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 ↔ C**

→$[A]_i$, $[B]_i$, $[C]_i$ – initial concentrations

→$[A]_e$, $[B]_e$, $[C]_e$ – equilibrium concentrations

→$\Delta[A]$, $\Delta[B]$, $\Delta[C]$, – change in the concentrations

→$[A]_e = [A]_i + \Delta[A]$ → same is valid for B and C

A + 2B ↔ C

→$\Delta[C] = +x$

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

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

$i + c = e$

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

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

→ 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**.

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

→ $[N_2]_i = [H_2]_i = 0$

→ $[NH_3]_e = 0.58$ M

$i + c = e$

[ ]	$2NH_3(g)$ ↔	$N_2(g)$ +	$3H_2(g)$
i	**1.00**	**0**	**0**
c	$-2x$	$+x$	$+3x$
e	$1.00 - 2x$	x	$3x$

→ $[NH_3]_e = 1.00 - 2x = 0.58$

⇒ $x = (1.00 - 0.58)/2 = 0.21$

→ $[N_2]_e = x = 0.21$ M

→ $[H_2]_e = 3x = 0.63$ 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 $2HI(g) \leftrightarrow H_2(g) + I_2(g)$.

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

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

$i + c = e$

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

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

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

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

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

$\Rightarrow [H_2]_e = [I_2]_e = x =$ **0.029 M**

$\Rightarrow [HI]_e = 0.25 - 2x = 0.25 - 2\times0.029 =$ **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 $2HI(g) \leftrightarrow H_2(g) + I_2(g)$.

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

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

$\rightarrow [I_2]_i = 0$

$i + c = e$

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

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

$$\frac{(0.15 + x)x}{(0.25 - 2x)^2} = 0.022 \Rightarrow \frac{0.15x + x^2}{0.25^2 - 2\times0.25\times2x + 4x^2} = 0.022$$

$$0.15x + x^2 = 0.022\times0.25^2 - 0.022\times4\times0.25x + 0.022\times4x^2$$

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

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

$$x_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$\rightarrow$ The (-) solution is meaningless

$$x = \frac{-0.172 + \sqrt{0.172^2 - 4\times0.912\times(-0.00138)}}{2\times0.912} = 0.00768$$

$\Rightarrow [I_2]_e = x =$ **0.0077 M**

$\Rightarrow [H_2]_e = 0.15 + x = 0.15 + 0.00768 =$ **0.16 M**

$\Rightarrow [HI]_e = 0.25 - 2x = 0.25 - 2\times0.00768 =$ **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 $\boldsymbol{K_c}$ **= 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***	**-3*x***	**+2*x***
e	**0.060 - *x***	**0.040 - 3*x***	**2*x***

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

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

$\rightarrow$ ***x*** is expected to be very small ($\boldsymbol{K_c}$ is quite small, so the product molarity, 2*x*, should be small too)

$\Rightarrow$ **Assumption** $\rightarrow$ ***x*** can be neglected in summations

$\Rightarrow 0.060 - x \approx 0.060$ and $0.040 - 3x \approx 0.040$

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

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

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

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

$\Rightarrow [NH_3]_e = 2x = 2 \times (3.1 \times 10^{-5}) = \mathbf{6.2 \times 10^{-5}\ M}$

- 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 $\boldsymbol{K_c}$ **= 10.** for $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$. Calculate the equilibrium concentration of NH_3.

$\rightarrow$ Using the assumption from the previous problem leads to:

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

$$x = 0.0031$$

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

(3×0.0031/0.040)×100% = 23% error

$\Rightarrow$ We must solve the equation without assumptions

- **Successive approximation**

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

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

$\rightarrow$ This formula allows the calculation of the **(n+1)**st approximation for ***x*** from the **n**th approximation

$\rightarrow$ For **n=0**, assume $\boldsymbol{x_0}$**=0** (***x*** is expected to be small)

$\rightarrow$ For **n=1** (1st iteration)

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

→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

$i + c = e$

[ ]	$H_2(g)$ +	$I_2(g)$ ↔	$2HI(g)$
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**