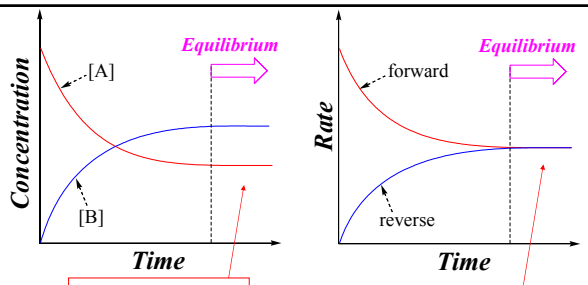
Equilibrium: The Extent of Reactions

– 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



[A] = constant
[B] = constant

$Rate_{fwd} = Rate_{rev}$

– 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 → B → C)

If the rates of step 1 and step 2 are equal, [B] remains constant → 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 ↔ B)

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

⇒ At equilibrium → $Rate_{fwd} = Rate_{rev}$

Example: N_2O_4(g; colorless) ↔ $2NO_2$(g; brown)

➢ The reaction can be started from pure N_2O_4(g; colorless) or from pure NO_2(g; brown).

➢ In both cases at equilibrium, the same light-brown color is reached (the same proportion of N_2O_4 and NO_2 is produced)

➢ The reaction has a single step mechanism (the forward and reverse reactions are elementary), so at equilibrium:

$Rate_1 = Rate_{-1} \rightarrow k_1[N_2O_4] = k_{-1}[NO_2]^2$

$$\Rightarrow \frac{k_1}{k_{-1}} = K = \frac{[NO_2]^2}{[N_2O_4]}$$

→ ***K*** is a constant which depends on ***T*** (***K*** = 0.211 at 100°C)
→ ***K*** determines the proportion of N_2O_4 and 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:

$aA + bB \leftrightarrow cC + dD$

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

→ K_c is the **equilibrium constant** in terms of concentration (depends on ***T*** and the specific reaction)
→ $[A]_e$, $[B]_e$, $[C]_e$, and $[D]_e$ are the **equilibrium concentrations** of the reactants and products
→ ***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:

$aA + bB \leftrightarrow cC + dD$

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

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

⇒ **At equilibrium → $Q = K$**

Example: Write the mass action expression for the reaction: $2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$

$$Q_c = \frac{[H_2O]^2}{[H_2]^2[O_2]} \qquad \textit{At equilibrium} \rightarrow Q_c = K_c$$

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

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

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

$A \leftrightarrow B$	or	$nA \leftrightarrow nB$
$Q_c = \frac{[B]}{[A]}$		$Q_c' = \frac{[B]^n}{[A]^n} = (Q_c)^n$

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

1. $A + B \leftrightarrow C$ $\quad Q_1 = [C]/[A][B]$
2. $C \leftrightarrow D$ $\quad Q_2 = [D]/[C]$

$A + B \leftrightarrow D$ $\quad Q_c = [D]/[A][B]$

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

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

Example: For the gas phase reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \leftrightarrow HCl(g)$$

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

$$2HCl(g) \leftrightarrow H_2(g) + Cl_2(g) \ ?$$

$\rightarrow$ 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

$\Rightarrow K_c' = (1/K_c)^2 = (1/3.6\times10^{-5})^2 = 7.7\times10^8$

Example: Given the following two reactions and their K_cs at a certain temperature:

$N_2O_4(g) \leftrightarrow 2NO_2(g)$ $\qquad K_{c1} = 2.2\times10^6$

$2NO_2(g) \leftrightarrow 2NO(g) + O_2(g)$ $\qquad K_{c2} = 1.6\times10^{-10}$

Calculate K_c at this temperature for the reaction

$$N_2O_4(g) \leftrightarrow 2NO(g) + O_2(g)$$

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

$\Rightarrow K_c = K_{c1} \times K_{c2} = (2.2\times10^6)\times(1.6\times10^{-10})$

$\Rightarrow K_c = 3.5\times10^{-4}$

Connection between Kinetics and Equilibrium

➢For an **elementary** reaction:

$$aA + bB \leftrightarrow cC + dD$$

$Rate_{fwd} = k_{fwd}[A]^a[B]^b$ and $Rate_{rev} = k_{rev}[C]^c[D]^d$

➢At equilibrium:

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

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

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

➢For an **overall** reaction (sum of elementary reactions), K_c is the product of the K_cs for the individual elementary steps:

$$K_c = K_c' \times K_c'' \times \ldots = \frac{k_{fwd}'}{k_{rev}'} \times \frac{k_{fwd}''}{k_{rev}''} \times \ldots$$

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

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

$\rightarrow$ Small K_c ($K_c << 1$) – 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

Example: $2H_2O(l) \leftrightarrow 2H_2(g) + O_2(g)$

$$Q_c' = \frac{[H_2(g)]^2[O_2(g)]}{[H_2O(l)]^2}$$

➢ The concentration of H_2O in pure liquid water is constant at a given temperature

$[H_2O] = mol/V = (m/MW)/V = d/MW$

➢ At 25°C:

$[H_2O] = (1.00\times10^3\ g/L)/(18.0\ g/mol) = 55.6\ mol/L$

$$Q_c' \times [H_2O(l)]^2 = [H_2(g)]^2[O_2(g)] = Q_c' \times (55.6)^2 = Q_c$$

$$\Rightarrow \quad Q_c = [H_2]^2[O_2]$$

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

Example: $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$

→ $AgCl(s)$ is a pure solid

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

Example: $S(s) + O_2(g) \leftrightarrow SO_2(g)$

→ $S(s)$ is a pure solid

$$\Rightarrow Q_c = [SO_2]/[O_2]$$

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

$$P_iV = n_iRT \qquad P_i/RT = n_i/V = C_i$$

➢ For a general reaction

$$aA(g) + bB(g) \leftrightarrow cC(g) \qquad Q_c = \frac{[C]^c}{[A]^a[B]^b}$$

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

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

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

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

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

→ Δn is the difference between the moles of gaseous products and reactants

$\Delta n = n$ (g, products) – n (g, reactants)

Example: For the reaction

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

$K_c = 2.6\times10^{-6}$ at 1000K. What is the partial pressure of CO_2 in the reaction mixture at this temperature?

→ Calculate K_p

→ $\Delta n = 1 - 0 = 1$

→ $K_p = K_c(RT)^{\Delta n} = 2.6\times10^{-6}(0.0821\times1000) = 2.1\times10^{-4}$

→ $K_p = Pco_2 \quad \Rightarrow \quad Pco_2 = \mathbf{2.1\times10^{-4}\ atm}$

➢ 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:

$$H_2S(g) + H_2O(l) \leftrightarrow H_3O^+(aq) + HS^-(aq)$$

$$K = [H_3O^+][HS^-]/P_{H_2S}$$

Example: Calculate K_c and K_p for the reaction

$$2BrCl(g) \leftrightarrow Br_2(g) + Cl_2(g)$$

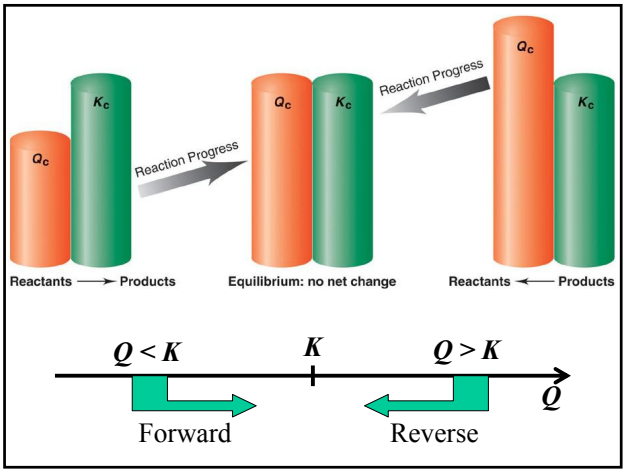
if at 500 K, the equilibrium concentrations of BrCl, Br_2 and Cl_2 are 0.131, 3.51 and 0.156 M, respectively.

$$K_c = \frac{[Br_2][Cl_2]}{[BrCl]^2} = \frac{3.51\times0.156}{0.131^2} = 31.9$$

→ $\Delta n = 1+1-2 = 0 \Rightarrow K_p = K_c(RT)^0 = 31.9\times1 = 31.9$

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

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

$K_p = 0.98$ at 298 K. Predict the direction of the reaction at 298 K, if the partial pressures of N_2O_4 and NO_2 are 2.4 and 1.2 atm, respectively.

$$Q_p = \frac{P_{NO_2}^{\,2}}{P_{N_2O_4}} = \frac{1.2^2}{2.4} = 0.60 \qquad K_p = 0.98$$

$\rightarrow Q_p < K_p \Rightarrow$ The reaction proceeds forward to produce more 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: $A + 2B \leftrightarrow C$
  - $\rightarrow [A]_i, [B]_i, [C]_i$ – initial concentrations
  - $\rightarrow [A]_e, [B]_e, [C]_e$ – equilibrium concentrations
  - $\rightarrow \Delta[A], \Delta[B], \Delta[C],$ – change in the concentrations
  - $\rightarrow [A]_e = [A]_i + \Delta[A] \rightarrow$ same is valid for B and C

$$A + 2B \leftrightarrow C$$

$\rightarrow \Delta[C] = +x$

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

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

e = c + i

[ ]	A	+ 2B	↔ C
i	$[A]_i$	$[B]_i$	$[C]_i$
c	$-x$	$-2x$	$+x$
e	$[A]_i - x$	$[B]_i - 2x$	$[C]_i + x$

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

$\rightarrow$ 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 NH_3 is sealed in a **1.00 L** container and heated to 500 K. Calculate K_c for $2NH_3(g) \leftrightarrow N_2(g) + 3H_2(g)$, if at equilibrium the concentration of NH_3 is **0.58 M**.

$\rightarrow [NH_3]_i = 1.00 \text{ mol}/1.00 \text{ L} = 1.00 \text{ M}$

$\rightarrow [N_2]_i = [H_2]_i = 0$

$\rightarrow [NH_3]_e = 0.58 \text{ M}$

$i + c = e$	[ ]	$2NH_3(g) \leftrightarrow$	$N_2(g)$	+	$3H_2(g)$
	i	1.00	0		0
	c	$-2x$	$+x$		$+3x$
	e	$1.00 - 2x$	x		$3x$

$\rightarrow [NH_3]_e = 1.00 - 2x = 0.58$

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

$\rightarrow [N_2]_e = x = 0.21$ M

$\rightarrow [H_2]_e = 3x = 0.63$ M

$$\Rightarrow K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{[0.21][0.63]^3}{[0.58]^2} = 0.16$$

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 $2HI(g) \leftrightarrow H_2(g) + I_2(g)$.

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

$\rightarrow [I_2]_i = [H_2]_i = 0$

$i + c = e$	[ ]	$2HI(g) \leftrightarrow$	$H_2(g)$	+	$I_2(g)$
	i	0.25	0		0
	c	$-2x$	$+x$		$+x$
	e	$0.25 - 2x$	x		x

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = 0.022$$

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

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

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

$\Rightarrow [H_2]_e = [I_2]_e = x = \mathbf{0.029\ M}$

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

➢Using the **quadratic formula**

Example: **0.50 mol** HI and **0.30 mol** H_2 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 $2HI(g) \leftrightarrow H_2(g) + I_2(g)$.

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

$\rightarrow [H_2]_i = 0.30$ mol/2.0 L = 0.15 M

$\rightarrow [I_2]_i = 0$

$i + c = e$	[ ]	$2HI(g) \leftrightarrow$	$H_2(g)$	+	$I_2(g)$
	i	0.25	0.15		0
	c	$-2x$	$+x$		$+x$
	e	$0.25 - 2x$	$0.15 + x$		x

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = 0.022$$

$$\frac{(0.15 + x)x}{(0.25 - 2x)^2} = 0.022 \Rightarrow \frac{0.15x + x^2}{0.25^2 - 2 \times 0.25 \times 2x + 4x^2} = 0.022$$

$$0.15x + x^2 = 0.022 \times 0.25^2 - 0.022 \times 4 \times 0.25x + 0.022 \times 4x^2$$

$$0.15x + x^2 = 0.00138 - 0.022x + 0.088x^2$$

$$0.912x^2 + 0.172x - 0.00138 = 0$$

$$x_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$ → The (-) solution is meaningless

$$x = \frac{-0.172 + \sqrt{0.172^2 - 4 \times 0.912 \times (-0.00138)}}{2 \times 0.912} = 0.00768$$

$\Rightarrow [I_2]_e = x = \mathbf{0.0077\ M}$

$\Rightarrow [H_2]_e = 0.15 + x = 0.15 + 0.00768 = \mathbf{0.16\ M}$

$\Rightarrow [HI]_e = 0.25 - 2x = 0.25 - 2 \times 0.00768 = \mathbf{0.23\ M}$

➢Using **simplifying assumptions**

Example: A mixture of **0.060 M** N_2 and **0.040 M** H_2 is heated to a temperature where $K_c = 0.0010$ for $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$. Calculate the equilibrium concentration of NH_3.

$\rightarrow [N_2]_i = 0.060$ M

$\rightarrow [H_2]_i = 0.040$ M

$\rightarrow [NH_3]_i = 0$

$i + c = e$	[ ]	$N_2(g)$	+	$3H_2(g) \leftrightarrow$	$2NH_3(g)$
	i	0.060		0.040	0
	c	$-x$		$-3x$	$+2x$
	e	$0.060 - x$		$0.040 - 3x$	$2x$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.0010$$

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

→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 $0.040 - 3x \approx 0.040$

$$\frac{4x^2}{(0.060)(0.040)^3} = 0.0010 \Rightarrow x = \sqrt{\frac{0.0010\times0.060\times0.040^3}{4}}$$

$$x = 3.1\times10^{-5}$$

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

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

⇒ $[NH_3]_e = 2x = 2\times(3.1\times10^{-5}) =$ **6.2×10^{-5} M**

➢Simplifying assumptions are not always justified

Example: A mixture of **0.060 M** N_2 and **0.040 M** H_2 is heated to a temperature where K_c **= 10.** for $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$. Calculate the equilibrium concentration of NH_3.

→ Using the assumption from the previous problem leads to:

$$\frac{4x^2}{(0.060)(0.040)^3} = 10. \Rightarrow x = \sqrt{\frac{10.\times0.060\times0.040^3}{4}}$$

$$x = 0.0031$$

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

$(3\times0.0031/0.040)\times100\% = 23\%$ 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)st** approximation for x from the **nth** approximation

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

→For **n=1** (1st iteration)

$$x_1 = \sqrt{\frac{10.\times(0.060 - 0)(0.040 - 3\times0)^3}{4}} = 0.0031$$

→For **n=2** (2nd iteration)

$$x_2 = \sqrt{\frac{10.\times(0.060 - 0.0031)(0.040 - 3\times0.0031)^3}{4}} = 0.0020$$

→For **n=3** (3rd iteration)

$$x_3 = \sqrt{\frac{10.\times(0.060 - 0.0020)(0.040 - 3\times0.0020)^3}{4}} = 0.0024$$

→For **n=4** (4th iteration)

$$x_4 = \sqrt{\frac{10.\times(0.060 - 0.0024)(0.040 - 3\times0.0024)^3}{4}} = 0.0023$$

→For **n=5** (5th iteration) → $x_5 = 0.0023$

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

⇒ $[NH_3]_e = 2x = 2\times(0.0023) =$ **0.0046 M**

Equilibrium Calculations for Reactions with Unknown Direction

Example: **0.50 mol** H_2, **0.50 mol** I_2 and **0.50 mol** HI are mixed in a **1.0 L** container and heated to a temperature where K_c **= 0.45** for the reaction $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$. Calculate [HI] at equilibrium.

→$[H_2]_i = [I_2]_i = [HI]_i = 0.50$ mol/1.0 L = **0.50 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

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.50^2}{0.50\times0.50} = 1 > K_c$$

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

$\Delta = \mathcal{P} + I$	[ ]	$H_{2(g)}$ +	$I_{2(g)}$ ↔	$2HI_{(g)}$
	i	0.50	0.50	0.50
	c	$+x$	$+x$	$-2x$
	e	$0.50 + x$	$0.50 + x$	$0.50 - 2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 0.45$$

$$\frac{(0.50-2x)^2}{(0.5+x)(0.5+x)} = 0.45 \Rightarrow \sqrt{\frac{(0.50-2x)^2}{(0.5+x)^2}} = \sqrt{0.45}$$

$$\frac{(0.50-2x)}{(0.5+x)} = \sqrt{0.45} \Rightarrow (0.50-2x) = \sqrt{0.45}\times(0.5+x)$$

$$0.50 - 0.67\times0.50 = 2x + 0.67x \Rightarrow x = \frac{0.165}{2+0.67} = 0.062$$

⇒ $[HI]_e = 0.50 - 2x = 0.50 - 2\times0.062 =$ **0.38 M**

17.6 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 $\mathbf{N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}}$. 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**

Example: $\mathbf{A(g) + B(g) \leftrightarrow C(g)}$

2 mol gas ↔ 1 mol 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 $\mathbf{N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}}$. How can the yield of NH_3 be increased by changing the pressure (volume) of the reaction mixture?

4 mol gas ↔ 2 mol gas

⇒ 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 $\mathbf{Cl_{2(g)} + H_{2(g)} \leftrightarrow 2HCl_{(g)}}$. What is the effect of increasing the volume of the reaction container?

2 mol gas ↔ 2 mol gas

⇒ 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 **favors the endothermic reaction** which consumes the added heat

➢**Decreasing *T*** by removing heat from the reaction mixture **favors the exothermic reaction** which produces heat

Example: $\mathbf{A + B \leftrightarrow C + D + }$ ***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) → $K = k_{fwd}/k_{rev}$ ⇒ If the forward reaction is endothermic, ***K*** increases

Example: Given $\mathbf{N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}}$ with ΔH = -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

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

→ The equation allows the calculation of ***K*** at one temperature knowing the value of ***K*** at another temperature and ΔH^o of the reaction

Example: Given $\mathbf{N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}}$ with ΔH = -92 kJ/mol. If K = 1 at C, what is K at C?