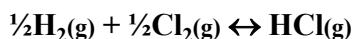


$$Q_c = \frac{[\text{D}]}{[\text{A}][\text{B}]}$$

$$Q_1 \times Q_2 = \frac{[\text{C}]}{[\text{A}][\text{B}]} \times \frac{[\text{D}]}{[\text{C}]} = \frac{[\text{D}]}{[\text{A}][\text{B}]} = Q_c$$

$\Rightarrow Q$  (or  $K$ ) of the sum of two or more reactions is the product of their  $Q$ s (or  $K$ s)

**Example:** For the gas phase reaction



$K_c$  is  $3.6 \times 10^{-5}$  at 1200 K. What is  $K_c'$  for the reaction

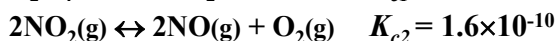


$\rightarrow$  The given reaction has been reversed  $\Rightarrow$  take the reciprocal of  $K_c$

$\rightarrow$  The given reaction has been multiplied by 2  $\Rightarrow$  take the square of  $K_c$

$$\Rightarrow K_c' = (1/K_c)^2 = (1/3.6 \times 10^{-5})^2 = 7.7 \times 10^8$$

**Example:** Given the following two reactions and their  $K_c$ s at a certain temperature:



Calculate  $K_c$  at this temperature for the reaction



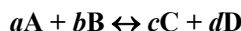
$\rightarrow$  The sum of the given reactions yields the desired reaction  $\Rightarrow$  multiply the  $K_c$

$$\Rightarrow K_c = K_{c1} \times K_{c2} = (2.2 \times 10^6) \times (1.6 \times 10^{-10})$$

$$\Rightarrow K_c = 3.5 \times 10^{-4}$$

## Connection between Kinetics and Equilibrium

$\triangleright$  For an elementary reaction:



$$\text{Rate}_{fwd} = k_{fwd}[\text{A}]^a[\text{B}]^b \quad \text{and} \quad \text{Rate}_{rev} = k_{rev}[\text{C}]^c[\text{D}]^d$$

$\triangleright$  At equilibrium:

$$\text{Rate}_{fwd} = \text{Rate}_{rev} \rightarrow k_{fwd}[\text{A}]^a[\text{B}]^b = k_{rev}[\text{C}]^c[\text{D}]^d$$

$$\Rightarrow \frac{k_{fwd}}{k_{rev}} = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} = Q_c = K_c \quad \Rightarrow \quad K_c = \frac{k_{fwd}}{k_{rev}}$$

$\rightarrow K_c$  is large when the forward reaction is fast and the reverse is slow ( $k_{fwd} \gg k_{rev}$ )

$\triangleright$  For an overall reaction (sum of elementary reactions),  $K_c$  is the product of the  $K_c$ s for the individual elementary steps:

$$K_c = K_c' \times K_c'' \times \dots = \frac{k'_{fwd}}{k'_{rev}} \times \frac{k''_{fwd}}{k''_{rev}} \times \dots$$

$\rightarrow$  The magnitude of  $K_c$  is an indication of how far a reaction proceeds toward products at a given  $T$

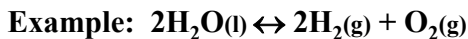
$\rightarrow$  Large  $K_c$  ( $K_c \gg 1$ ) – products dominate

$\rightarrow$  Small  $K_c$  ( $K_c \ll 1$ ) – reactants dominate

$\rightarrow$  Intermediate  $K_c$  ( $K_c \sim 1$ ) – significant amounts of both reactants and products are present at equilibrium

### Form of $Q$ and $K$ for Heterogeneous Equilibria

– **Heterogeneous** equilibria – reactants and products in different phases



$$Q'_c = \frac{[\text{H}_2(g)]^2 [\text{O}_2(g)]}{[\text{H}_2\text{O}(l)]^2}$$

➤ The concentration of  $\text{H}_2\text{O}$  in pure liquid water is constant at a given temperature

$$[\text{H}_2\text{O}] = \text{mol}/V = (m/MW)/V = d/MW$$

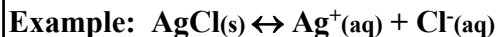
➤ At  $25^\circ\text{C}$ :

$$[\text{H}_2\text{O}] = (1.00 \times 10^3 \text{ g/L}) / (18.0 \text{ g/mol}) = 55.6 \text{ mol/L}$$

$$Q'_c \times [\text{H}_2\text{O}(l)]^2 = [\text{H}_2(g)]^2 [\text{O}_2(g)] = Q'_c \times (55.6)^2 = Q_c$$

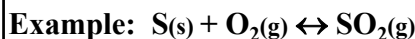
$$\Rightarrow Q_c = [\text{H}_2]^2 [\text{O}_2]$$

⇒ The molarities of **pure liquids** and **solids** remain constant during the reaction and can be **eliminated** from the expressions for  $Q$  and  $K$



→  $\text{AgCl}(s)$  is a pure solid

$$\Rightarrow Q_c = [\text{Ag}^+][\text{Cl}^-]$$



→  $\text{S}(s)$  is a pure solid

$$\Rightarrow Q_c = [\text{SO}_2] / [\text{O}_2]$$

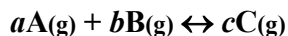
### 17.3 Equilibria Involving Gases

– Gases are quantified easier through partial pressures rather than molarities

➤ For a gaseous reactant or product, the molarity,  $C_i$ , and partial pressure,  $P_i$ , are related by the ideal gas law

$$P_i V = n_i RT \quad P_i / RT = n_i / V = C_i$$

➤ For a general reaction



$$Q_c = \frac{[\text{C}]^c}{[\text{A}]^a [\text{B}]^b}$$

$$Q_c = \frac{(P_C / RT)^c}{(P_A / RT)^a (P_B / RT)^b} = \frac{P_C^c}{P_A^a P_B^b} \times \frac{1}{(RT)^{c-(a+b)}}$$

$$Q_c = \frac{P_C^c}{P_A^a P_B^b} \times \frac{1}{(RT)^{\Delta n}} \quad \Delta n = c - (a + b)$$

$$Q_c = Q_p \times \frac{1}{(RT)^{\Delta n}} \quad Q_p = \frac{P_C^c}{P_A^a P_B^b}$$

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

→  $Q_p$  and  $K_p$  are the reaction quotient and equilibrium constant in terms of partial pressures ( $P$  is in atm,  $R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$ ,  $T$  is in K)

→  $\Delta n$  is the difference between the moles of gaseous products and reactants

$$\Delta n = n(\text{g, products}) - n(\text{g, reactants})$$

**Example:** For the reaction



$K_c = 2.6 \times 10^{-6}$  at  $1000\text{K}$ . What is the partial pressure of  $\text{CO}_2$  in the reaction mixture at this temperature?

→ Calculate  $K_p$

$$\rightarrow \Delta n = 1 - 0 = 1$$

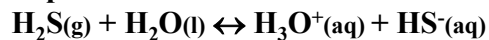
$$\rightarrow K_p = K_c (RT)^{\Delta n} = 2.6 \times 10^{-6} (0.0821 \times 1000) = 2.1 \times 10^{-4}$$

$$\rightarrow K_p = P_{\text{CO}_2} \quad \Rightarrow \quad P_{\text{CO}_2} = 2.1 \times 10^{-4} \text{ atm}$$

➤ Use  $K_c$  (or  $Q_c$ ) if molarities are given,  $K_p$  (or  $Q_p$ ) if partial pressures are given, or  $K$  (or  $Q$ ) for mixed expressions

➤ Omit the subscript “e” from all expressions for  $K$

**Example:**



$$K = [\text{H}_3\text{O}^+][\text{HS}^-] / P_{\text{H}_2\text{S}}$$

**Example:** Calculate  $K_c$  and  $K_p$  for the reaction



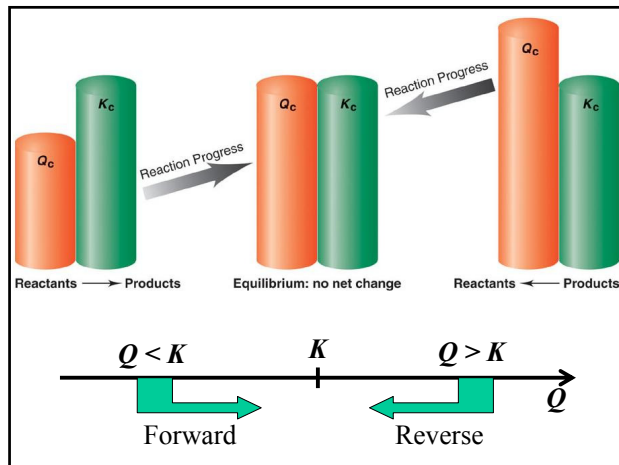
if at  $500 \text{ K}$ , the equilibrium concentrations of  $\text{BrCl}$ ,  $\text{Br}_2$  and  $\text{Cl}_2$  are  $0.131$ ,  $3.51$  and  $0.156 \text{ M}$ , respectively.

$$K_c = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2} = \frac{3.51 \times 0.156}{0.131^2} = 31.9$$

$$\rightarrow \Delta n = 1 + 1 - 2 = 0 \quad \Rightarrow \quad K_p = K_c (RT)^0 = 31.9 \times 1 = 31.9$$

## 17.4 The Direction of Reaction

- The direction of a reaction can be predicted by comparing the current value of  $Q$  to the value of  $K$  at the temperature of the reaction
- As the reaction approaches equilibrium,  $Q$  approaches  $K$ 
  - If  $Q < K$ , the concentration of reactants is too high, while that of products is too low  
 $\Rightarrow$  the reaction **proceeds forward**
  - If  $Q > K$ , the concentration of reactants is too low, while that of products is too high  
 $\Rightarrow$  the reaction **proceeds in reverse**
  - If  $Q = K$ , the reaction is **at equilibrium**



**Example:** For the reaction



$K_p = 0.98$  at 298 K. Predict the direction of the reaction at 298 K, if the partial pressures of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are 2.4 and 1.2 atm, respectively.

$$Q_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{1.2^2}{2.4} = 0.60 \quad K_p = 0.98$$

$\rightarrow Q_p < K_p \Rightarrow$  The reaction proceeds forward to produce more  $\text{NO}_2$

## 17.5 Solving Equilibrium Problems

- Calculation of  $K_c$  (or  $K_p$ ) values from measured equilibrium concentrations (or pressures)
- Calculation of equilibrium concentrations (or pressures) from  $K_c$  (or  $K_p$ ) values
- Equilibrium tables** (“*ice*” tables) – give the initial, *i*, change of, *c*, and equilibrium, *e*, concentrations of reactants and products
  - For a general reaction:  $\text{A} + 2\text{B} \leftrightarrow \text{C}$
  - $\rightarrow [\text{A}]_i, [\text{B}]_i, [\text{C}]_i$  – initial concentrations
  - $\rightarrow [\text{A}]_e, [\text{B}]_e, [\text{C}]_e$  – equilibrium concentrations
  - $\rightarrow \Delta[\text{A}], \Delta[\text{B}], \Delta[\text{C}]$ , – change in the concentrations
  - $\rightarrow [\text{A}]_e = [\text{A}]_i + \Delta[\text{A}] \rightarrow$  same is valid for B and C



$$\rightarrow \Delta[\text{C}] = +x$$

$$\rightarrow \Delta[\text{A}] = -\Delta[\text{C}] \times (1 \text{ mol A} / 1 \text{ mol C}) = -\Delta[\text{C}] = -x$$

$$\rightarrow \Delta[\text{B}] = -\Delta[\text{C}] \times (2 \text{ mol B} / 1 \text{ mol C}) = -2\Delta[\text{C}] = -2x$$

| [ ]      | A                  | + 2B                | $\leftrightarrow$ | C                  |
|----------|--------------------|---------------------|-------------------|--------------------|
| <i>i</i> | $[\text{A}]_i$     | $[\text{B}]_i$      |                   | $[\text{C}]_i$     |
| <i>c</i> | $-x$               | $-2x$               |                   | $+x$               |
| <i>e</i> | $[\text{A}]_i - x$ | $[\text{B}]_i - 2x$ |                   | $[\text{C}]_i + x$ |

$$\Rightarrow K_c = \frac{[\text{C}]}{[\text{A}][\text{B}]^2} = \frac{([\text{C}]_i + x)}{([\text{A}]_i - x)([\text{B}]_i - 2x)^2}$$

$\rightarrow$  The equation can be used to calculate  $K_c$  if  $x$  is known or to calculate  $x$  if  $K_c$  is known

## Using Equilibrium Quantities to Calculate $K$

- If all equilibrium concentrations are given, substitute in the mass action expression to find  $K$
- If the initial concentrations and one equilibrium concentration are given, use an *ice* table to find  $K$

**Example:** 1.00 mol of  $\text{NH}_3$  is sealed in a 1.00 L container and heated to 500 K. Calculate  $K_c$  for  $2\text{NH}_3(\text{g}) \leftrightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ , if at equilibrium the concentration of  $\text{NH}_3$  is 0.58 M.

$$\rightarrow [\text{NH}_3]_i = 1.00 \text{ mol} / 1.00 \text{ L} = 1.00 \text{ M}$$

$$\rightarrow [\text{N}_2]_i = [\text{H}_2]_i = 0$$

$$\rightarrow [\text{NH}_3]_e = 0.58 \text{ M}$$

|           |     |   |    |     |
|-----------|-----|---|----|-----|
|           | [ ] | 2NH <sub>3</sub> (g) ↔ N <sub>2</sub> (g) + 3H <sub>2</sub> (g) |    |     |
| i + c = e | i   | 1.00  | 0  | 0   |
|           | c   | -2x   | +x | +3x |
|           | e   | 1.00 - 2x   | x  | 3x  |

$$\rightarrow [\text{NH}_3]_e = 1.00 - 2x = 0.58$$

$$\rightarrow x = (1.00 - 0.58)/2 = 0.21$$

$$\rightarrow [\text{N}_2]_e = x = 0.21 \text{ M}$$

$$\rightarrow [\text{H}_2]_e = 3x = 0.63 \text{ M}$$

$$\Rightarrow K_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{[0.21][0.63]^3}{[0.58]^2} = 0.16$$

### Using $K$ to Calculate Equilibrium Quantities

- If  $K$  and all but one equilibrium concentrations are given, substitute in the mass action expression for  $K$  to find the unknown concentration
- If the initial concentrations and  $K$  are given, use an *ice* table to find the equilibrium concentrations

**Example:** 0.50 mol of HI is sealed in a 2.0 L reactor and heated to 700°C. Calculate the equilibrium concentrations of all species if at 700°C,  $K_c = 0.022$  for  $2\text{HI}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ .

$$\rightarrow [\text{HI}]_i = 0.50 \text{ mol}/2.0 \text{ L} = 0.25 \text{ M}$$

$$\rightarrow [\text{I}_2]_i = [\text{H}_2]_i = 0$$

|           |     |  |    |    |  |
|-----------|-----|--|----|----|--|
|           | [ ] | 2HI(g) ↔ H <sub>2</sub> (g) + I <sub>2</sub> (g) |    |    | $K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 0.022$ |
| i + c = e | i   | 0.25   | 0  | 0  |  |
|           | c   | -2x  | +x | +x |  |
|           | e   | 0.25 - 2x  | x  | x  |  |

$$\frac{x \cdot x}{(0.25 - 2x)^2} = 0.022 \Rightarrow \sqrt{\frac{x^2}{(0.25 - 2x)^2}} = \sqrt{0.022}$$

$$\frac{x}{0.25 - 2x} = \sqrt{0.022} \Rightarrow x = \sqrt{0.022} \times 0.25 - \sqrt{0.022} \times 2x$$

$$x + 0.297x = 0.0371 \Rightarrow x = \frac{0.0371}{1 + 0.297} = 0.029$$

$$\Rightarrow [\text{H}_2]_e = [\text{I}_2]_e = x = 0.029 \text{ M}$$

$$\Rightarrow [\text{HI}]_e = 0.25 - 2x = 0.25 - 2 \times 0.029 = 0.19 \text{ M}$$

### ➤ Using the quadratic formula

**Example:** 0.50 mol HI and 0.30 mol H<sub>2</sub> are sealed in a 2.0 L reactor and heated to 700°C. Calculate the equilibrium concentrations of all species if at 700°C,  $K_c = 0.022$  for  $2\text{HI}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ .

$$\rightarrow [\text{HI}]_i = 0.50 \text{ mol}/2.0 \text{ L} = 0.25 \text{ M}$$

$$\rightarrow [\text{H}_2]_i = 0.30 \text{ mol}/2.0 \text{ L} = 0.15 \text{ M}$$

$$\rightarrow [\text{I}_2]_i = 0$$

|           |     |  |          |    |  |
|-----------|-----|--|----------|----|--|
|           | [ ] | 2HI(g) ↔ H <sub>2</sub> (g) + I <sub>2</sub> (g) |          |    | $K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 0.022$ |
| i + c = e | i   | 0.25   | 0.15     | 0  |  |
|           | c   | -2x  | +x       | +x |  |
|           | e   | 0.25 - 2x  | 0.15 + x | x  |  |

|   |
|---|
| $\frac{(0.15 + x)x}{(0.25 - 2x)^2} = 0.022 \Rightarrow \frac{0.15x + x^2}{0.25^2 - 2 \times 0.25 \times 2x + 4x^2} = 0.022$ |
| $0.15x + x^2 = 0.022 \times 0.25^2 - 0.022 \times 4 \times 0.25x + 0.022 \times 4x^2$                                       |
| $0.15x + x^2 = 0.00138 - 0.022x + 0.088x^2$   |
| $0.912x^2 + 0.172x - 0.00138 = 0$   |
| $x_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \rightarrow \text{The } (-) \text{ solution is meaningless}$                  |
| $x = \frac{-0.172 + \sqrt{0.172^2 - 4 \times 0.912 \times (-0.00138)}}{2 \times 0.912} = 0.00768$                           |
| $\Rightarrow [\text{I}_2]_e = x = 0.0077 \text{ M}$   |
| $\Rightarrow [\text{H}_2]_e = 0.15 + x = 0.15 + 0.00768 = 0.16 \text{ M}$   |
| $\Rightarrow [\text{HI}]_e = 0.25 - 2x = 0.25 - 2 \times 0.00768 = 0.23 \text{ M}$  |

### ➤ Using simplifying assumptions

**Example:** A mixture of 0.060 M N<sub>2</sub> and 0.040 M H<sub>2</sub> is heated to a temperature where  $K_c = 0.0010$  for  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$ . Calculate the equilibrium concentration of NH<sub>3</sub>.

$$\rightarrow [\text{N}_2]_i = 0.060 \text{ M}$$

$$\rightarrow [\text{H}_2]_i = 0.040 \text{ M}$$

$$\rightarrow [\text{NH}_3]_i = 0$$

|           |     |   |            |     |   |
|-----------|-----|---|------------|-----|---|
|           | [ ] | N <sub>2</sub> (g) + 3H <sub>2</sub> (g) ↔ 2NH <sub>3</sub> (g) |            |     | $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 0.0010$ |
| i + c = e | i   | 0.060   | 0.040      | 0   |   |
|           | c   | -x  | -3x        | +2x |   |
|           | e   | 0.060 - x   | 0.040 - 3x | 2x  |   |

$$\frac{(2x)^2}{(0.060 - x)(0.040 - 3x)^3} = 0.0010$$

→  $x$  is expected to be very small ( $K_c$  is quite small, so the product molarity,  $2x$ , should be small too)

⇒ **Assumption** →  $x$  can be neglected in summations  
 ⇒  $0.060 - x \approx 0.060$  and  $0.040 - 3x \approx 0.040$

$$\frac{4x^2}{(0.060)(0.040)^3} = 0.0010 \Rightarrow x = \sqrt{\frac{0.0010 \times 0.060 \times 0.040^3}{4}}$$

$$x = 3.1 \times 10^{-5}$$

→ Must check the assumption ( $x \ll 0.06$  and  $3x \ll 0.04$ )

→ The **assumption is justified** since  $x$  and  $3x$  are less than 5% of 0.060 and 0.040 → The **5% rule**

⇒  $[\text{NH}_3]_e = 2x = 2 \times (3.1 \times 10^{-5}) = 6.2 \times 10^{-5} \text{ M}$

➤ Simplifying assumptions are not always justified

**Example:** A mixture of **0.060 M**  $\text{N}_2$  and **0.040 M**  $\text{H}_2$  is heated to a temperature where  $K_c = 10$ . for  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$ . Calculate the equilibrium concentration of  $\text{NH}_3$ .

→ Using the assumption from the previous problem leads to:

$$\frac{4x^2}{(0.060)(0.040)^3} = 10. \Rightarrow x = \sqrt{\frac{10 \times 0.060 \times 0.040^3}{4}}$$

$$x = 0.0031$$

→ The **assumption is not justified** since  $x$  and  $3x$  are more than 5% of 0.060 and 0.040

$$(3 \times 0.0031 / 0.040) \times 100\% = 23\% \text{ error}$$

⇒ We must solve the equation without assumptions

➤ **Successive approximation**

→ Using the same formula as in the previous problem without neglecting  $x$  and  $3x$  leads to:

$$x_{n+1} = \sqrt{\frac{10 \times (0.060 - x_n)(0.040 - 3x_n)^3}{4}}$$

→ This formula allows the calculation of the **(n+1)<sup>st</sup>** approximation for  $x$  from the **n<sup>th</sup>** approximation

→ For **n=0**, assume  $x_0 = 0$  ( $x$  is expected to be small)

→ For **n=1** (1<sup>st</sup> iteration)

$$x_1 = \sqrt{\frac{10 \times (0.060 - 0)(0.040 - 3 \times 0)^3}{4}} = 0.0031$$

→ For **n=2** (2<sup>nd</sup> iteration)

$$x_2 = \sqrt{\frac{10 \times (0.060 - 0.0031)(0.040 - 3 \times 0.0031)^3}{4}} = 0.0020$$

→ For **n=3** (3<sup>rd</sup> iteration)

$$x_3 = \sqrt{\frac{10 \times (0.060 - 0.0020)(0.040 - 3 \times 0.0020)^3}{4}} = 0.0024$$

→ For **n=4** (4<sup>th</sup> iteration)

$$x_4 = \sqrt{\frac{10 \times (0.060 - 0.0024)(0.040 - 3 \times 0.0024)^3}{4}} = 0.0023$$

→ For **n=5** (5<sup>th</sup> iteration) →  $x_5 = 0.0023$

→ Since  $x_5 \approx x_4$  (convergence) ⇒  $x = 0.0023$

⇒  $[\text{NH}_3]_e = 2x = 2 \times (0.0023) = 0.0046 \text{ M}$

### Equilibrium Calculations for Reactions with Unknown Direction

**Example:** **0.50 mol**  $\text{H}_2$ , **0.50 mol**  $\text{I}_2$  and **0.50 mol**  $\text{HI}$  are mixed in a **1.0 L** container and heated to a temperature where  $K_c = 0.45$  for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2\text{HI}(\text{g})$ . Calculate  $[\text{HI}]$  at equilibrium.

→  $[\text{H}_2]_i = [\text{I}_2]_i = [\text{HI}]_i = 0.50 \text{ mol} / 1.0 \text{ L} = 0.50 \text{ M}$

→ Since all reactants and products are present initially, the direction of the reaction must be determined first  
 ⇒  $Q_c$  must be calculated and compared to  $K_c$

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{0.50^2}{0.50 \times 0.50} = 1 > K_c$$

→  $Q_c > K_c$  ⇒ the reaction proceeds to the left

|             |     |                        |   |                        |                   |                        |   |
|-------------|-----|------------------------|---|------------------------|-------------------|------------------------|---|
|             | [I] | $\text{H}_2(\text{g})$ | + | $\text{I}_2(\text{g})$ | $\leftrightarrow$ | $2\text{HI}(\text{g})$ | $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 0.45$ |
| $i + c = e$ | i   | 0.50                   |   | 0.50                   |                   | 0.50                   |   |
|             | c   | +x                     |   | +x                     |                   | -2x                    |   |
|             | e   | $0.50 + x$             |   | $0.50 + x$             |                   | $0.50 - 2x$            |   |

$$\frac{(0.50 - 2x)^2}{(0.50 + x)(0.50 + x)} = 0.45 \Rightarrow \sqrt{\frac{(0.50 - 2x)^2}{(0.50 + x)^2}} = \sqrt{0.45}$$

$$\frac{(0.50 - 2x)}{(0.50 + x)} = \sqrt{0.45} \Rightarrow (0.50 - 2x) = \sqrt{0.45} \times (0.50 + x)$$

$$0.50 - 0.67 \times 0.50 = 2x + 0.67x \Rightarrow x = \frac{0.165}{2 + 0.67} = 0.062$$

⇒  $[\text{HI}]_e = 0.50 - 2x = 0.50 - 2 \times 0.062 = 0.38 \text{ M}$

## 17.6 Changing Reaction Conditions and the Equilibrium State

- **Le Chatelier's principle** – when a system at equilibrium is disturbed, the equilibrium “shifts” in a direction that minimizes the effect of the disturbance

– A chemical system can be disturbed by changing the values of  $Q$  or  $K$  so that temporarily  $Q \neq K$

- Changing concentrations of reactants or products ( $Q$  changes)
- Changing pressure for gas reactions ( $Q$  changes)
- Changing temperature ( $K$  changes)

**Example:** Given  $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ . How can the yield of  $NH_3$  be increased by manipulating the concentrations of reactants and products?

- Add more  $N_2$  and  $H_2$
- Remove some  $NH_3$

### Changing Pressure or Volume

- Affects the concentrations of gaseous reactants and products (changes  $Q$ )

- **Changing the partial pressure** of a gaseous reactant or product

→ The concentration of the reactant or product changes and the equilibrium shifts accordingly as described before

#### ➤ Expansion ( $\downarrow P$ by $\uparrow V$ )

→ The equilibrium shifts in a direction that produces more gases and increases the pressure

⇒ The equilibrium **shifts toward the side with more moles of gas**

➤ Compression and expansion do not affect reactions in which the number of moles of gases is the same on both sides of the equation

- **Changing the total pressure** of the reaction mixture by **adding an inert gas**

→ The equilibrium **is not affected** because the partial pressures and concentrations of the components do not change

## Changing Concentration

- If the concentration increases, the system reacts to consume some of it; If the concentration decreases, the system reacts to produce some of it

- **Adding reactants or removing products**

→ The equilibrium **shifts toward the products** in order to consume the added reactants or generate the removed products

→  $Q$  decreases →  $Q < K$  → reaction **shifts forward**

- **Adding products or removing reactants**

→ The equilibrium **shifts toward the reactants** in order to consume the added products or generate the removed reactants

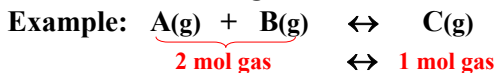
→  $Q$  increases →  $Q > K$  → reaction **shifts in reverse**

- **Changing the total pressure** of the reaction mixture by **changing its volume**

- **Compression** ( $\uparrow P$  by  $\downarrow V$ )

→ The equilibrium shifts in a direction that consumes gases and relieves the pressure

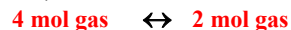
⇒ The equilibrium **shifts toward the side with fewer moles of gas**



$$Q_p = \frac{P_C}{P_A P_B} = \frac{(n_C RT / V)}{(n_A RT / V)(n_B RT / V)} = \frac{n_C}{n_A n_B} \times \frac{V}{RT}$$

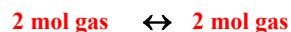
⇒ As  $V$  is reduced,  $Q$  decreases ( $Q < K$ ) and the reaction shifts forward

**Example:** Given  $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ . How can the yield of  $NH_3$  be increased by changing the pressure (volume) of the reaction mixture?



⇒ Increasing the pressure (compression) shifts the equilibrium to the right toward less moles of gas (4 mol → 2 mol) and improves the yield of  $NH_3$

**Example:** Given  $Cl_2(g) + H_2(g) \leftrightarrow 2HCl(g)$ . What is the effect of increasing the volume of the reaction container?



⇒ Increasing the volume (expansion) has no effect on the reaction since the number of moles of gas is the same on both sides of the equation

## Changing Temperature

- Affects the value of  $K$

➤ **Increasing  $T$**  by adding heat to the reaction mixture **favours the endothermic reaction** which consumes the added heat

➤ **Decreasing  $T$**  by removing heat from the reaction mixture **favours the exothermic reaction** which produces heat

**Example:**  $A + B \leftrightarrow C + D + \text{heat}$      $\Delta H < 0$

→ The forward reaction is exothermic, while the reverse reaction is endothermic

⇒ Increasing  $T$  favors the endothermic reaction so the reaction shifts in reverse

➤ Changing  $T$  changes the value of  $K$

➤ Increasing  $T$  increases  $K$  for endothermic reactions

➤ Increasing  $T$  decreases  $K$  for exothermic reactions

→ Increasing  $T$  increases more the rate constant of the endothermic reaction (which has higher activation energy) →  $K = k_{\text{fwd}}/k_{\text{rev}}$  ⇒ If the forward reaction is endothermic,  $K$  increases

**Example:** Given  $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$  with  $\Delta H^\circ = -92$  kJ/mol. How can the yield of  $NH_3$  be increased by manipulating the temperature?

→ The forward reaction is exothermic

⇒ Lowering the temperature facilitates the forward reaction and improves the yield of  $NH_3$

➤ The  $T$  dependence of  $K$  is given by the van't Hoff equation

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{\text{rxn}}^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

→ The equation allows the calculation of  $K$  at one temperature knowing the value of  $K$  at another temperature and  $\Delta H^\circ$  of the reaction

**Example:** Given  $N_2(g) + O_2(g) \leftrightarrow 2NO(g)$  with  $\Delta H^\circ = 181$  kJ/mol. If  $K_p = 4.3 \times 10^{-31}$  at 298 K, what is  $K_p$  at 3000 K?

$$T_1 = 298 \text{ K} \quad K_{p1} = 4.3 \times 10^{-31}$$

$$T_2 = 3000 \text{ K} \quad K_{p2} = ?$$

$$\ln \frac{K_{p2}}{4.3 \times 10^{-31}} = -\frac{181 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{3000 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\frac{K_{p2}}{4.3 \times 10^{-31}} = \exp \left( -\frac{181 \times 10^3}{8.314} \left( \frac{1}{3000} - \frac{1}{298} \right) \right)$$

$$K_{p2} = 4.3 \times 10^{-31} \times \exp \left( -\frac{181 \times 10^3}{8.314} \left( \frac{1}{3000} - \frac{1}{298} \right) \right)$$

$$K_{p2} = 1.6 \times 10^{-2}$$

→  $K_p$  is much larger at 3000 K because the forward reaction is endothermic and therefore is favored by  $\uparrow T$

## The Effect of Catalysts

➤ Catalysts **do not affect the equilibrium state** and the value of  $K$  because they speed up equally both the forward and reverse reactions

➤ Catalysts only shorten the time needed to reach equilibrium

**Example:** Given  $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$  with  $\Delta H^\circ = -92$  kJ/mol. What are the optimum conditions for the synthesis of  $NH_3$ ?

→ Pump in more  $N_2$  and  $H_2$  and remove  $NH_3$  ( $NH_3$  can be removed by cooling → condensation)

→ Increase  $P$  and decrease  $T$

→ At lower  $T$ , a catalyst is needed to speed up the process

**Table 17.4** Effect of Various Disturbances on an Equilibrium System

| Disturbance  | Net Direction of Reaction   | Effect on Value of $K$   |
|--|---|--|
| <b>Concentration</b>                               |   |  |
| Increase [reactant]                                | Toward formation of product   | None   |
| Decrease [reactant]                                | Toward formation of reactant  | None   |
| Increase [product]                                 | Toward formation of reactant  | None   |
| Decrease [product]                                 | Toward formation of product   | None   |
| <b>Pressure</b>                                    |   |  |
| Increase $P$<br>(decrease $V$ )                    | Toward formation of fewer moles of gas  | None   |
| Decrease $P$<br>(increase $V$ )                    | Toward formation of more moles of gas   | None   |
| Increase $P$<br>(add inert gas, no change in $V$ ) | None; concentrations unchanged  | None   |
| <b>Temperature</b>                                 |   |  |
| Increase $T$                                       | Toward absorption of heat   | Increases if $\Delta H_{\text{rxn}}^\circ > 0$<br>Decreases if $\Delta H_{\text{rxn}}^\circ < 0$ |
| Decrease $T$                                       | Toward release of heat  | Increases if $\Delta H_{\text{rxn}}^\circ < 0$<br>Decreases if $\Delta H_{\text{rxn}}^\circ > 0$ |
| Catalyst added                                     | None; forward and reverse equilibrium attained sooner; rates increase equally | None   |