

# **INTRODUCTORY PHYSICAL CHEMISTRY CALCULATIONS**

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**B.Sc (Ago-Iwoye), M.Sc (Ibadan)**

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## **DEDICATION**

To Almighty Allaah,  
The Most Beneficent,  
The Most Merciful

## ACKNOWLEDGEMENT

Writing a book is really a challenge to one's authority in the field of endeavour. The challenge is even more when it's a field that is perceived to be difficult. However, with encouragement from colleagues, friends and family, there is no task that is insurmountable. I therefore wish to express my sincere appreciation to the following:

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- iv. My family members for their understanding and love.

## **PREFACE**

Physical chemistry is perceived by a good number of students as a difficult course to study. Their fears are not unconnected the enormous calculations involved in it. This book has been written to aid the performances of students offering physical chemistry at the introductory level. It is believed that simplicity coupled with more the examples and number of calculations practised in a mathematical course, the better the understanding of the principles that form the basis and the more confident a student will be. Unfortunately, conventional physical chemistry textbooks can offer at most two to three examples on principles being taught, although, with much exercises. This book is therefore written, putting students that dislike calculations into consideration. It is believed that with the number of examples given on each principle, the fundamentals will be understood and students can be confident to treat the exercises that follow. The textbook will also serve to refresh Higher National Diploma students offering chemical kinetics, electrochemistry, thermochemistry and chemical equilibrium in physical chemistry.

The book consists of five chapters in all. Each chapter has three parts – Key concepts, Examples and Exercises. No chapter has less than ten examples and exercises each.

Every effort has been made to ensure the correctness of all the calculations. The author cannot say the book is error-free. The attention of the author should be called to error(s) if detected. Also, suggestions on how to improve the textbook are welcome.

Abdulzaeez A. Oderinde

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# CHAPTER ONE

## THERMOCHEMISTRY

### ***KEY CONCEPTS***

Thermochemistry is an aspect of thermodynamics that study the heat flow that accompanies chemical reactions.

Heat can flow from a system into the surrounding or from the surrounding into the system. The part of the universe on which attention is directed is called the system while the remaining part of the universe at that instance is the surrounding. The heat flow is designated with  $q$ .  $q$  is positive if heat flows from the surrounding into the system.  $q$  is negative when heat flows out of the system into the surrounding.

An endothermic system is a chemical reaction or physical change in which heat is absorbed ( $q$  is positive i.e.  $q > 0$ ).

An exothermic system is a chemical reaction or physical change in which heat is evolved ( $q$  is negative i.e.  $q < 0$ ).

For a pure substance of a certain mass, the expression for  $q$  can be written as  $q = mass \times c \times \Delta t$



The quantity  $c$  is called the specific heat or specific heat capacity. Specific heat is defined as the amount of heat required to raise the temperature of one gram of a substance one degree Celsius. When the mass of that substance is equal to its molar mass, then  $c$  is called the molar heat capacity.

exothermic reaction:  $q = \Delta H < 0$   $H_{\text{products}} < H_{\text{reactants}}$

endothermic reaction:  $q = \Delta H > 0$   $H_{\text{products}} > H_{\text{reactants}}$

Enthalpy (denoted  $H$ ) is an extensive property of a substance that can be used to obtain the heat absorbed or evolved in a chemical reaction.

The change in enthalpy for a reaction,  $\Delta H$ , at a given temperature and pressure (called the enthalpy of reaction) is obtained by subtracting the enthalpy of the reactants from the enthalpy of the products.

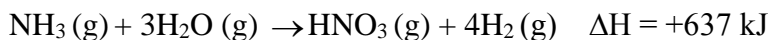
$$\Delta H = H_{\text{products}} - H_{\text{reactant}}$$

$\Delta H$  and  $\Delta E$  are related to each other by the relation  $\Delta H = \Delta E + \Delta nRT$ .  $\Delta n$  is the difference of the number of moles of gaseous products and gaseous reactants.

The sum of the kinetic and potential energies of the particles making up a substance is referred to as the internal energy,  $U$ , of

the substance. The difference of internal energy of the products  $E_P$ , and that of reactants  $E_R$  is change in internal energy denoted by  $\Delta E$  (i.e.  $\Delta E = E_P - E_R$ ). If  $\Delta E$  is positive (+), the reaction is exothermic and if  $\Delta E$  is negative (–), then the reaction is endothermic. It represents the amount of heat required to raise the temperature of the system  $1^\circ\text{C}$  and has the units  $\text{J}/^\circ\text{C}$ .

A chemical equation that shows the enthalpy relation between products and reactants is called a thermochemical equation. This type of equation contains, at the right of the balanced chemical equation, the appropriate value and sign for  $\Delta H$ . For example,



For thermochemical reactions:

- i. the sign of  $\Delta H$  indicates whether the reaction, when carried out at constant pressure, is endothermic (positive  $\Delta H$ ) or exothermic (negative  $\Delta H$ ).
- ii. in interpreting a thermochemical equation, the coefficients represent numbers of moles ( $\Delta H$  is +637 kJ when  $1 \text{ mol NH}_3 + 3 \text{ mol H}_2\text{O} \rightarrow 1 \text{ mol HNO}_3 + 4 \text{ mol H}_2$ ).
- iii. the phases (physical states) of all species must be specified, using the symbols (s), (l), (g), or (aq). The enthalpy of one mole of  $\text{H}_2\text{O}(\text{g})$  at  $25^\circ\text{C}$  is 44 kJ larger than that of one mole

of  $\text{H}_2\text{O}(l)$ ; the difference, which represents the heat of vaporization of water, is clearly significant.

- iv. the value quoted for  $\Delta H$  applies when products and reactants are at the same temperature, ordinarily taken to be  $25^\circ\text{C}$  unless specified otherwise.
- v. The magnitude of  $\Delta H$  is directly proportional to the amount of reactant or product.
- vi.  $\Delta H$  for a reaction is equal in magnitude but opposite in sign to  $\Delta H$  for the reverse reaction.
- vii. The value of  $\Delta H$  for a reaction is the same whether it occurs in one step or in a series of steps

The standard enthalpy of formation,  $\Delta H_f^\circ$ , is defined as the enthalpy change of the reaction in which the only reaction product is 1 mol of the species of interest, and only pure elements in their most stable state of aggregation under the standard state conditions appear as reactants.

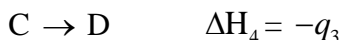
The standard enthalpy change,  $\Delta H^\circ$ , for a given thermochemical equation is equal to the sum of the standard enthalpies of formation of the product compounds minus the sum of the standard enthalpies of formation of the reactant compounds.

$$\Delta H^{\circ} = \sum \Delta H_{f(\text{product})}^{\circ} - \sum \Delta H_{f(\text{reactants})}^{\circ}$$

Hess's law of constant heat of formation states that at constant pressure, the total heat change accompanying a chemical reaction is the same no matter by which method the change is brought about. For a reaction



and for the reaction

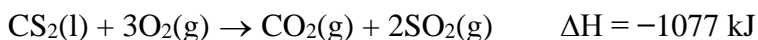


According to Hess's law,  $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$

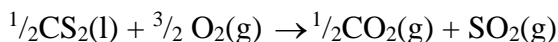
$$\begin{aligned} \text{Or} \quad -Q_1 &= -q_1 + (-q_2) + (-q_3) \\ &= -(q_1 + q_2 + q_3) \end{aligned}$$

## EXAMPLES

**EXAMPLE 1.** Carbon disulphide burns in air, producing carbon dioxide and sulphur dioxide.



What is  $\Delta H$  for the following equation?



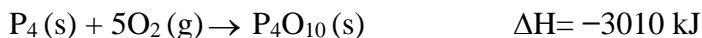
**SOLUTION**

$\Delta H$  is related to stoichiometry. Since the number of moles of reactants and products in the desired equation are halves of those in the proceeding equation,  $\Delta H$  of the desired equation will also be half that of the proceeding equation.

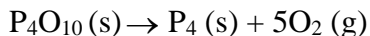
$$\Delta H = \left( \frac{1}{2} \times -1077 \right) \text{ KJ}$$

$$\Delta H = -538.5 \text{ KJ}$$

**EXAMPLE 2.** When white phosphorus burns in air, it produces phosphorus (v) oxide.



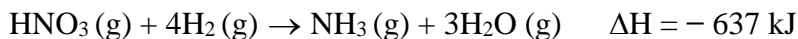
What is  $\Delta H$  for the following equation?

**SOLUTION**

The desired equation is the reverse of the proceeding equation. Therefore, the enthalpy change  $\Delta H$ , for the desired equation will have the same magnitude but opposite sign

$$\Delta H = +3010 \text{ kJ}$$

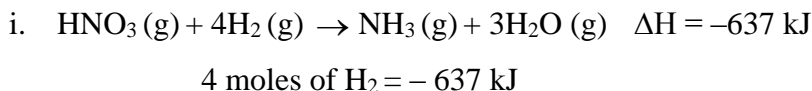
**EXAMPLE 3.** In the late eighteenth century Priestley prepared ammonia by reacting  $\text{HNO}_3(\text{g})$  with hydrogen gas. The thermodynamic equation for the reaction is



- i. Calculate  $\Delta H$  where one mole of hydrogen gas reacts.

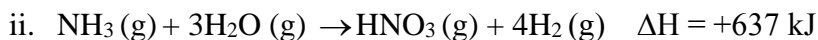
- ii. What is  $\Delta H$  when 10.00 g of  $\text{NH}_3$  (g) are made to react with an excess of steam to form  $\text{HNO}_3$  and  $\text{H}_2$  gases?

### SOLUTION



Therefore,

$$\begin{aligned} 1 \text{ mole of } \text{H}_2 &= \frac{1 \text{ mole} \times -637 \text{ kJ}}{4 \text{ moles}} \\ &= \mathbf{-159 \text{ kJ}} \end{aligned}$$



The enthalpy change,  $\Delta H$  for the reversed equation is +637 kJ

From the reaction equation,

$$1 \text{ mole of } \text{NH}_3(\text{g}) \equiv +637 \text{ kJ}$$

and

$$\begin{aligned} 1 \text{ mole of } \text{NH}_3(\text{g}) &= (14 + 3(1)) \text{ g of } \text{NH}_3(\text{g}) \\ &= 17.00 \text{ g of } \text{NH}_3(\text{g}) \end{aligned}$$

it implies that,

$$17.00 \text{ g of } \text{NH}_3(\text{g}) \equiv +637 \text{ kJ of energy}$$

therefore,

$$\begin{aligned} 10.00 \text{ g of } \text{NH}_3(\text{g}) &\equiv \frac{10.00 \text{ g} \times +637 \text{ kJ}}{17.00 \text{ g}} \\ &= \mathbf{+375 \text{ kJ}} \end{aligned}$$

**EXAMPLE 4.** Strontium metal is responsible for the red colour in fireworks. Fireworks manufacture use strontium carbonate, which can be produced by combining strontium meal, graphite (C), and oxygen gas. The formation of one mole of  $\text{SrCO}_3$  releases  $1.220 \times 10^3 \text{ kJ}$  of energy. What is  $\Delta H$  when 10.00 L of oxygen at 25 °C and 1.00 atm are used by the reaction?  $R = 0.0821 \text{ L.atm/mol.k}$

### SOLUTION

**Given:**  $P = 1.00 \text{ atm}$ ;  $V = 10.00 \text{ L}$ ;  $T = 25 \text{ °C}$ ;  $R = 0.0821$

$\text{L.atm/mol.k}$



For oxygen,

$$PV = nRT$$

therefore,

$$n = PV/RT$$

$$T = 25 \text{ °C} = (25+273) \text{ K} = 298\text{K}$$

$$n = \left( \frac{1.00 \times 10.00}{0.0821 \times 298} \right) \text{ mol}$$

$$n = 0.4087 \text{ mol of O}_2$$

but,

$$\frac{3}{2} \text{ mol of O}_2 \equiv -1.220 \times 10^3 \text{ kJ of energy}$$

therefore,

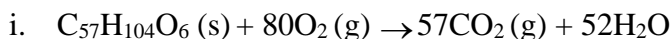
$$0.0487 \text{ mol of O}_2 \equiv \left( \frac{0.4087 \times -1.220 \times 10^3 \times 2}{3} \right) \text{ kJ}$$

$$= -332.41 \text{ kJ}$$

**EXAMPLE 5.** A typical fat in the body is glyceryl trioleate,  $\text{C}_{57}\text{H}_{104}\text{O}_6$ . When it is metabolised in the body, it combines with oxygen to produce carbon dioxide, water and  $3.022 \times 10^4$  kJ of heat per mole of fat.

- i. How many kilojoules of energy must be evolved in the form of heat if you want to get rid of 2.27 kg of this fat by combustion?
- ii. How many nutritional calories is this? (1 nutritional calories =  $1 \times 10^3$  calories)
- iii. How many grammes of the fat would have to be burned to heat 100.0 mL of water ( $d = 1.00 \text{ g/mL}$ ) from  $22^\circ\text{C}$  to  $25^\circ\text{C}$ . The specific heat capacity of water is  $4.18 \text{ J/g}^\circ\text{C}$ ?

### SOLUTION



$$\Delta H = -3.022 \times 10^4 \text{ kJ}$$

1 mole of  $\text{C}_{57}\text{H}_{104}\text{O}_6 = (57(12) + 104(1) + 6(16)) \text{ g} = 884 \text{ g}$

$$884 \text{ g of C}_{57}\text{H}_{104}\text{O}_6 \equiv -3.022 \times 10^4 \text{ kJ of heat}$$

Therefore,  $2.27 \times 10^3 \text{ g of C}_{57}\text{H}_{104}\text{O}_6 =$



$$\left( \frac{2.27 \times 10^3 \times -3.022 \times 10^4}{884} \right) \text{ kJ} = -77.601 \times 10^3 \text{ kJ}$$

ii. 1 nutritional calorie =  $1 \times 10^3$  calories

1 nutritional calorie = 1 kcal

but,

1 kcal = 4.184kJ

i.e. 4.184kJ of energy = 1 nutritional calorie

therefore,

$-77.601 \times 10^3$  kJ of energy =

$$\left( \frac{77.601 \times 10^3 \times 1}{4.184} \right) \text{ nutr. calories}$$

= 18.547 nutritional calories.

iii. Given: d = 1.00g/mL; v = 100.0mL

Using density,  $d = m/v$

where m= mass of water (g)

v = volume (mL)

$m = d \times v$

= 1.00 g/mL x 100.0mL

= 100.0 g

Using  $q = m c \Delta T$

where q = quantity of heat (J)

$\Delta T$  = heat change ( $^{\circ}\text{C}$ )

$\Delta T = (25.00 - 22.00) ^{\circ}\text{C} = 3 ^{\circ}\text{C}$

$$c = 4.18 \text{ J/g. } ^\circ\text{C and } m = 100.0 \text{ g}$$

therefore,

$$\begin{aligned} q &= 100.0 \times 4.18 \times 3 \\ &= 1254 \text{ J} \end{aligned}$$

Quality of heat required by 100.0g of water = 1254g

$$884 \text{ g of fat} = 3.022 \times 10^4 \text{ kJ of heat}$$

i.e.  $3.022 \times 10^4 \text{ J}$  of heat would be evolved by 884g of fat

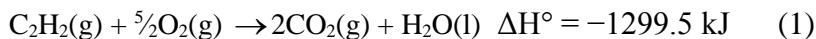
Therefore,

$$\begin{aligned} 1254 \text{ J of heat would be evolved by } &\left( \frac{1254 \times 884}{3.022 \times 10^4} \right) \text{ g of fat} \\ &= \mathbf{3.668 \times 10^{-2} \text{ g of fat}} \end{aligned}$$

**EXAMPLE 6.** Calculate the enthalpy for this reaction:



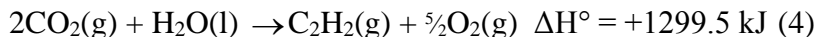
Given the following thermochemical equations:



## SOLUTION

### Steps:

- i. Flip Eqn. (1) so that  $\text{C}_2\text{H}_2$  becomes a product
- ii. Multiply Eqn. (2) by two to get 2 moles of C
- iii. Rewrite all three equations with changes applied



Notice that the  $\Delta H$  values changed for the reversed and multiplied equations.

- iv. Add up Eqns. (4), (5), and (6). Examine what cancels:

$2\text{CO}_2$ : Eqns. (4) and (5)

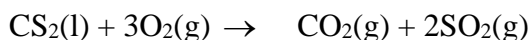
$\text{H}_2\text{O}$ : Eqns. (4) and (6)

$\frac{5}{2}\text{O}_2$ : Eqn. (4) and sum of Eqn. (5) and (6).

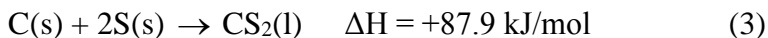
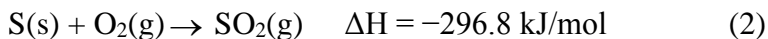
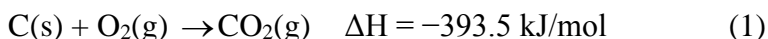
- v. Add up  $\Delta H$  values

$$\begin{aligned} &+1299.5 \text{ kJ} + (-787 \text{ kJ}) + (-285.8 \text{ kJ}) \\ &= \mathbf{+226.7 \text{ kJ}} \end{aligned}$$

**EXAMPLE 7.** Calculate the enthalpy of the following chemical reaction



Given the following thermochemical reactions:



## SOLUTION

### Steps:

- i. Leave Eqn. (1) untouched (want  $\text{CO}_2$  as a product)

ii. Multiply Eqn. (2) by 2 (want to cancel 2S, also want 2SO<sub>2</sub> on product side)

iii. Flip Eqn. (3) (want CS<sub>2</sub> as a reactant)

iv. Rewrite the three equations with the changes applied



v. Add the three revised equations – (4), (5), and (6).

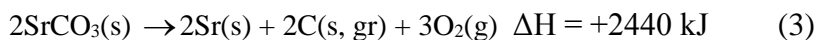
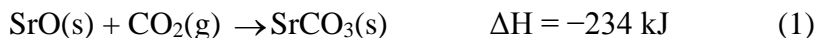
C and 2S will cancel.

vi. Add the three enthalpies for the final answer.

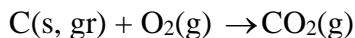
$$\Delta H = -393.5 \text{ kJ/mol} + (-593.6 \text{ kJ/mol}) + (-87.9 \text{ kJ/mol})$$

$$= -1075 \text{ kJ/mol}$$

**EXAMPLE 8.** Given the following data:



Find the  $\Delta H$  of the following reaction:



## SOLUTION

### Steps:

i. Flip Eqn. (1) to put CO<sub>2</sub> on the product side

ii. Divide Eqn. (2) through by 2 to cancel one SrO

- iii. Flip Eqn. (3) to put the  $\text{SrCO}_3$  on the other side and divide by two so that we can cancel one  $\text{SrCO}_3$

*Notice that what we did to the third equation also sets up the Sr to be cancelled. Why not also multiply first equation by two (to get 2SrO for canceling)? Because we only want one  $\text{CO}_2$  in the final answer, not two. Notice also that the oxygen is ignored. If everything is right, the oxygen will take care of itself.*

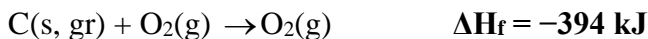
- iv. Rewrite all the equations with the changes ( $\Delta H$  values inclusive)



- v. Add the equations, eliminate  $\text{SrCO}_3$ ,  $\text{SrO}$ ,  $\text{Sr}$ ,  $\frac{1}{2}\text{O}_2$  and add the  $\Delta H$  values

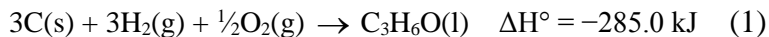
$$\Delta H = +234 \text{ kJ} + (+592 \text{ kJ}) + (-1220 \text{ kJ})$$

$$= -394 \text{ kJ}$$



Notice the subscripted f. This is the enthalpy of formation of  $\text{CO}_2$ .

**EXAMPLE 9.** Using the following thermochemical equations, calculate the standard enthalpy of combustion for one mole of liquid acetone ( $\text{C}_3\text{H}_6\text{O}$ ).

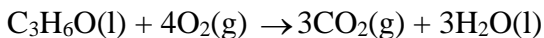


### SOLUTION

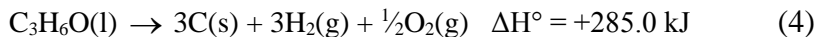
#### Steps:

- i. The combustion of liquid acetone is the target equation.

Write (and balance) it:



- ii. Reverse eqn (1), so as to put acetone on the reactant side. Here are all three data equations with the first one changed:



Note the sign change in the enthalpy when the equation is reversed.

- iii. Multiply eqn (2) by 3 to create a situation where the  $3\text{C(s)}$  will cancel when the equations are added together:



Note that the enthalpy was also multiplied by three.

- iv. Multiply eqn (3) by 3 to remove the  $\text{H}_2$  from the final answer. Another multiplication by 3 is used:



Note that the enthalpy was also multiplied by three.

- v. Add equations (4), (5), and (6) together to obtain the desired reaction equation. Note the following:

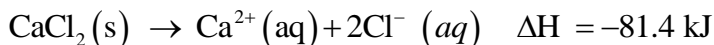
$\frac{1}{2}\text{O}_2(\text{g})$  will cancel from each side, leaving  $4\text{O}_2(\text{g})$  on the left-hand side.

$$\Delta\text{H}^\circ = +285.0 \text{ kJ} + (-1182.0 \text{ kJ}) + (-858.0 \text{ kJ})$$

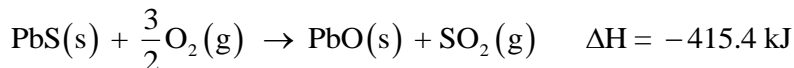
The standard enthalpy of combustion for one mole of liquid acetone ( $\text{C}_3\text{H}_6\text{O}$ ) = **-1755 kJ**

## EXERCISES

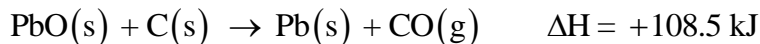
- Calcium chloride is a compound frequently found in first-aid packs. It gives off heat when dissolved in water. The following reaction takes place.



- What is  $\Delta\text{H}$  when one mole of calcium chloride precipitates from solution?
  - What is  $\Delta\text{H}$  when 10.00 g of calcium chloride precipitate?
- A lead ore, galena, consisting mainly of lead(II) sulfide, is the principal source of lead. To obtain the lead, the ore is first heated in the air to form lead oxide.



The oxide is then reduced to metal with carbon.



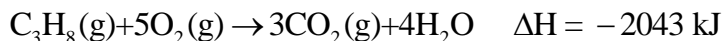
Calculate  $\Delta H$  for the reaction of one mole of lead(II) sulfide with oxygen and carbon, forming lead, sulfur dioxide, and carbon monoxide.

3. Colourless nitric oxide, NO, combines with oxygen to form nitrogen dioxide, NO<sub>2</sub>, a brown gas.

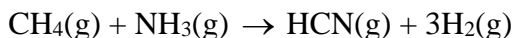


What is the enthalpy change per gram of hydrogen?

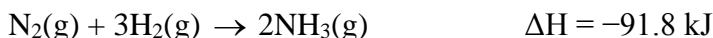
4. Propane, C<sub>3</sub>H<sub>8</sub>, is a common fuel gas. Use the following to calculate the grammes of propane you would need to provide 369 kJ of heat.



5. Calculate  $\Delta H$  for this reaction:

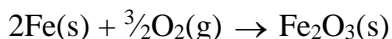


Given:

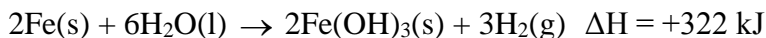




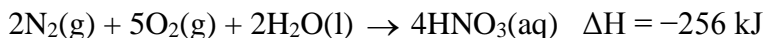
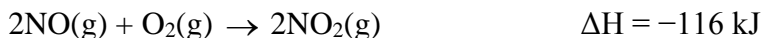
6. Determine the heat of reaction for the oxidation of iron



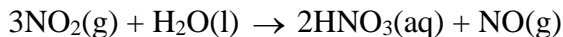
given the thermochemical equations:



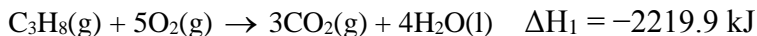
7. Given the following information:



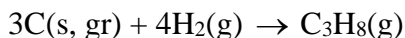
Calculate the enthalpy change for the reaction below:



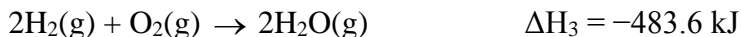
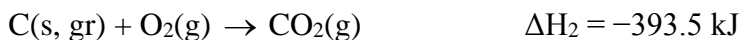
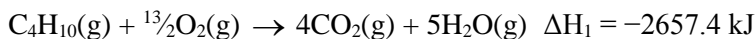
8. The standard enthalpy change of formation of propane is impossible to measure directly. That is because carbon and hydrogen will not directly react to make propane. However, standard enthalpy changes of combustion are relatively easy to measure.



Determine the enthalpy of formation for propane.

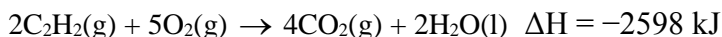
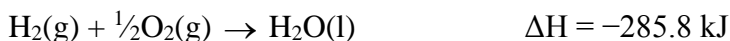
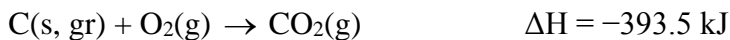


9. Determine the standard enthalpy of formation for butane, using the following data:

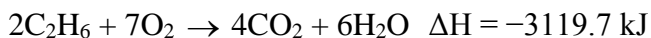


Comment: note that the first and third equations are not standard combustion equations. The water in each equation is as a gas. In standard combustion equations, water is a liquid (its standard state).

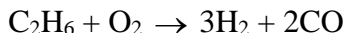
10. Calculate the enthalpy of formation for acetylene ( $\text{C}_2\text{H}_2$ ), given the following data:



11. Given:



Calculate  $\Delta H$  for the following reaction:



## CHAPTER FIVE

### COLLIGATIVE PROPERTIES OF SOLUTIONS

#### ***KEY CONCEPTS***

Colligative properties of solutions are those solution properties that depend primarily on the concentration of solute particles rather than their nature.

These properties include vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure.

When a non-volatile solute is dissolved in a solvent, the vapour pressure of the solution is lowered than that of the pure solvent. The lowering of vapour pressure relative to the vapour pressure of the pure solvent is equal to the mole fraction of the solute in the solution

$$P_1^{\circ} - P_1 = X_2 P_1^{\circ}$$

$P_1$  is the vapor pressure of solvent over the solution,  $P_1^{\circ}$  is the vapor pressure of the pure solvent at the same temperature, and  $X_2$  is the mole fraction of solute.

When a non-volatile solute is added to a pure solvent with boiling point,  $T_b^o$ , it lowers the vapour pressure. The solution will require being heated to a higher temperature,  $T_b$ , before the vapour pressure will be equal to the atmospheric pressure. The increase in boiling point is referred to as boiling point elevation,  $\Delta T_b$ .

$$\Delta T_b = T_b - T_b^o$$

Boiling point elevation is related to the moles of solute dissolved in 1 kg of solvent by the equation

$$\Delta T_b = i \times K_b \times m$$

where  $i$  = van't Hoff factor ( $i = 1$  for non-electrolytes and its value depend on species involved for electrolytes),  $K_b$  is the molal boiling point constant ( $^{\circ}\text{C}/m$ ), and  $m$  is the molality of solution ( $m$ ).

The addition of a non-volatile solute to a solvent of freezing point,  $T_f^o$ , lowers the vapour pressure and freezing point decreases to a new value,  $T_f$ . The difference of the freezing point of pure solvent and solution is called the freezing point lowering or depression,  $\Delta T_f$ . It is given by

$$\Delta T_f = T_f^o - T_f$$

Freezing point depression,  $\Delta T_f$ , is related to the moles of solute dissolved in 1 kg of solvent by the equation

$$\Delta T_f = i \times K_f \times m$$

where  $i$  = van't Hoff factor ( $i = 1$  for non-electrolytes and its value depend on species involved for electrolytes),  $K_f$  is the molal boiling point constant ( $^{\circ}\text{C}/m$ ), and  $m$  is the molality of solution ( $m$ ).

The amount by which the pressure in the solution is raised is known as the osmotic pressure,  $\pi$ . For any non-electrolyte,  $\pi$  is directly proportional to molarity,  $M$ . The equation relating these two quantities is very similar to the ideal gas law

$$\pi = \frac{nRT}{V} = iMRT$$

Where  $i$  = van't Hoff factor. ( $i = 1$  for non-electrolytes and its value depend on species involved for electrolytes),  $n$  is the number of moles of solute,  $R$  is the gas law constant,  $0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$ ,  $T$  is the temperature (K), and  $V$  is the volume of solution (L).

**EXAMPLES**

**EXAMPLE 1.** Calculate the mole fractions of glucose and water in a solution containing 56 g of glucose in 200 g of solution (Glucose = 180.2 g/mol; water = 18.02 g/mol).

**SOLUTION**

**Given:** mass of solute (glucose) = 56 g; mass of solution = 200 g.

**Required:** Vapour pressure of solution

The moles of solute and solvent must be calculated first.

The mass of water is the difference between the mass of solute and solution.

$$\begin{aligned}\text{mass of water} &= (200 - 56) \text{ g} \\ &= 144 \text{ g}\end{aligned}$$

$$\text{mole of substance} = \frac{\text{mass of substance}}{\text{molar mass of substance}}$$

$$\text{mole of glucose} = \frac{\text{mass of glucose}}{\text{molar mass of glucose}}$$

$$\begin{aligned}\text{mole of glucose} &= \frac{56}{180.2} \text{ mol} \\ &= 0.311 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{mole of water} &= \frac{144}{18.02} \text{ mol} \\ &= 7.991 \text{ mol}\end{aligned}$$

Mole fraction of glucose

$$X_{Glu} = \frac{\text{mole of Glucose}}{\text{total moles}}$$

$$X_{Glu} = \frac{0.311}{0.311 + 7.991}$$

$$X_{Glu} = \frac{0.311}{8.302}$$

$$X_{Glu} = \mathbf{0.037}$$

Mole fraction of water

$$X_{H_2O} = \frac{\text{mole of } H_2O}{\text{total moles}}$$

$$X_{H_2O} = \frac{7.991}{0.311 + 7.991}$$

$$X_{H_2O} = \frac{7.991}{8.302}$$

$$X_{H_2O} = \mathbf{0.963}$$

Note: The sum of mole fractions,  $X_{Total} = X_A + X_B + X_C + \dots = 1$ . From the above example,  $X_{Total} = 0.037 + 0.963 = 1$

**EXAMPLE 2.** Calculate the vapour pressure of a solution consisting of 3 moles of a non-volatile solute A and 15 moles of water at 25 °C, given that the vapour pressure of water at 25 °C is 23.76 mm Hg.

### SOLUTION

**Given:** number of moles of B = 3 moles; number of moles of water = 15 moles; vapour pressure of water = 23.78 mm Hg

**Required:** Vapour pressure of solution

Remember that the vapour pressure is related to mole fractions. There is a need to calculate mole fraction of the solvent first.

Using mole fraction  $X_A = \frac{\text{moles of A}}{\text{total moles}}$

$$X_{H_2O} = \frac{\text{mole of } H_2O}{\text{total moles}}$$

$$= \frac{15}{18} = 0.83$$

Then, Substitute into Raoult's law and solve

$$P = X_B P_B^{\circ}$$

$$P = 23.76 \times 0.83$$

$$P = \mathbf{19.8 \text{ mm Hg}}$$

**EXAMPLE 3.** A solution contains 80.0 g of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , in 300.0 g of water. Calculate the vapour pressure of the solution at 25 °C (vapour pressure of pure water at 25 °C = 23.76 mm Hg;  $\text{C}_6\text{H}_{12}\text{O}_6 = 180.2 \text{ g/mol}$ ;  $\text{H}_2\text{O} = 18.02 \text{ g/mol}$ ).

### SOLUTION

**Given:** mass of solute (glucose) = 80.0 g; mass of solvent (water); vapour pressure of water = 23.76 mm Hg

**Required:** Vapour pressure of solution

Here, unlike in Example 1, the moles of solute and solvent must be calculated first.

$$\text{mole of substance} = \frac{\text{mass of substance}}{\text{molar mass of substance}}$$

$$\text{mole of glucose} = \frac{\text{mass of glucose}}{\text{molar mass of glucose}}$$

$$\begin{aligned} \text{mole of glucose} &= \frac{80.0}{180.2} \text{ mol} \\ &= 0.444 \text{ mol} \end{aligned}$$

$$\text{mole of water} = \frac{300.0}{18.02} \text{ mol}$$



$$= 16.648 \text{ mol}$$

Water is the solvent, therefore there is a need to calculate its mole fraction.

$$X_{\text{H}_2\text{O}} = \frac{\text{mole of H}_2\text{O}}{\text{total moles}}$$

$$X_{\text{H}_2\text{O}} = \frac{16.648}{0.444 + 16.648}$$

$$X_{\text{H}_2\text{O}} = \frac{16.648}{17.092}$$

$$X_{\text{H}_2\text{O}} = 0.974$$

Then, substitute into Raoult's law and solve

$$P_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{\circ}$$

$$P_{\text{H}_2\text{O}} = 23.76 \times 0.974$$

$$P_{\text{H}_2\text{O}} = \mathbf{23.14 \text{ mm Hg}}$$

**EXAMPLE 4.** A solution contains 0.0653 g of a compound in 8.31 g of ethanol. The molality of the solution is 0.0368 m. Calculate the molecular mass of the compound.

## SOLUTION

**Given:** Mass of solute = 0.0653 g; Mass of solvent = 8.31 g;

Molality of solution = 0.0368 m

**Desired:** Molecular mass of the compound

Remember that,

$$\text{Molality} = \frac{\text{mole of solute}}{\text{kg of solvent}}$$

Convert the mass of ethanol from gramme to kilogramme

$$8.31 \text{ g of ethanol} \equiv 8.31 \times 10^{-3} \text{ kg of ethanol}$$

Therefore,

$$0.0368 = \frac{\text{mole of solute}}{8.31 \times 10^{-3}}$$

Make mole of solute the subject of the formula

$$\begin{aligned} \text{mole of solute} &= 0.0368 \times 8.31 \times 10^{-3} \\ &= 3.06 \times 10^{-4} \text{ mol} \end{aligned}$$

But,

$$\text{mole of solute} = \frac{\text{mass of solute}}{\text{molecular mass}}$$

$$\text{molecular mass} = \frac{\text{mass of solute}}{\text{mole of solute}}$$

$$\text{Molecular mass} = \frac{0.0653}{3.06 \times 10^{-4}}$$

$$\text{Molecular mass} = \mathbf{213.53 \text{ g/mol}}$$

**EXAMPLE 5.** Urea,  $(\text{NH}_2)_2\text{CO}$ , is dissolved in 100.0 g of water.

The solution freezes at  $0.085^\circ\text{C}$ . How many grammes of urea were dissolved to make the solution?

## SOLUTION

**Given:** Formula of urea; mass of water = 100.0 g; freezing point of mixture =  $0.085^\circ\text{C}$ .

**Desired:** Mass of urea dissolved in solution.

This problem is related to freezing point depression.

For freezing point depression,

$$\Delta T_f = K_f \times m$$

and

$$\Delta T_f = T_f^o - T_f$$

Therefore,

$$\begin{aligned}\Delta T_b &= (0 - (-0.085))\text{ }^{\circ}\text{C} \\ &= 0.085\text{ }^{\circ}\text{C}\end{aligned}$$

Also,

$$\text{molality, } m = \frac{\Delta T_f}{K_f}$$

$$m = \left( \frac{0.085}{1.858} \right) m$$

$$m = 0.0457\text{ m}$$

$$\text{but molality, } m = \frac{\text{mole of solute}}{\text{kg of solvent}}$$

Solvent used = water = 100.0 g

Convert the mass of water from gramme to kilogramme

$$100.0\text{ g of water} = 100.0 \times 10^{-3}\text{ kg of water}$$

$$\begin{aligned}\text{Mole of solute} &= 0.0457 \times 100.0 \times 10^{-3} \\ &= 4.57 \times 10^{-3}\text{ mol}\end{aligned}$$

Also,

$$\text{mole of solute} = \frac{\text{mass of solute}}{\text{molar mass of solute}}$$

$$\text{mass of solute} = \text{mole of solute} \times \text{molar mass of solute}$$

$$\begin{aligned}\text{molar mass of urea, (NH}_2\text{)}_2\text{CO} &= 2 (14) + 4 (1) + 12 + 16 \\ &= 60 \text{ g/mol}\end{aligned}$$

$$\text{Mass of solute} = (60 \times 4.57 \times 10^{-3}) \text{ g}$$

$$\text{Mass of solute} = 0.27 \text{ g}$$

$$\text{Mass of urea dissolved in solution} = \mathbf{0.27 \text{ g}}$$

**EXAMPLE 6.** What is the boiling point of a solution of 0.150 g of glycerol,  $\text{C}_3\text{H}_8\text{O}_3$ , in 20.0 g of water?  $K_b = 0.512 \text{ }^\circ\text{C/m}$

### SOLUTION

**Given:** Mass of glycerol = 0.150 g; Formula of glycerol =  $\text{C}_3\text{H}_8\text{O}_3$ ; mass of water = 20.0 g;  $K_b = 0.512 \text{ }^\circ\text{C/m}$

**Desired:** Boiling point of solution ( $^\circ\text{C}$ )

This problem is related to boiling point elevation.

For boiling point elevation,

$$\Delta T_b = K_b \times m$$

and

$$\Delta T_b = T_b - T_b^o$$

therefore,

substitute  $T_b - T_b^\circ$  for  $\Delta T_b$

$$T_b - 100 = 0.512 \times m$$

But  $m = \frac{\text{mole of solute}}{\text{molar mass of solute}}$

Molar mass of Glycerol,  $\text{C}_3\text{H}_8\text{O}_3 = (12) + 8(1) + 3(16)$   
 $= 92 \text{ g/mol}$

Mole of solute  $= \frac{0.150}{92}$

$$= 1.6 \times 10^{-3} \text{ mol}$$

$$m = \left( \frac{1.6 \times 10^{-2}}{20.0 \times 10^{-3}} \right) m$$

$$= 0.082$$

Therefore,  $T_b - 100 = 0.512 \times 0.082$

$$T_b - 100 = 0.042$$

$$T_b = (0.042 + 100)^\circ\text{C}$$

$$T_b = \mathbf{100.04}^\circ\text{C}$$

**EXAMPLE 7.** Butylated hydroxytoluene (BHT) is used as an antioxidant in processed foods. A solution of 2.500 g of BTH in 100.0 g of benzene had a freezing point of  $4.880^\circ\text{C}$ . What is the molecular mass of BTH?  $K_f = 5.10^\circ\text{C}/m$ ;  $T_f^\circ = 5.50^\circ\text{C}$

**SOLUTION**

**Given:** Mass of solute = 2.500 g; Mass of solvent = 100.0 g;

Freezing point of solution,  $T_f = 4.880\text{ }^{\circ}\text{C}$

**Desired:** Molecular mass of Butylated hydroxytoluene (BHT)

Using

$$\Delta T_f = K_f \times m$$

where  $\Delta T_f$  = freezing point depression ( $^{\circ}\text{C}$ )

$K_f$  = molal freezing point constant ( $^{\circ}\text{C}/m$ )

$m$  = solution molality ( $m$ )

$$\Delta T_f = 5.10 \times m$$

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

$$\text{mole of solute} = \frac{\text{mass of solute}}{\text{molecular mass of solute}}$$

$$\text{mass of solute} = 100.0\text{ g}$$

$$= 100.0 \times 10^{-3}\text{ kg}$$

$$\Delta T_f = K_f \times m$$

$$T_f^{\circ} - T_f = K_f \times m$$

$$5.50 - 4.880 = 5.10 \times m$$

$$0.62 = 5.10m$$

$$m = \frac{0.62}{5.10}$$

$$= 0.122 \text{ m}$$

But,

$$\text{mole of solute} = m \times \text{kg of solvent}$$

$$\text{molecular mass} = \frac{\text{mass of solute}}{m \times \text{kg of solvent}}$$

$$\text{molecular mass} = \frac{2.500}{0.122 \times 100.0 \times 10^{-3}}$$

$$\text{molecular mass} = \mathbf{204.92 \text{ g/mol}}$$

**EXAMPLE 8.** In a mountainous location, the boiling point of pure water is found to be  $95^\circ\text{C}$ . How many grams of sodium chloride must be added to 1 kg of water to bring the boiling point back to  $100^\circ\text{C}$ ? Assume that,  $i = 2$ ;  $K_b = 0.512^\circ\text{C/m}$

### SOLUTION

**Given:**  $T_b^\circ = 95^\circ\text{C}$  ;  $T_b = 100^\circ\text{C}$ ; mass of water = 1 kg;  $i = 2$ ;

$K_b = 0.512^\circ\text{C/m}$

**Desired:** Mass of solute (NaCl)

Using

$$\Delta T_b = i \times K_b \times m$$

$$\Delta T_b = (100 - 95)^\circ\text{C}$$

$$= 5^\circ\text{C}$$

$$m = \frac{\Delta T_b}{i \times K_b}$$

$$= \left( \frac{5}{2 \times 0.512} \right) m$$

$$m = 4.88 \text{ m}$$

But,

$$m = \frac{\text{mole of solute}}{\text{kg of solvent}}$$

$$\text{mole of solute} = m \times \text{kg of solvent}$$

$$= 4.88 \times 1$$

$$= 4.88 \text{ mole}$$

$$\text{NaCl} = (23 + 35.5) \text{ g/mol}$$

$$1 \text{ mol of NaCl} = 58.5 \text{ g}$$

Therefore,

$$4.88 \text{ mole of NaCl} = 4.88 \times 58.5$$

$$= \mathbf{285.64 \text{ g}}$$

**EXAMPLE 9.** Pepsin is an enzyme involved in the process of digestion. Its molar mass was determined to be about  $3.50 \times 10^4$  g/mol, experimentally. What is the osmotic pressure in mmHg at 30 °C of a 0.250 g sample of pepsin in 55.0 mL of an aqueous solution?



**SOLUTION**

**Given:** Molar mass =  $3.50 \times 10^4$  g/mol; Temperature,  $T = 30^\circ\text{C}$ ; Mass of solute = 0.250 g; Volume of solution = 55.0 mL;

**Desired:** Osmotic pressure,  $\pi$

Using

$$\pi = MRT$$

where  $M$  = Molarity of pepsin solution

$$M = \frac{\text{mole of solute}}{\text{litre of solution}}$$

$$\text{Volume of solution} = 55.0 \text{ mL} = 55.0 \times 10^{-3} \text{ L}$$

$$\text{Mole of solute} = \frac{\text{mass of solute}}{\text{molar mass of solute}}$$

$$= \frac{0.250}{3.50 \times 10^4}$$

$$= 7.14 \times 10^{-6} \text{ mol}$$

$$\text{molarity of solution, } M = \frac{7.14 \times 10^{-6}}{55.0 \times 10^{-3}}$$

$$= 1.30 \times 10^{-4} \text{ M}$$

But,

$$\pi = MRT$$

$R$  = gas constant, 0.0821 L.atm/mol.K

Temperature,  $T$  (K)

$$= (30 + 273) \text{ K} = 303 \text{ K}$$

Therefore,

$$\pi = 1.30 \times 10^{-4} \times 0.0821 \times 303$$

$$\pi = 0.00323 \text{ atm}$$

But

$$1 \text{ atm} = 760 \text{ mmHg}$$

Therefore;

$$0.00323 \text{ atm} = (0.00323 \times 760) \text{ mmHg}$$

$$\pi = \mathbf{2.46 \text{ mmHg}}$$

**EXAMPLE 10.** When 8.79 g of benzoic acid,  $\text{C}_7\text{H}_6\text{O}_2$ , are mixed with 325 g of phenol, the mixture freezes at  $39.26^\circ\text{C}$ . The freezing point of pure phenol is  $40.90^\circ\text{C}$ . What is the freezing point constant for phenol?

### SOLUTION

**Given:** Mass of benzoic acid = 8.79 g; Formula of benzoic acid =  $\text{C}_7\text{H}_6\text{O}_2$ ; Mass of phenol = 323 g; Freezing point of mixture,  $T_f = 39.26^\circ\text{C}$ ; Freezing point of pure phenol,  $T_f^\circ = 40.90^\circ\text{C}$ .

**Desired:** Freezing point constant,  $K_f$  ( $^\circ\text{C}/\text{m}$ )

Using

$$T_f^\circ - T_f = k_f \times m$$

$m$  = molality of solution

$$m = \frac{\text{mole of solute}}{\text{kg of solvent}}$$

$$\text{mole of solute} = \frac{\text{mass of solute}}{\text{molar mass of solute}}$$

The solute is benzoic acid. Therefore,

$$\text{Mass of solute} = 8.79 \text{ g}$$

$$\begin{aligned}\text{Molar mass of benzoic acid} &= (7(12) + 6(1) + 2(16)) \text{ g/mol} \\ &= (84 + 6 + 2) \text{ g/mol} = 122 \text{ g/mol}\end{aligned}$$

The solvent is phenol. Therefore,

$$\text{Mass of solvent} = 325 \text{ g}$$

Convert the mass of the solvent from grammes to kilogramme

$$325 \text{ g} = 325 \times 10^{-3} \text{ kg}$$

$$\begin{aligned}\text{mole of solution} &= \left( \frac{8.79}{122} \right) \text{ mole} \\ &= 0.072 \text{ mole of benzoic acid}\end{aligned}$$

$$\begin{aligned}\text{molarity of solution} &= \left( \frac{0.072}{325 \times 10^{-3}} \right) \\ &= 0.222 \text{ m}\end{aligned}$$

But,

$$\Delta T_f = T_f^o - T_f$$

Therefore,

$$\Delta T_f = (40.90 - 9.26) ^\circ\text{C}$$

And,

$$K_f = \frac{\Delta T_f}{m}$$

$$K_f = \left( \frac{1.64}{0.222} \right) ^\circ\text{C} / m$$

$$K_f = 7.39 ^\circ\text{C}/m$$

**EXAMPLE 11.** Insulin is a hormone responsible for the regulation of glucose level in the blood. An aqueous solution of insulin has an osmotic pressure of 2.5 mmHg at 25 °C. It is prepared by dissolving 0.100 g of insulin in enough water to make 125 mL of solution. What is the molar mass of insulin?

### SOLUTION

**Given:** Osmotic pressure,  $\pi = 2.5$  mm Hg; Temperature 25 °C;  
mass of insulin = 0.100 g; volume of solution = 125 mL; R =  
0.0821 L.atm/mol.K

**Desired:** Molar mass of insulin

Using

$$\pi = MRT$$

Temperature,  $T = 25 ^\circ\text{C} = (25 + 273) \text{ K} = 298 \text{ K}$

Volume of solution = 125 mL =  $125 \times 10^{-3} \text{ L}$

The solute is insulin.

And,

$$760 \text{ mmHg} = 1 \text{ atm}$$

$$\therefore 2.5 \text{ mmHg} = \left( \frac{2.5 \times 1}{760} \right) \text{ atm}$$

$$2.5 \text{ mmHg} = 0.0033 \text{ atm}$$

$$M = \left( \frac{0.0033}{0.0821 \times 298} \right) M$$

$$M = 1.34 \times 10^{-4}$$

But,

$$M = \frac{\text{mole of solute}}{\text{litre of solution}}$$

$$\text{mole of solute} = (1.34 \times 10^{-4} \times 125 \times 10^{-3})$$

$$= 1.68 \times 10^{-5} \text{ mol}$$

Also,

$$\text{mole of solute} = \frac{\text{mass of solute}}{\text{molar mass of solute}}$$

Therefore,

$$\text{molar mass of solute} = \frac{\text{mass of solute}}{\text{mole of solute}}$$

$$= \left( \frac{0.100}{1.68 \times 10^{-5}} \right) \text{ g/mol}$$

Molar mass of Insulin = **5952.4 g/mol**

**EXAMPLE 12.** The Rast method uses camphor ( $\text{C}_{10}\text{H}_{16}\text{O}$ ) as a solvent for determining the molar mass of a compound. When 2.50 g of cortisone acetate is dissolved in 50.00 g of camphor, ( $K_f = 40.0\text{ }^\circ\text{C/m}$ ), the freezing point of the mixture is determined to be  $173.44\text{ }^\circ\text{C}$ ; that of pure camphor is  $178.40\text{ }^\circ\text{C}$ . What is the molar mass of cortisone acetate?

### SOLUTION

**Given:** Camphor,  $\text{C}_{10}\text{H}_{16}\text{O}$ ; mass of cortisone acetate = 2.50 g; mass of Camphor = 50.00 g;  $K_f = 40.0\text{ }^\circ\text{C/m}$ ; freezing point of mixture,  $T_f = 173.44\text{ }^\circ\text{C}$ ; freezing point of pure camphor,  $T_f = 178.40\text{ }^\circ\text{C}$ .

**Derived:** Molar mass of cortisone acetate

Using

$$\Delta T_f = T_f^o - T_f$$

and,

$$T_f^o - T_f = K_f \times m$$

$$\Delta T_f = (178.40 - 173.44)\text{ }^\circ\text{C}$$

$$= 4.96\text{ }^\circ\text{C}$$

$$m = \left( \frac{\Delta T_f}{K_f} \right)$$

$$= \left( \frac{4.96}{40.0} \right) \text{ m}$$

$$m = 0.124 \text{ m}$$

but,

$$m = \frac{\text{mole of solute}}{\text{kg of solvent}}$$

$$\text{mole of solute} = m \times \text{kg of solvent}$$

$$= (0.124 \times 50.00 \times 10^{-3})$$

$$\text{mole of solute} = 6.2 \times 10^{-4} \text{ mol}$$

But,

$$\text{mole of solute} = \frac{\text{mass of solute}}{\text{molar mass of solute}}$$

Therefore,

$$\begin{aligned} \text{molar mass of solute} &= \frac{\text{mass of solute}}{\text{mole of solute}} \\ &= \left( \frac{2.50}{6.2 \times 10^{-4}} \right) \text{ g/mol} \end{aligned}$$

$$\text{Molar mass of solute} = 4032.26 \text{ g/mol}$$

$$\text{Molar mass of cortisone acetate} = \mathbf{4032.26 \text{ g/mol}}$$

## ***EXERCISES***

1. Calculate the vapour pressure of water over each of the following ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) solutions at 22 °C (vp

pure water = 19.83 mm Hg). Ethylene glycol can be assumed to be non-volatile.

- i.  $X_{\text{ethylene glycol}} = 0.288$
  - ii. % ethylene glycol by mass = 39.0%
  - iii. 2.42 *m* ethylene glycol
2. Calculate the vapour pressure at 35 °C of a solution made by dissolving 20.2 g of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , in 70.1 g of water. The vapour pressure of pure water at 35 °C is 42.2 mmHg. What is the vapour-pressure lowering of the solution? (Sucrose is non-volatile.)
  3. What is the vapour pressure at 23 °C of a solution of 1.20 g of naphthalene,  $\text{C}_{10}\text{H}_8$ , in 25.6 g of benzene,  $\text{C}_6\text{H}_6$ ? The vapour pressure of pure benzene at 23 °C is 86.0 mmHg; the vapour pressure of naphthalene can be neglected. Calculate the vapour pressure lowering of the solution.
  4. The vapour pressure of pure  $\text{CCl}_4$  at 65 °C is 504 mm Hg. How many grams of naphthalene ( $\text{C}_{10}\text{H}_8$ ) must be added to 25.00 g of  $\text{CCl}_4$  so that the vapour pressure of  $\text{CCl}_4$  over the solution is 483 mm Hg? Assume the vapour pressure of naphthalene at 65 °C is negligible.
  5. The boiling point of water is 100 °C. If 3 g of a non-volatile solute is dissolved in 200 g of it and the solution has a  $K_b$  of 0.52 °C/m, what is the boiling point of the solution?



6. 12.5 g of the solute when dissolved in 170 g of water results in the elevation of boiling point by  $0.63^{\circ}\text{C}$ . Calculate the molecular mass of the solute if the  $K_b$  of water is  $0.52^{\circ}\text{C/m}$ .
7. When 13.66 g of lactic acid,  $\text{C}_3\text{H}_6\text{O}_3$ , are mixed with 115 g of stearic acid, the mixture freezes at  $62.7^{\circ}\text{C}$ . The freezing point of pure stearic acid is  $69.4^{\circ}\text{C}$ . What is the freezing point constant of stearic acid.
8. What is the boiling point of a solution of 0.150 g of glycerol,  $\text{C}_3\text{H}_8\text{O}_3$ , in 20.0 g of water ( $K_f = 1.86^{\circ}\text{C/m}$ )? What is the freezing point?
9. 4.50 g of a substance dissolved in 125 g of  $\text{CCl}_4$  leading to an elevation of the boiling point of  $0.650^{\circ}\text{C}$ . Calculate the freezing point depression, the molar mass of the substance, and the factor by which the vapour pressure of  $\text{CCl}_4$  is lowered.
10. Safrole is contained in oil of sassafras and was once used to flavor root beer. A 2.39 mg sample of safrole was dissolved in 103.0 mg of diphenyl ether. The solution had a melting point of  $25.70^{\circ}\text{C}$ . Calculate the molecular mass of safrole.

11. A solution contains 0.0653 g of a compound in 8.31 g of ethanol. The molality of the solution is 0.0368 *m*. Calculate the molecular mass of the compound.
12. The molar mass of phenolphthalein, an acid-base indicator, was determined by osmotic pressure measurements. A student obtained an osmotic pressure of 14.6 mm Hg at 25 °C for a 2.00 L solution containing 500.0 mg of phenolphthalein. What is the molar mass of phenolphthalein?
13. Arginine vasopressin is a pituitary hormone. It helps regulate the amount of water in the blood by reducing the flow of urine from the kidneys. An aqueous solution containing 21.6 mg of vasopressin in 100.0 mL of solution has an osmotic pressure at 25 °C of 3.70 mmHg. What is the molecular mass of the hormone?
14. Lysozyme, extracted from egg whites, is an enzyme that cleaves bacterial cell walls. A 20.0 mg sample of this enzyme is dissolved in enough water to make 225 mL of solution. At 23 °C the solution has an osmotic pressure of 0.118 mm Hg. Estimate the molar mass of lysozyme.
15. Dextran is a polymeric carbohydrate produced by certain bacteria. It is used as a blood plasma substitute. An aqueous solution contains 0.582 g of dextran in 106 mL of

solution at 21 °C. It has an osmotic pressure of 1.47 mmHg.

What is the average molecular mass of the dextran?

16. What is the freezing point of 0.0075 *m* aqueous calcium chloride,  $\text{CaCl}_2$ ? Use the formula of the salt to obtain *i*.
17. An aqueous solution of  $\text{LiX}$  is prepared by dissolving 3.58 g of the electrolyte in 283 mL of  $\text{H}_2\text{O}$  ( $d = 1.00 \text{ g/mL}$ ;  $K_f = 1.86 \text{ }^\circ\text{C/m}$ ). The solution freezes at 21.818C. What is  $\text{X}^-$ ? (Assume complete dissociation of  $\text{LiX}$  to  $\text{Li}^+$  and  $\text{X}^-$ ).
18. Calculate the osmotic pressure generated at 298 K if a cell with a total solute concentration of 0.500 M is immersed in pure water. The cell wall is permeable to water molecules, but not to the solute molecules.

# CHAPTER THREE

## CHEMICAL KINETICS

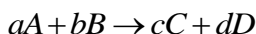
### **KEY CONCEPTS**

Chemical kinetics is an aspect of chemistry concerned with the speeds or rates at which a chemical reaction occurs.

The rate of reaction is a positive quantity that expresses how the concentration of a reactant or product changes with time (m/s). The concentration of reactants decreases during the course of the reaction, while that of products increases.

The rate expression should take into consideration, the moles of reactants and products under consideration.

For the general equation



$$rate = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

The rate of reaction depends on and is directly proportional to the concentration.

i.e. Rate  $\propto$  concentration

$$rate = k[X]$$

Where X is any reactant

The equation,  $rate = k[X]$  is referred to as the rate expression.

The proportionality constant k is called the rate constant.

For the process  $A \rightarrow Products$

The rate expression has the general form

$$rate = k[A]^m$$

The power to which the concentration of the reactant A is raised in the rate expression is called the order of the reaction, m, and is determined experimentally. From the rate expression, the order of reaction can be determined using

$$\frac{rate_2}{rate_1} = \left( \frac{[A]_2}{[A]_1} \right)^m$$

where  $rate_1$  and  $rate_2$  are the rates of reaction at two different concentrations of A,  $[A]_1$  and  $[A]_2$ , respectively.

Once the order of a reaction is known, the rate constant, k, is readily calculated.

With the order and rate constant known, the rate of reaction at any concentration can be calculated.

For reactions involving more than one reactant the general form of rate expression is

$$rate = k[A]^m \times [B]^n$$

In the rate expression,  $m$  and  $n$  are the orders of reaction with respect to A and B. The overall order of reaction is the sum of the expression,  $m + n$ .

When more than one reactant is involved, the order can be determined by holding the initial concentration of one reactant constant while varying that of the other reactant. From rates measured under these conditions, it is possible to deduce the order of the reaction with respect to the reactant whose initial concentration is varied. consider the reaction between A and B referred to above. Suppose we run two different experiments in which the initial concentrations of A differ ( $[A]_1$ ,  $[A]_2$ ) but that of B is held constant at  $[B]$ . Then the value of  $m$  can be determined.

$$rate_1 = k[A]_1^m \times [B]^n ; rate_2 = k[A]_2 \times [B]^n$$

$$\frac{rate_2}{rate_1} = \left( \frac{[A]_2}{[A]_1} \right)^m$$

The integrated rate equations relate the concentration of reactants to time for different orders of reaction.

For a first order reaction,

$$\ln[A] = -kt + \ln[A]_o$$

$[A]_0$  is the initial concentration of reactant A, and  $[A]$  is the concentration of reactant A after a time,  $t$ .

A plot of  $\ln[A]$  versus  $t$  should be a straight line with an intercept of  $\ln[A]_0$  on the vertical axis and a slope of  $-k$ .

For gas-phase reaction, concentration is replaced with pressure of the gaseous reactant.

$$\ln[P] = -kt + \ln[P]_0$$

The half-life of a first-order reaction is given by the expression

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

where  $t_{1/2}$  is the half-life of the reaction, and  $k$ , the rate constant.

The half-life,  $t_{1/2}$ , is the time required for the concentration of reactant to decrease to half of its initial concentration. It is independent of the concentration of reactant.

A second-order reaction is that whose rate depends on the concentration of one reactant raised to the second power or on the concentration of two different reactants, each raised to the first power.

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

A plot of  $\frac{1}{[A]}$  versus  $t$  gives a straight line with slope  $k$  and intercept  $\frac{1}{[A]_o}$  on the y-axis.

The half-life of a second-order reaction is  $1/k[A]_o$

For a zero-order reaction,

$$\text{rate} = k[A]^0 = k$$

Thus, the rate of a zero-order reaction is a constant, independent of reactants concentrations. The concentration-time relations for a zero-order reaction is

$$[A] = -kt + [A]_o$$

The plot of concentration versus time is linear with intercept  $[A]_o$  and slope  $-k$ .

The half-life of a zero-order reaction is  $[A]_o/2k$

The dependence of the rate constant of a reaction on temperature can be expressed by the Arrhenius equation given as

$$k = Ae^{-E_a/RT}$$

where  $A$  = the collision frequency i.e. frequency factor. It is a constant;  $E_a$  = Activation energy of the reaction (KJ/mol);  $R$  = Gas constant (8.314 J/K.mol);  $T$  = Absolute temperature (K);  $e$  = Base of the natural logarithm



Taking the natural log of both sides of the equation, and rearranging,

$$\ln k = \left( \frac{-E_a}{R} \right) \left( \frac{1}{T} \right) + \ln A$$

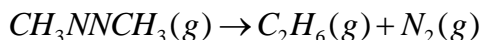
A plot of  $\ln k$  against  $\frac{1}{T}$  gives a straight line with slope  $\frac{-E_a}{R}$  and intercept  $\ln A$ .

The Arrhenius equation can also be used to calculate the activation energy or find the rate constant at another temperature if the  $E_a$  is known.

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \text{ or } \ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

## EXAMPLES

**EXAMPLE 1.** In experiments on the decomposition of azomethane,



the following data were obtained:

Experiment	Initial concentration of azomethane	Initial rate (M/s)
1	$1.13 \times 10^{-2} \text{ M}$	$2.8 \times 10^{-6}$
2	$2.26 \times 10^{-2} \text{ M}$	$5.6 \times 10^{-6}$

What is the rate law? What is the value of the rate constant?

**SOLUTION**

Note that the reaction involves a single reactant. Answering the questions require writing hypothetical rate law, solving for the order or reaction and then calculating the rate constant.

Hypothetical rate law:

$$rate = k[CH_3NNCH_3]^m$$

To solve for  $m$ , using

$$\frac{rate_2}{rate_1} = \left( \frac{[CH_3NNCH_3]_2}{[CH_3NNCH_3]_1} \right)^m$$

$$\frac{5.6 \times 10^{-6}}{2.8 \times 10^{-6}} = \left( \frac{2.26 \times 10^{-2}}{1.13 \times 10^{-2}} \right)^m$$

$$2^1 = 2^m$$

$$m = 1$$

therefore,

$$rate = k[CH_3NNCH_3]^1$$

$$\mathbf{rate = k[CH_3NNCH_3]}$$

To calculate the rate constant, either of the experiments can be used. The values of the initial concentration of azomethane and initial rate of reaction are substituted into the rate law and the rate constant calculated.

Using Expt 1:

$$2.8 \times 10^{-6} = k(1.13 \times 10^{-2})$$

$$k = \left( \frac{2.8 \times 10^{-6}}{1.13 \times 10^{-2}} \right) \frac{M/s}{M}$$

$$k = \mathbf{2.48 \times 10^{-4} s^{-1}}$$

Using Expt 2:

$$5.6 \times 10^{-6} = k(2.26 \times 10^{-2})$$

$$k = \left( \frac{5.6 \times 10^{-6}}{2.26 \times 10^{-2}} \right) \frac{M/s}{M}$$

$$k = \mathbf{2.48 \times 10^{-4} s^{-1}}$$

The above showed that rate constant remains the same for any reaction and can be determined using any of the experiments.

**EXAMPLE 2.** For a reaction involving the decomposition of Y, the following data are obtained:

Experiment	1	2	3	4
Rate (mol/L.min)	0.288	0.245	0.202	0.158
[Y] (mol/L)	0.200	0.170	0.140	0.110

- Determine the order of the reaction.
- Write the rate expression for the decomposition of Y.
- Calculate  $k$  for the experiment above.

**SOLUTION**

The problem is solved just like Example 1.

Hypothetical rate law:

$$rate = k[Y]^m$$

To determine the order of reaction, choose any pair of experiments to determine  $m$

Using Experiments 2 and 4:

$$\frac{rate_4}{rate_2} = \left( \frac{[Y]_4}{[Y]_2} \right)^m$$

$$\frac{0.158}{0.245} = \left( \frac{0.110}{0.170} \right)^m$$

$$0.65^1 = 0.65^m$$

$$m = 1$$

**The order of reaction of Y = 1**

The rate expression for the decomposition of Y:

$$rate = k[Y]^1$$

$$rate = k[Y]$$

To calculate  $k$  for the experiment, choose any of the experiments and substitute for the rate and concentration.

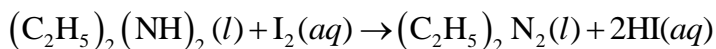
Using Experiment 1:

$$0.288 = k(0.200)$$

$$k = \left( \frac{0.288}{0.200} \right) \frac{\text{mol/L} \cdot \text{min}}{\text{mol/L}}$$

$$k = 1.44 \text{ min}^{-1}$$

**EXAMPLE 3.** Diethylhydrazine reacts with iodine according to the following equation:



The rate of the reaction is followed by monitoring the disappearance of the purple color due to iodine. The following data are obtained at a certain temperature.

Expt.	$[(\text{C}_2\text{H}_5)_2(\text{NH})_2]$	$[\text{I}_2]$	Initial Rate (mol/L.s)
1	0.150	0.250	$1.08 \times 10^{-4}$
2	0.150	0.3620	$1.56 \times 10^{-4}$
3	0.200	0.400	$2.30 \times 10^{-4}$
4	0.300	0.400	$3.44 \times 10^{-4}$

- What is the order of the reaction with respect to diethylhydrazine, iodine, and overall?
- Write the rate expression for the reaction.
- Calculate  $k$  for the reaction.
- What must  $[(\text{C}_2\text{H}_5)_2(\text{NH})_2]$  be so that the rate of the reaction is  $5.00 \times 10^{-4}$  mol/L.h when  $[\text{I}_2] = 0.500 \text{ M}$ ?

**SOLUTION**

This example involves more than one reactant. The concentrations of the reactants were varied at some points in the experiments. To determine the order of reaction with respect to a particular reactant, choose two experiments in which the desired reactant has different concentrations while other reactant has the same concentrations.

Hypothetical rate law:

$$\text{rate} = k \left[ (\text{C}_2\text{H}_5)_2 (\text{NH})_2 \right]^m [\text{I}_2]^n$$

Order of reaction with respect to hydrogen:

Using Expt. 3 and 4, diethylhydrazine has two different concentrations while the concentration of iodine is constant.

Therefore,

$$\frac{\text{rate}_4}{\text{rate}_3} = \left( \frac{[(\text{C}_2\text{H}_5)_2 (\text{NH})_2]_4}{[(\text{C}_2\text{H}_5)_2 (\text{NH})_2]_3} \right)^m$$

$$\frac{3.44 \times 10^{-4}}{2.30 \times 10^{-4}} = \left( \frac{0.300}{0.200} \right)^m$$

$$1.5^1 = 1.5^m$$

$$m = 1$$

**The order of reaction with respect to diethylhydrazine = 1**

Order of reaction with respect to iodine:

Using Expt. 1 and 2, iodine has two different concentrations while the concentration of diethylhydrazine is constant.

$$\frac{rate_2}{rate_1} = \left( \frac{[I_2]_2}{[I_2]_1} \right)^n$$

$$\frac{1.56 \times 10^{-4}}{1.08 \times 10^{-4}} = \left( \frac{0.3620}{0.250} \right)^n$$

$$1.4^1 = 1.4^n$$

$$n = 1$$

**The order of reaction with respect to iodine = 1**

Overall order of reaction:

Overall order of reaction =  $m + n$

$$m + n = 1 + 1 = 2$$

**The overall order of reaction = 2**

Rate expression for the reaction:

From the rate law and the order of reaction with respect to the two reactants, the rate expression

$$rate = k \left[ (C_2H_5)_2(NH)_2 \right]^1 [I_2]^1$$

$$rate = k \left[ (C_2H_5)_2(NH)_2 \right] [I_2]$$

To calculate k:

Choose any of the experiments and substitute for rate and concentrations.

Using Expt. 3:

$$2.30 \times 10^{-4} = k(0.200)(0.400)$$

$$k = \left( \frac{2.30 \times 10^{-4}}{0.200 \times 0.400} \right) \frac{\text{mol/L.h}}{\text{mol/L} \times \text{mol/L}}$$

$$\mathbf{k = 2.9 \times 10^{-3} \text{ L/mol.h}}$$

Concentration of diethylhydrazine at given rate and concentration of iodine:

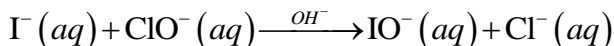
$$\text{rate} = k[(C_2H_5)_2(NH)_2][I_2]$$

$$5.00 \times 10^{-4} = 2.9 \times 10^{-3} \left( [(C_2H_5)_2(NH)_2] \right) (0.500)$$

$$\left( [(C_2H_5)_2(NH)_2] \right) = \left( \frac{5.00 \times 10^{-4}}{2.9 \times 10^{-3} \times 0.500} \right) \frac{\text{mol/L.h}}{\text{L/mol.h} \times \text{mol/L}}$$

$$\left[ (C_2H_5)_2(NH)_2 \right] = \mathbf{0.345 \text{ M}}$$

**EXAMPLE 4.** Iodide ion,  $I^-$ , is oxidized to hypiodite ion,  $IO^-$ , by hypochlorite ion,  $ClO^-$ , in basic solution. The equation is



The following initial-rate experiments were run and, for each, the initial rate of formation of  $IO^-$  was determined.



Experiment	Initial Concentrations (mol/L)			Initial Rate (mol/L.s)
	I <sup>-</sup>	ClO <sup>-</sup>	OH <sup>-</sup>	
Expt. 1	0.010	0.020	0.010	12.2×10 <sup>-2</sup>
Expt. 2	0.020	0.010	0.010	12.2×10 <sup>-2</sup>
Expt. 3	0.010	0.010	0.010	6.1×10 <sup>-2</sup>
Expt. 4	0.010	0.010	0.020	3.0×10 <sup>-2</sup>

Find the rate law and the value of the rate constant.

### SOLUTION

This example involves three reactants. The concentrations of the reactants were varied at some points in the experiments. To determine the order of reaction with respect to a particular reactant, choose two experiments in which the desired reactant has different concentrations while other reactants have constant concentrations.

Hypothetical rate law:

$$rate = k[I^-]^l[ClO^-]^m[OH^-]^n$$

Order of reaction with respect to I<sup>-</sup> :

Using Expt. 2 and 3, I<sup>-</sup> has two different concentrations while the other reactants have constant concentrations.

$$\frac{rate_3}{rate_2} = \left( \frac{[I^-]_3}{[I^-]_2} \right)^l$$

$$\frac{6.1 \times 10^{-2}}{12.2 \times 10^{-2}} = \left( \frac{0.010}{0.020} \right)^l$$

$$0.5^l = 0.5^l$$

$$l = 1$$

### Order of reaction with respect to $\text{I}^- = 1$

Order of reaction with respect to  $\text{ClO}^-$  :

Using Expt. 1 and 3,  $\text{ClO}^-$  has two different concentrations while the other reactants have constant concentrations.

$$\frac{\text{rate}_3}{\text{rate}_1} = \left( \frac{[\text{ClO}^-]_3}{[\text{ClO}^-]_1} \right)^m$$

$$\frac{6.1 \times 10^{-2}}{12.2 \times 10^{-2}} = \left( \frac{0.010}{0.020} \right)^m$$

$$0.5^l = 0.5^m$$

$$m = 1$$

### Order of reaction with respect to $\text{ClO}^- = 1$

Order of reaction with respect to  $\text{OH}^-$  :

Using Expt. 3 and 4,  $\text{OH}^-$  has two different concentrations while the other reactants have constant concentrations.

$$\frac{\text{rate}_4}{\text{rate}_3} = \left( \frac{[\text{OH}^-]_4}{[\text{OH}^-]_3} \right)^n$$

$$\frac{3.0 \times 10^{-2}}{6.1 \times 10^{-2}} = \left( \frac{0.020}{0.010} \right)^n$$

$$0.5 = 2^n$$

Taking the log of both sides

$$\log 0.5 = \log 2^n$$

$$\log 0.5 = n \log 2$$

$$n = \frac{\log 0.5}{\log 2}$$

$$n = -1$$

**Order of reaction with respect to  $\text{OH}^- = -1$**

**Rate law:**  $rate = k [\text{I}^-]^l [\text{ClO}^-]^m [\text{OH}^-]^n$

$$rate = k [\text{I}^-]^1 [\text{ClO}^-]^1 [\text{OH}^-]^{-1}$$

$$\mathbf{rate = k [\text{I}^-] [\text{ClO}^-] [\text{OH}^-]^{-1}}$$

The value of the rate constant:

Using Expt. 1:

$$12.2 \times 10^{-2} = k(0.010)(0.020)(0.010)^{-1}$$

$$k = \left( \frac{12.2 \times 10^{-2}}{(0.010)(0.020)(0.010)^{-1}} \right) \frac{\text{mol/L.s}}{\text{mol/L} \times \text{mol/L} \times \text{mol/L}}$$

$$k = \left( \frac{12.2 \times 10^{-2} \times 0.010}{0.010 \times 0.020} \right) \frac{\text{mol/L.s} \times \text{mol/L}}{\text{mol/L} \times \text{mol/L}}$$

$$k = 1.1s^{-1}$$

**EXAMPLE 5.** Sulfuryl chloride,  $SO_2Cl_2$ , decomposes when heated.



In an experiment, the initial concentration of  $SO_2Cl_2$  was 0.0248 mol/L. If the rate constant is  $2.2 \times 10^{-5} s^{-1}$ , what is the concentration of  $SO_2Cl_2$  after 2.0 h? The reaction is first order.

**SOLUTION**

**Given:** Initial concentration of  $SO_2Cl_2 = 0.0248$  mol/L; rate constant =  $2.2 \times 10^{-5} s^{-1}$ ; time,  $t = 2.0$  h.

**Desired:** concentration of  $SO_2Cl_2$  after 2.0 h.

The reaction is a first order reaction involving variation of concentration with time.

$$\text{Using: } \ln[SO_2Cl_2] = -kt + \ln[SO_2Cl_2]_o$$

where  $[SO_2Cl_2]_o$  = initial concentration of  $SO_2Cl_2$

$[SO_2Cl_2]$  = concentration of  $SO_2Cl_2$  after 2.0 h

$t$  = time

$k$  = rate constant

There is a need for units of expression to agree. Therefore, the time will be converted from hours to seconds

$$1 \text{ h} = 3600 \text{ s}$$

Therefore,  $2 \text{ h} = (2 \times 3600) \text{ s}$

$$t = 7200 \text{ s}$$

substituting into the equation above,

$$\ln[\text{SO}_2\text{Cl}_2] = -(2.2 \times 10^{-5})(7200) + \ln 0.0248$$

$$\ln[\text{SO}_2\text{Cl}_2] = -58.56$$

$$[\text{SO}_2\text{Cl}_2] = e^{-58.56}$$

$$[\text{SO}_2\text{Cl}_2] = 3.70 \times 10^{-26} \text{ M}$$

**EXAMPLE 6.** The first-order rate constant for the decomposition of a certain hormone in water at 25 °C is  $3.42 \times 10^{-4} \text{ day}^{-1}$ .

- i. If a 0.0200 *M* solution of the hormone is stored at 25 °C for two months, what will its concentration be at the end of that period?
- ii. How long will it take for the concentration of the solution to drop from 0.0200 *M* to 0.00350 *M*?
- iii. What is the half-life of the hormone?

### SOLUTION

*i. Given:* Initial concentration of hormone = 0.0200 *M*; rate constant =  $3.42 \times 10^{-4} \text{ day}^{-1}$ ; time, *t* = 2 months.

*Desired:* concentration of hormone after 2 months.

**ii. Given:** Initial concentration of hormone = 0.0200 M; final concentration of hormone = 0.00350 M.

**Desired:** time, t, required for decrease in hormone concentration.

**iii. Desired:** half-life of the hormone.

The reaction is a first order reaction involving variation of concentration with time.

Let the hormone be designated as H.

i.

Using:  $\ln[H] = -kt + \ln[H]_o$

where  $[H]_o$  = initial concentration of hormone

$[H]$  = concentration of hormone after 2 months

t = time

k = rate constant

There is a need for units of expression to agree. Therefore, the time will be converted from months to days.

Assume a month is 30 days.

1 month = 30 days

Therefore, 2 months = (2 × 30) days

t = 60 days

substituting into the equation above,

$$\ln[H] = -(4.42 \times 10^{-4})(60) + \ln 0.0200$$

$$\ln[H] = -3.89$$

$$[H] = e^{-3.89}$$

$$[H] = 2.05 \times 10^{-2} M$$

ii. Using:  $\ln[H] = -kt + \ln[H]_o$

where  $[H]_o$  = initial concentration of hormone

$[H]$  = concentration of hormone after time,  $t$

$t$  = unknown time

$k$  = rate constant

$$\ln 0.00350 = -(3.42 \times 10^{-4})t + \ln 0.0200$$

$$\ln 0.00350 - \ln 0.0200 = -3.42 \times 10^{-4} t$$

$$\ln\left(\frac{0.00350}{0.0200}\right) = -3.42 \times 10^{-4} t$$

$$\ln 0.175 = -3.42 \times 10^{-4} t$$

$$-1.743 = -3.42 \times 10^{-4} t$$

$$t = \left(\frac{-1.743}{-3.42 \times 10^{-4}}\right) \text{ days}$$

$$t = \mathbf{5096 \text{ days}}$$

iii.

Half-life of the hormone:

$$\text{Using } t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \left( \frac{0.693}{3.42 \times 10^{-4}} \right) \text{ days}$$

$$t_{1/2} = \mathbf{2026 \text{ days}}$$

**EXAMPLE 7.** A reaction of the form  $aA \rightarrow \text{Products}$  is second order with a rate constant of 0.169 L/mol.s. If the initial concentration of A is 0.159 mol/L, how many seconds would it take for the concentration of A to decrease to  $6.07 \times 10^{-3}$  mol/L?

### SOLUTION

**Given:** rate constant = 0.169 L/mol.s; initial concentration = 0.159 mol/L; final concentration =  $6.07 \times 10^{-3}$  mol/L.

**Desired:** time,  $t$ , required for the concentration to decrease.

$$\text{Using } \frac{1}{[A]} = kt + \frac{1}{[A]_o}$$

where  $[A]_o$  = initial concentration of reactant A,

$[A]$  = concentration of reactant A after a time,  $t$ .

$$\frac{1}{6.07 \times 10^{-3}} = 0.169t + \frac{1}{0.159}$$

$$164.74 = 0.169t + 6.29$$

$$158.45 = 0.169t$$



$$t = \left( \frac{158.45}{0.169} \right) s$$

$$t = \mathbf{937.57\ s}$$

**EXAMPLE 8.** For the zero-order decomposition of ammonia on tungsten the rate constant is  $2.08 \times 10^{-4}$  mol/L.s. What is the half-life of a 0.250 *M* solution of ammonia? How long will it take for the concentration of ammonia to drop from 1.25 *M* to 0.388 *M*?

### SOLUTION

*i. Given:* rate constant =  $2.08 \times 10^{-4}$  L/mol.s; initial concentration = 0.250 *M*

*Desired:* half-life of the decomposition of ammonia.

*ii. Given:* initial concentration = 1.25 *M*; final concentration = 0.388 *M*

i.

$$\text{Using } t_{1/2} = \frac{[\text{NH}_3]_o}{2k}$$

where  $[\text{NH}_3]_o$  = initial concentration of ammonia

$$t_{1/2} = \left( \frac{0.250}{2 \times 2.08 \times 10^{-4}} \right) s$$

$$t_{1/2} = \mathbf{601\ s}$$

ii.

$$\text{Using } [\text{NH}_3] = -kt + [\text{NH}_3]_o$$

$$0.388 = -(2.08 \times 10^{-4})t + 1.25$$

$$-0.862 = -2.08 \times 10^{-4}t$$

$$t = \left( \frac{-0.862}{-2.08 \times 10^{-4}} \right) s$$

$$t = \mathbf{4144\text{ s}}$$

**EXAMPLE 9.** The rate constant of a first-order reaction is  $3.46 \times 10^{-2} \text{ s}^{-1}$  at 298 K. What is the rate constant at 350 K if the  $E_a$  for the reaction is 50.2 kJ/mol?  $R = 8.314 \text{ J/K.mol}$

### SOLUTION

**Given:** initial rate constant,  $k_1 = 3.46 \times 10^{-2} \text{ s}^{-1}$ ; initial temperature,  $T_1 = 298 \text{ K}$ ; final temperature,  $T_2 = 350 \text{ K}$ ; activation energy,  $E_a = 50.2 \text{ kJ/mol}$ .

**Desired:** final rate constant,  $k_2$

Convert the activation energy,  $E_a$  to J/mol

$$1 \text{ kJ/mol} = 1000 \text{ J/mol}$$

Therefore,

$$50.2 \text{ kJ/mol} = 50.2 \times 10^3 \text{ J/mol}$$

$$E_a = 50.2 \times 10^3 \text{ J/mol}$$

$$\text{Using } \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \text{ or } \ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{3.46 \times 10^{-2}}{k_2} = \frac{50.2 \times 10^3}{8.314} \left( \frac{1}{350} - \frac{1}{298} \right)$$

$$\ln(3.46 \times 10^{-2}) - \ln k_2 = 6.04 \times 10^3 (-4.99 \times 10^{-4})$$

$$\ln k_2 = -3.36 + 3.01$$

$$\ln k_2 = -0.35$$

$$k_2 = e^{-0.35}$$

$$k_2 = 0.702 \text{ s}^{-1}$$

**EXAMPLE 10.** In a series of experiments on the decomposition of dinitrogen pentoxide,  $\text{N}_2\text{O}_5$ , rate constants were determined at two different temperatures. At  $35^\circ\text{C}$ , the rate constant was  $1.4 \times 10^{-4} \text{ s}^{-1}$ ; at  $45^\circ\text{C}$ , the rate constant was  $5.0 \times 10^{-4} \text{ s}^{-1}$ . What is the activation energy for this reaction?  $R = 8.314 \text{ J/K.mol}$

### SOLUTION

**Given:** initial temperature,  $T_1 = 35^\circ\text{C}$ ; initial rate constant,  $k_1 = 1.4 \times 10^{-4} \text{ s}^{-1}$ ; final temperature,  $T_2 = 45^\circ\text{C}$ ; final rate constant,  $k_2 = 5.0 \times 10^{-4} \text{ s}^{-1}$ .

**Desired:** activation energy,  $E_a$

Convert the temperatures from  $^\circ\text{C}$  to K

Therefore,

$$T_1 = 35\text{ }^{\circ}\text{C} = (35 + 273)\text{ K}$$

$$T_1 = 308\text{ K}$$

$$T_2 = 45\text{ }^{\circ}\text{C} = (45 + 273)\text{ K}$$

$$T_2 = 318\text{ K}$$

$$\text{Using } \ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{1.4 \times 10^{-4}}{5.0 \times 10^{-4}} = \frac{E_a}{8.314} \left( \frac{1}{318} - \frac{1}{308} \right)$$

$$\ln 0.28 = \frac{E_a}{8.314} (0.00314 - 0.00325)$$

$$-1.273 = \frac{E_a}{8.314} (-0.00011)$$

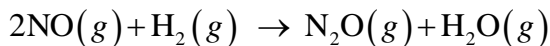
$$\frac{-1.273}{-0.00011} = \frac{E_a}{8.314}$$

$$E_a = (11572.72 \times 8.314)\text{ J/mol}$$

$$\mathbf{E_a = 96215.65\text{ J / mol}}$$

## ***EXERCISES***

1. Nitrogen monoxide, NO, reacts with hydrogen to give nitrous oxide, N<sub>2</sub>O, and water.



In a series of experiments, the following initial rates of disappearance of NO were obtained:

Experiment	Initial concentration (mol/L)		Initial rate (mol/L.s)
	[NO]	[H <sub>2</sub> ]	
1	$6.4 \times 10^{-3}$	$2.2 \times 10^{-3}$	$2.6 \times 10^{-5}$
2	$12.8 \times 10^{-3}$	$2.2 \times 10^{-3}$	$1.0 \times 10^{-4}$
3	$6.4 \times 10^{-3}$	$4.5 \times 10^{-3}$	$5.1 \times 10^{-5}$

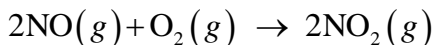
Find the rate law and the value of the rate constant for the reaction of NO.

2. For the reaction:  $A \rightarrow \text{products}$

The following data are obtained.

Experiment	1	2	3	4
Rate (mol/L.min)	0.0167	0.0107	0.00601	0.00267
[A]	0.100	0.0800	0.0600	0.0400

- Determine the order of the reaction.
  - Write the rate expression for the reaction.
  - Calculate  $k$  for the experiment above.
3. In a kinetic study of the reaction

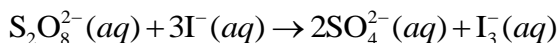


the following data were obtained for the initial rates of disappearance of NO:

Experiment	Initial concentration (mol/L)		Initial rate (mol/L.s)
	[NO]	[O <sub>2</sub> ]	
1	0.0125	0.0253	0.0281
2	0.0250	0.0253	0.112
3	0.0125	0.0506	0.0561

Obtain the rate law. What is the value of the rate constant?

4. The peroxysulfate ion reacts with the iodide ion in aqueous solution according to the following equation:

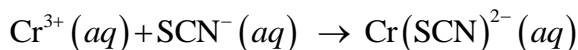


The following data are obtained at a certain temperature:

Expt.	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ]	[I <sub>2</sub> ]	Initial Rate (mol/L.min)
1	0.0200	0.0155	1.15 × 10 <sup>-4</sup>
2	0.0250	0.0200	1.85 × 10 <sup>-4</sup>
3	0.0300	0.0200	2.22 × 10 <sup>-4</sup>
4	0.0300	0.0275	3.06 × 10 <sup>-4</sup>

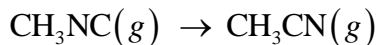
- i. What is the order of the reaction with respect to  $[S_2O_8^{2-}]$ ,  $[I_2]$  and overall?
  - ii. Write the rate expression for the reaction.
  - iii. Calculate  $k$  for the reaction.
  - iv. When  $[S_2O_8^{2-}] = 0.105\text{ M}$  and  $[I_2] = 0.0875\text{ M}$ , what is the rate of the reaction at the temperature of the experiment?
5. The decomposition of dimethyl ether ( $CH_3OCH_3$ ) to methane, carbon monoxide, and hydrogen gases is found to be first-order. At  $500\text{ }^\circ\text{C}$ , a  $150.0\text{-mg}$  sample of dimethyl ether is reduced to  $43.2\text{ mg}$  after three quarters of an hour. Calculate
- i. the rate constant.
  - ii. the half-life at  $500^\circ\text{C}$ .
  - iii. how long it will take to decompose 95% of the dimethyl ether.
6. Cyclopropane,  $C_3H_6$ , is converted to its isomer propylene,  $CH_2=CHCH_3$ , when heated. The rate law is first order in cyclopropane, and the rate constant is  $6.0 \times 10^{-4}\text{ s}^{-1}$  at  $500\text{ }^\circ\text{C}$ . If the initial concentration of cyclopropane is  $0.0226\text{ mol/L}$ , what is the concentration after  $899\text{ s}$ ?

7. Copper-64 is one of the metals used to study brain activity. Its decay constant is  $0.0546\text{ h}^{-1}$ . If a solution containing 5.00 mg of Cu-64 is used, how many milligrams of Cu-64 remain after eight hours?
8. The first-order rate constant for the decomposition of a certain drug at  $25^{\circ}\text{C}$  is  $0.215\text{ month}^{-1}$ .
  - i. If 10.0 g of the drug is stored at  $25^{\circ}\text{C}$  for one year, how many grams of the drug will remain at the end of the year?
  - ii. What is the half-life of the drug?
  - iii. How long will it take to decompose 65% of the drug?
9. In the presence of excess thiocyanate ion,  $\text{SCN}^{-}$ , the following reaction is first order in chromium(III) ion,  $\text{Cr}^{3+}$ ; the rate constant is  $2.0 \times 10^{-6}\text{ s}^{-1}$ .



If 85.0% reaction is required to obtain a noticeable color from the formation of the  $\text{Cr}(\text{SCN})^{2-}$  ion, how many hours are required?

10. Methyl isocyanide,  $\text{CH}_3\text{NC}$ , isomerizes, when heated, to give acetonitrile (methyl cyanide),  $\text{CH}_3\text{CN}$ .





The reaction is first order. At 230 °C, the rate constant for the isomerization is  $6.3 \times 10^{-4} \text{ s}^{-1}$ . What is the half-life? How long would it take for the concentration of  $\text{CH}_3\text{NC}$  to decrease to 50.0% of its initial value? to 25.0% of its initial value?

11. The reaction  $2\text{NOCl}(g) \rightarrow 2\text{NO}(g) + \text{Cl}_2(g)$  has rate-constant values for the reaction of  $\text{NOCl}$  of  $9.3 \times 10^{-6} \text{ s}^{-1}$  at 350 K and  $6.9 \times 10^{-4} \text{ s}^{-1}$  at 400 K. Calculate activation energy for the reaction. What is the rate constant at 435 K?
12. The rate of a particular reaction triples when the temperature is increased from 25 °C to 35 °C. Calculate the activation energy for this reaction.
13. Cold-blooded animals decrease their body temperature in cold weather to match that of their environment. The activation energy of a certain reaction in a cold-blooded animal is 65 kJ/mol. By what percentage is the rate of the reaction decreased if the body temperature of the animal drops from 35 °C to 22 °C?
14. The chirping rate of a cricket,  $X$ , in chirps per minute, near room temperature is

$$X = 7.2t - 32$$

where  $t$  is the temperature in  $^{\circ}\text{C}$ .

- i. Calculate the chirping rates at  $25^{\circ}\text{C}$  and  $35^{\circ}\text{C}$ .
- ii. Use your answers in (a) to estimate the activation energy for the chirping.
- iii. What is the percentage increase for a  $10^{\circ}\text{C}$  rise in temperature?

# CHAPTER FOUR

## ELECTROCHEMISTRY

### *KEY CONCEPTS*

Electrochemistry is the study of the inter-conversion of electrical and chemical energy.

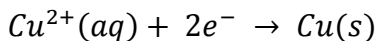
The conversion takes place in an electrochemical cell which may be a voltaic/galvanic cell or an electrolytic cell.

In a voltaic (galvanic) cell, a spontaneous reaction generates electrical energy. Its oxidation occurs at the anode and its reduction at the cathode. The electrons produced at the anode are transferred to the cathode where they are consumed by an external circuit.

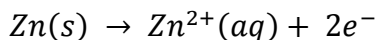
In an electrolytic cell electrical energy is used to bring about a non-spontaneous reaction.

Electrochemical processes are redox (oxidation-reduction) reactions.

In an electrochemical cell, oxidation and reduction half-reactions take place at two different electrodes. Reduction occurs at the cathode e.g.



Oxidation occurs at the anode e.g.



In an electrochemical cell, anions move to the anode while cations move to the cathode.

The loss of electrons by an element during oxidation is marked by an increase in the element's oxidation number.

In reduction, there is a decrease in oxidation number resulting from a gain of electrons by an element.

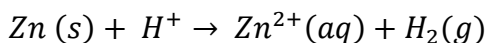
The cell reaction can be summarized in a cell notation. For example, the cell reaction above is often abbreviated as



If we assume that the concentrations of the  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions are 1M, thus the cell notation is written as

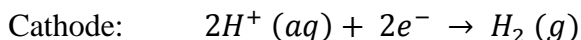
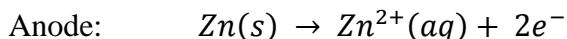


For a voltaic cell involving a spontaneous reaction between zinc metal and  $\text{H}^{+}$  ions.



No metal is involved in the cathode half-reaction. An inert electrode that conducts an electric current is used.

The half-reaction occurring in the cells are:



The cell notation is



The symbol Pt is used to indicate the presence of an inert platinum support electrode.

The cause of the spontaneous reaction in a voltaic cell is measured by the cell voltage which is dependent on the nature of the redox reaction and the concentration of the species involved.

The standard emf (voltage/ potential) of a cell,  $E_{cell}^{\circ}$ , is a contribution from both the anode and cathode is given by

$$E_{cell}^{\circ} = E_{red}^{\circ} + E_{ox}^{\circ}$$

$$\text{OR } E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$$

Standard half-cell voltages are ordinarily obtained from a list of standard potentials (Appendix A). The potentials however, are the standard voltages for reduction half-reactions.

$$\text{i.e. Standard Potential} = E_{red}^{\circ}$$

To obtain the standard voltage for an oxidation half reaction, the sign of the standard potential listed is changed.

To determine whether a given redox reaction is spontaneous, the calculated cell voltage is considered. If the calculated voltage is a positive quantity, the reaction is spontaneous. If the calculated voltage is negative, the reaction is non-spontaneous.

The standard free energy change,  $\Delta G^\circ$ , is also a general criterion for reaction spontaneity. Thermodynamically,  $E^\circ$  and  $\Delta G^\circ$  are related by

$$\Delta G^\circ = -nFE^\circ$$

where  $\Delta G^\circ$  = Standard free energy change (gases at 1atm, spp in solution at 1M) for the reaction

$E^\circ$  = Standard voltage for the cell reaction

$F$  = Faraday constant ( $9.648 \times 10^4$  g/mol or  $9.648 \times 10$  C/mol/ $e^-$  or  $9.648 \times 10^4$  J/mol)

$n$  = No of moles of  $e^-$  transferred in the reaction

$\Delta G^\circ$  and  $E^\circ$  have opposite signs. A spontaneous reaction is that for which  $\Delta G^\circ$  is negative and  $E^\circ$  is positive.

The equilibrium constant for a redox reaction can be calculated from the standard voltage,  $E^\circ$  by the relation:

$$E^{\circ} = \frac{RT \ln K}{nF}$$

where R = gas constant (8.314J/mol.K)

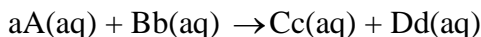
T = Temperature (Kelvin)

Under standard state conditions,

$$E^{\circ} = \frac{0.0257V}{n} \ln K \text{ or } E^{\circ} = \frac{0.0592V}{n} \log K$$

K = equilibrium constant

To obtain a quantitative relation between cell voltage and concentration, general equation



is considered. The cell voltage and the standard cell potential are related by the Nernst equation

$$E = E^{\circ} - \frac{RT \ln Q}{nF} = E^{\circ} - \frac{(0.0257V)}{n} \ln Q$$

E = cell voltage

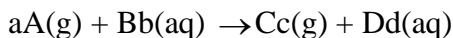
E<sup>o</sup> = standard voltage

n = number of moles of electrons involved in the reaction

Q = Reaction quotient

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

For gaseous species, pressure is considered instead of concentration



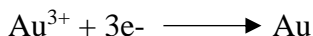
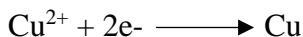
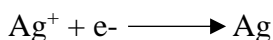
$$Q = \frac{P_C^c \times [D]^d}{P_A^a \times [B]^b}$$

In an electrolytic cell, a spontaneous redox reaction is made to occur by pumping electrical energy into the system.

A storage battery provides a source of dc, from the terminals of the battery, two wires lead to the electrolytic cell.

The cell consists of two electrodes, dipping into a solution containing ions.

The amount of electricity passed through an electrolytic cell determines the amount of substance produced by redox at the electrodes. For example, from the balanced half-equation



It can be deduced that

1mol of electron = 1mole of Ag i.e. 107.9g of Ag

2mol of e<sup>-</sup> = 1mol of Cu i.e. 63.55g of Cu

3mol of e<sup>-</sup> = 1mol of Au i.e. 197.0g of Au

The coulomb, C, is related to the charge carried by a mole of electron through the Faraday constant.



$$1\text{mol of electrons} \equiv 9.648 \times 10^4 \text{ C}$$

When a current of 1amp passes through an electron circuit, 1 coulomb passes a given point in the circuit in 1 second.

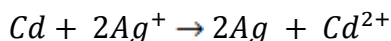
$$\text{i.e. } Q = It \text{ i.e. } I = Q/t \quad (\text{C/s})$$

$$IJ = IC.V,$$

when a charge of 1C moves through a potential difference of 1V, it acquires an energy of IJ.

### EXAMPLES

**EXAMPLE 1.** Calculate  $E^o$  for cell reaction

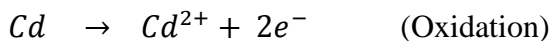
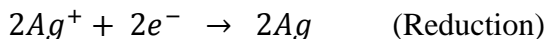


### SOLUTION

The table of standard reduction potentials (APPENDIX A) is required

#### Steps:

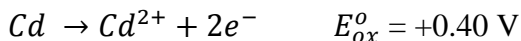
- i. Split into two half reactions



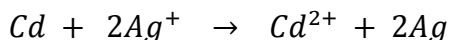
- ii. From the table of reduction potentials, obtain the  $E_{red}^o$  of both reactions.



- iii. Change reduction potential of the oxidation half reaction to  $E_{ox}^o$  as appropriate



- iv. Add the reactions



$$\text{Therefore, } E^o = E_{red}^o + E_{ox}^o$$

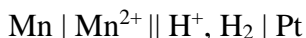
$$E^o = (0.80 + 0.40) \text{ V}$$

$$E^o = +1.20 \text{ V}$$

**Note:**

- i.  $E^o$  is always positive for a voltaic cell reaction.
- ii.  $E^o$ ,  $E_{ox}^o$  and  $E_{red}^o$  are independent of how the cell reaction equation is written. Coefficients of balanced equation is not to be used to multiply their values.

**EXAMPLE 2.** Calculate  $E^o$  for the following cells



**SOLUTION**

**Steps:**

- i. Write the half-cell reactions



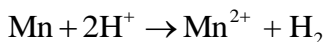
- ii. From the table of reduction potentials, obtain the  $E_{red}^o$  of both reactions.



- iii. Change reduction potential of the oxidation half reaction to  $E_{ox}^o$  as appropriate



- iv. Add the reactions

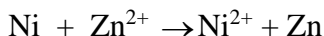


Therefore,  $E^o = E_{red}^o + E_{ox}^o$

$$E^o = (0.00 + 1.18) \text{ V}$$

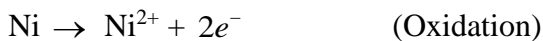
$$E^o = +1.18 \text{ V}$$

**EXAMPLE 3.** Consider an overall cell reaction represented as



Is the redox reaction spontaneous?

**SOLUTION**



For oxidation,

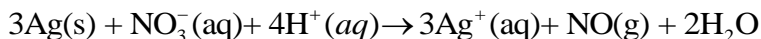


$$E^{\circ} = (0.24 + (-0.76))\text{V}$$

$$E^{\circ} = -0.526 \text{ V}$$

**The reaction is not spontaneous.**

**EXAMPLE 4.** For the reaction

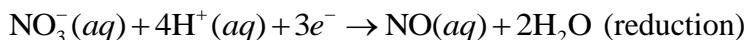


Use the table of standard reduction potentials to calculate at 25 °C, (a)  $\Delta G^{\circ}$  (b) K

**SOLUTION**

**Steps:**

- i. Split equation into oxidation and reduction



- ii. Calculate  $E^{\circ}$

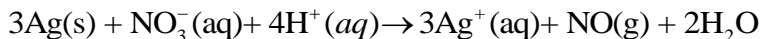


Change reduction potential of the oxidation half reaction to

$E_{ox}^{\circ}$  as appropriate



Add and calculate the cell potentials to get  $E^o$



$$E^o = E_{red}^o + E_{ox}^o$$

$$E^o = (+0.96 + (-0.80))\text{V}$$

$$E^o = 0.16\text{ V}$$

iii. Calculate  $\Delta G^o$  using  $-nFE^o$

Using  $\Delta G^o = -nFE^o$

$n = 3$  i.e. three moles of electrons were involved in the overall balanced reaction

$$\Delta G^o = -(3)(9.648 \times 10^4)(0.16)$$

$$\Delta G^o = -46310\text{ J}$$

$$\Delta G^o = \mathbf{-4.6\text{ kJ}}$$

iv. Calculate  $K$  using  $E^o = \frac{0.0257\text{ V}}{n} \ln k$

$$0.16 = \frac{0.0257}{3} \ln k$$

$$0.16 \times 3 = 0.0257 \ln k$$

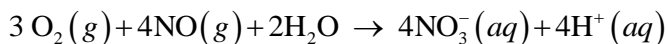
$$\ln k = \frac{0.16 \times 3}{0.0257}$$

$$\ln k = 18.68$$

$$k = e^{18.68}$$

$$\mathbf{k = 12.9 \times 10^7}$$

**EXAMPLE 5.** Consider a voltaic cell at 25 °C in which the following reaction takes place.



- i. Calculate  $E^\circ$ .
- ii. Write the Nernst equation for the cell.
- iii. Calculate  $E$  under the following conditions:

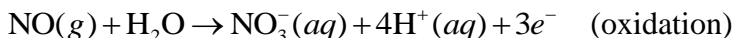
$$[\text{NO}_3^-] = 0.750 \text{ M}, \quad P_{\text{NO}} = 0.993 \text{ atm}, P_{\text{O}_2} = 0.515 \text{ atm},$$

$$[\text{H}^+] = 0.0014 \text{ M}$$

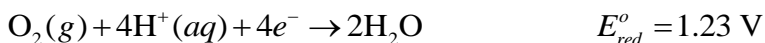
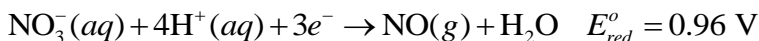
## SOLUTION

### Steps:

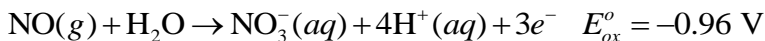
- i. Separate the overall equation into half-cell reactions



- ii. Obtain  $E_{red}^\circ$  from the table of reduction potentials



- iii. Change reduction potential of the oxidation half reaction  
to  $E_{ox}^o$  as appropriate



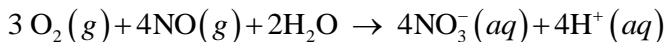
- iv. Calculate  $E^o$  using  $E^o = E_{\text{red}}^o + E_{\text{ox}}^o$

$$E^o = ((1.23) + (-0.96)) \text{ V}$$

$$E^o = \mathbf{0.27 \text{ V}}$$

The general Nernst equation:  $E = E^o - \frac{0.0257\text{V}}{n} \ln Q$

From the balanced equation of reaction:



$$Q = \frac{[\text{NO}_3^-]^4 \times [\text{H}^+]^4}{\text{P}_{\text{O}_2}^3 \times \text{P}_{\text{NO}}^4}$$

The Nernst equation for the reaction is

$$E = 0.27 - \frac{0.0257\text{V}}{12} \ln \left( \frac{[\text{NO}_3^-]^4 \times [\text{H}^+]^4}{\text{P}_{\text{O}_2}^3 \times \text{P}_{\text{NO}}^4} \right)$$

$$E = \mathbf{0.27 - 0.0021 \ln \left( \frac{[\text{Ag}^+]^3 \times \text{P}_{\text{NO}}}{[\text{NO}_3^-] \times [\text{H}^+]^4} \right)}$$

To calculate E

$$Q = \frac{(0.750)^4 (0.0014)^4}{(0.515)^3 (0.993)^4}$$

$$Q = \frac{1.22 \times 10^{-12}}{1.33 \times 10^{-1}}$$

$$Q = 9.19 \times 10^{-12}$$

Substituting for Q in the Nernst equation

$$E = (0.27 - 0.0021 \ln(9.19 \times 10^{-11})) \text{ V}$$

$$E = (0.27 - (0.0021)(-25.41)) \text{ V}$$

$$E = (0.27 + 0.05) \text{ V} = \mathbf{0.32 \text{ V}}$$

**EXAMPLE 6.** A solution containing a metal ion ( $M^{3+}(\text{aq})$ ) is electrolyzed by a current of 5.00 A. After 10.0 minutes, 1.19 g of the metal is plated out. How many coulombs are supplied by the battery. What is the metal? (Assume 100 % efficiency).

### SOLUTION

**Given:** Metal ion,  $M^{3+}(\text{aq})$ ; current,  $I = 5.00 \text{ A}$ ; metal plated out = 1.19 g; Efficiency = 100%

**Desired:** Coulombs, C of electricity supplied by the battery;

Name of metal M.

Using  $Q = It$

where Q = quantity of electricity (C)

I = current (A)

t = time (s)



Convert the time in minutes to seconds

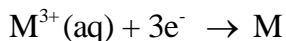
$$t = 10.0 \text{ min} = (10 \times 60) \text{ s}$$

$$Q = (5.00 \times 10 \times 60) \text{ C}$$

$$= 3000 \text{ C}$$

Coulombs supplied by the battery = **3000 C**

For a metal ion  $M^{3+}$ ,



1 mole of metal  $M \equiv 3$  moles of electron

and,

$$1 \text{ mole of electron} \equiv 9.648 \times 10^4 \text{ C}$$

therefore,

$$3 \text{ moles of electron} \equiv 3 \times 9.648 \times 10^4 \text{ C}$$

$$= 289440 \text{ C}$$

it implies that,

$$289440 \text{ C} \equiv 1 \text{ mole of } M$$

but,

3000 C plated 1.19 g of M

$$\therefore 289440 \text{ C} \equiv \left( \frac{289440 \times 1.19}{3000} \right) \text{ g of metal } M$$

$$= 114.8 \text{ g of } M$$

From the periodic table of elements, **metal M is Indium, In.**

**EXAMPLE 7.** A constant electric current flow for 3.75 h through two electrolytic cells connected in series. One contains a solution of  $\text{AgNO}_3$  and the second a solution of  $\text{CuCl}_2$ . During this time, 2.00 g of silver are deposited in the first cell. How many grams of copper are deposited in the second cell? What is the current flowing, in amperes?

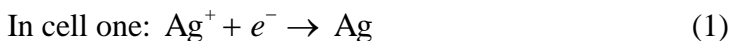
### SOLUTION

**Given:** Time,  $t = 3.75$  h; Cells of  $\text{AgNO}_3$  and  $\text{CuCl}_2$  in series;

Ag metal deposited in the first cell = 2.00 g

**Desired:** mass of copper deposited in the second cell; current flowing (A)

**Note:** The cells are connected in series. That implies that the current flow will be the same in both.



Using  $Q = It$

where  $Q$  = quantity of electricity (C)

$I$  = current (A)

$t$  = time (s)

Convert the time given in minutes to seconds

Time,  $t = 3.75$  h =  $(3.75 \times 60 \times 60)$  s

= 135364 s

Amount of silver deposited = 2.00 g

From eqn (1),

1 mole of  $e^- \equiv 107.9$  g of Ag

i.e.  $9.648 \times 10^4$  C  $\equiv 107.9$  g of Ag

$$\begin{aligned} 2.00 \text{ g of Ag will be deposited by } & \left( \frac{2.00 \times 9.648 \times 10^4}{107.9} \right) \text{ C} \\ & = 1788.2 \text{ C} \end{aligned}$$

Therefore, the quantity of electricity passed through cell one = 1788.2 C

Since the cells are connected in series, the same quantity of electricity passed through cell two.

From eqn (2),

2 moles of  $e^- \equiv 63.5$  g of Cu

i.e.  $2 \times 9.648 \times 10^4$  C  $\equiv 63.5$  g of Cu

Therefore,

1788.2 C of electricity will deposit

$$\begin{aligned} & \left( \frac{1788.2 \times 63.5}{2 \times 9.648 \times 10^4} \right) \text{ g of Cu} \\ & = \mathbf{0.59 \text{ g of Cu}} \end{aligned}$$

ii. Current flowing in amperes

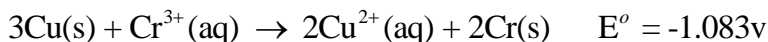
Using  $Q = It$

$$I = \frac{Q}{t}$$

$$I = \frac{1788.32}{135364}$$

Current, I, flowing = **0.13 A**

**EXAMPLE 8.** An electrolytic cell consists of 100.0 g strip of copper in 0.200 M  $\text{Cu}(\text{NO}_3)_2$  and 100.0 g strip of chromium in 0.200 M  $\text{Cr}(\text{NO}_3)_3$ . The overall reaction is



An external battery provides 3 A for 70 min and 20 s with 100% efficiency. What is the mass of the copper strip after the battery has been disconnected?

### SOLUTION

**Given:** mass of Cu and Cr strips before electrolysis = 100.0 g each; current, A = 3 A; time, t = 70 min 20 s; efficiency = 100%.

**Desired:** Mass of Cu strip after electrolysis

Using  $Q = It$

where Q = quantity of electricity (C)

I = current (A)

t = time (s)

Convert time in minutes to seconds

$$t = 70 \text{ min and } 20 \text{ secs} = ((70 \times 60) + 20) \text{ s} \\ = 4220 \text{ s}$$

therefore,

$$Q = (3 \times 4220) \text{ C}$$

$$Q = 12660 \text{ C}$$

For Cu,



$$2 \text{ moles of } \text{e}^{-} \equiv 6.5 \text{ g of Cu}$$

it implies that,

$$2 \times 9.648 \times 10^4 \text{ C} \equiv 6.5 \text{ g Cu}$$

therefore,

$$12660 \text{ C} \equiv \left( \frac{12660 \times 6.5}{2 \times 9.648 \times 10^4} \right) \text{ g of Cu} \\ = 4.12 \text{ g of Cu}$$

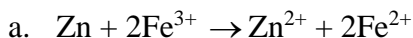
Mass of Cu strip remaining (g) = (Initial mass – Mass dissociated) g

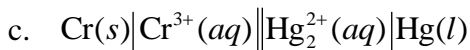
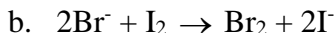
$$= (100.0 - 4.12) \text{ g}$$

Mass of Cu strip remaining = **95.8 g of Cu**

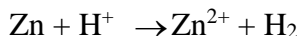
## ***EXERCISES***

1. Calculate the standard cell potential for the cells



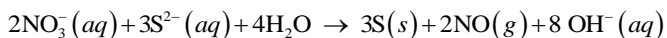


2. For a  $\text{Ni} | \text{Ni}^{2+} || \text{Cu}^{2+} | \text{Cu}$  cell, is the cell reaction spontaneous.
3. Consider the following reactions. Are they spontaneous in the direction written, under standard conditions at 25 °C?
  - i.  $\text{Sn}^{4+}(aq) + 2\text{Fe}^{2+}(aq) \rightarrow \text{Sn}^{2+}(aq) + 2\text{Fe}^{3+}(aq)$
  - ii.  $4\text{MnO}_4^-(aq) + 12\text{H}^+(aq) \rightarrow 4\text{Mn}^{2+}(aq) + 5\text{O}_2(g) + 6\text{H}_2\text{O}(l)$
4. What is the standard cell potential you would obtain from a cell at 25 °C using an electrode in which  $\text{I}^-(aq)$  is in contact with  $\text{I}_2(s)$  and an electrode in which a chromium strip dips into a solution of  $\text{Cr}^{3+}(aq)$ ?
5. Which of the following reactions is (are) spontaneous at standard conditions?
  - i.  $2\text{NO}_3^-(aq) + 18\text{H}^+(aq) + 6\text{Cl}^-(aq) \rightarrow 2\text{NO}(g) + 4\text{H}_2\text{O} + 3\text{Cl}_2(g)$
  - ii.  $\text{O}_2(g) + 4\text{H}^+(aq) + 4\text{Cl}^-(aq) \rightarrow 2\text{H}_2\text{O} + 2\text{Cl}_2(g)$
  - iii.  $3\text{Fe}(s) + 2\text{AuCl}_4^-(aq) \rightarrow 2\text{Au}(s) + 8\text{Cl}^-(aq) + 3\text{Fe}^{2+}(aq)$
6. Calculate  $E^\circ$ ,  $\Delta G^\circ$  and  $K$  at 25 °C for the reaction
 
$$3\text{S}^{2-} + 2\text{NO}_3^- + 4\text{H}_2\text{O} \rightarrow 3\text{S} + 2\text{NO} + 8\text{OH}^-$$
7. Calculate  $E^\circ$ ,  $\Delta G^\circ$  and  $K$  at 25 °C for the reaction
 
$$3\text{Mn}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$$
8. Consider a voltaic cell in which the reaction is



It was found that the voltage is +0.560 V when  $[\text{Zn}^{2+}] = 1.0 \text{ M}$ ,  $P_{\text{H}_2} = 1.0 \text{ atm}$ . What must be the concentration of  $\text{H}^+$  in the  $\text{H}_2 - \text{H}^+$  half-cell?

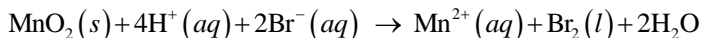
9. Consider a voltaic cell in which the following reaction takes place in basic medium at 25 °C.



- Calculate  $E^\circ$ .
- Write the Nernst equation for the cell voltage  $E$ .
- Calculate  $E$  under the following conditions:

$$P_{\text{NO}} = 0.994 \text{ atm}, \text{ pH} = 13.7, [\text{S}^{2-}] = 0.154 \text{ M}, [\text{NO}_3^-] = 0.472 \text{ M}$$

10. Consider the reaction at 25 °C.



At what pH is the voltage zero if all other species are at standard conditions?

# CHAPTER FIVE

## CHEMICAL EQUILIBRIUM

### *KEY CONCEPTS*

Chemical equilibrium is the state reached by a reaction mixture when the rates of forward and reverse reactions have become equal.

If you observe the reaction mixture, you see no net change, although the forward and reverse reactions are continuing.

To obtain the composition of an equilibrium mixture, you need to determine the amount of only one of the substances. The amounts of the others can be calculated from the amounts



originally placed in the vessel and the equation that represents the reaction.

Chemical equilibrium problem is essentially one of stoichiometry. It involves initial, or *starting*, amounts of reactants. These amounts *change* as reaction occurs. Later, the reaction comes to *equilibrium*, and you analyze the reaction mixture for the amount of one of the reactants or products.

It is convenient to solve this problem by first setting up a table (ICE table) in which you write the initial (starting), change, and equilibrium values of each substance under the balanced equation.

You fill in the starting amounts from the values given in the problem statement. You are not given explicit values for the changes that occur, so you let  $x$  be the molar change.

- i. Each product increases by  $x$  moles multiplied by the coefficients of the substances in the balanced equation.
- ii. Reactants decrease by  $x$  moles multiplied by the corresponding coefficients. The decrease is indicated by a negative sign.
- iii. Equilibrium values are equal to starting values plus the changes.

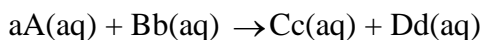
The equilibrium composition depends on the amounts of starting substances.

All equilibrium compositions for a reaction at a given temperature are related by a quantity called the *equilibrium constant*

The equilibrium-constant expression for a reaction is an expression obtained by multiplying the concentrations of products, dividing by the concentrations of reactants, and raising each concentration term to a power equal to the coefficient in the chemical equation.

The equilibrium constant  $K_c$  is the value obtained for the equilibrium-constant expression when equilibrium concentrations are substituted.

Consider the reaction



where A, B, C, and D denote reactants and products, and  $a$ ,  $b$ ,  $c$ , and  $d$  are coefficients in the balanced chemical equation.

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

The law of mass action is a relation that states that the values of the equilibrium-constant expression  $K_c$  are constant for a

particular reaction at a given temperature, whatever equilibrium concentrations are substituted

The equilibrium-constant expression is defined in terms of the balanced chemical equation. If the equation is rewritten with different coefficients, the equilibrium-constant expression will be changed.

It is the usual practice to write equilibrium constants without units.

Equilibrium constants can also be stated in terms of molar concentrations as  $K_c$

In gas-phase equilibria, equilibrium constant is often written in terms of partial pressures of gases,  **$K_p$** , rather than concentrations.

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

If a given chemical equation can be obtained by taking the sum of other equations, the equilibrium constant for the given equation equals the product of the equilibrium constants of the other equations.

A homogeneous equilibrium is an equilibrium that involves reactants and products in a single phase

A heterogeneous equilibrium is an equilibrium involving reactants and products in more than one phase.

In writing the equilibrium-constant expression for a heterogeneous equilibrium, you omit concentration terms for pure solids and liquids.

The concentration of a gas can have various values, the concentration of a pure solid or a pure liquid is a constant at a given temperature.

If  $K_c$  for a reaction, is large, the equilibrium mixture is mostly products.

If  $K_c$  is small, the equilibrium mixture is mostly reactants.

When  $K_c$  is around 1, the equilibrium mixture contains appreciable amounts of both reactants and products.

## ***EXAMPLES***

**EXAMPLE 1.** Carbon monoxide and hydrogen react according to the following equation:



When 1.000 mol CO and 3.000 mol H<sub>2</sub> are placed in a 10.00-L vessel at 927 °C and allowed to come to equilibrium, the mixture is found to contain 0.387 mol H<sub>2</sub>O. What is the molar composition of the equilibrium mixture? That is, how many moles of each substance are present?

## SOLUTION

Using the information given in the problem, you set up the following table:

Amount (mol)	CO	3H <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O
Initial	1.000	3.000	0	0
Change	-x	-3x	+x	+x
Equilibrium	1.000 - x	3.000 - 3x	+x	x = 0.387

The problem statement gives the equilibrium amount for H<sub>2</sub>O. This tells you that  $x = 0.387$  mol. You calculate equilibrium amounts for other substances from the expressions given in the table, using this value of  $x$ .

$$\text{Equilibrium amount of CO} = 1.000 - 0.387 = 0.613 \text{ mol}$$

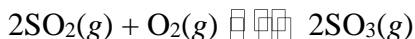
$$\text{Equilibrium amount of H}_2 = 3.000 - 3(0.387) = 1.839 \text{ mol}$$

Equilibrium amount of  $\text{CH}_4 = 0.387 \text{ mol}$

Equilibrium amount of  $\text{H}_2\text{O} = 0.387 \text{ mol}$

**Therefore, the amounts of substances in the equilibrium mixture are 0.613 mol  $\text{CO}$ , 1.839 mol  $\text{H}_2$ , 0.387 mol  $\text{CH}_4$ , and 0.387 mol  $\text{H}_2\text{O}$ .**

**EXAMPLE 2.** In the contact process, sulfuric acid is manufactured by first oxidizing  $\text{SO}_2$  to  $\text{SO}_3$ , which is then reacted with water. The reaction of  $\text{SO}_2$  with  $\text{O}_2$  is



A 2.000 L flask was filled with 0.0400 mol  $\text{SO}_2$  and 0.0200 mol  $\text{O}_2$ . At equilibrium at 900 K, the flask contained 0.0296 mol  $\text{SO}_3$ . How many moles of each substance were in the flask at equilibrium?

**SOLUTION**

Set up an ICE table.

Amount (mol)	$2\text{SO}_2$	$\text{O}_2$	$2\text{SO}_3$
Initial	0.0400	0.0200	0
Change	$-2x$	$-x$	$+2x$
Equilibrium	$0.0400 - 2x$	$0.0200 - x$	$+2x$

The problem statement gives the equilibrium amount for  $\text{SO}_3$ .

This tells you that  $2x = 0.0296 \text{ mol}$ .

Therefore,  $x = \frac{0.0296}{2} = 0.0148 \text{ mol}$

You calculate equilibrium amounts for other substances from the expressions given in the table, using this value of  $x$ .

$$\text{Equilibrium amount of SO}_2 = 0.0400 - 0.0296 = 0.0104 \text{ mol}$$

$$\text{Equilibrium amount of O}_2 = 0.0200 - 0.0148 = 0.0052 \text{ mol}$$

$$\text{Equilibrium amount of SO}_3 = 0.0296 \text{ mol}$$

**Therefore, the amounts of substances in the equilibrium mixture are 0.0104 mol SO<sub>2</sub>, 0.0052 mol O<sub>2</sub>, 0.0296 mol SO<sub>3</sub>.**

**EXAMPLE 3.** The following reaction was allowed to come to equilibrium at 430 K.



The equilibrium concentrations were analyzed and found to be:

$$[\text{SO}_2] = 1.31 \text{ M}, [\text{NO}_2] = 1.42 \text{ M}, [\text{NO}] = 9.67 \text{ M}, [\text{SO}_3] = 12.2 \text{ M}$$

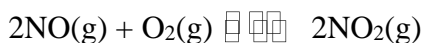
What is the value of  $K_c$ ?

$$K_c = \frac{[\text{NO}][\text{SO}_3]}{[\text{SO}_2][\text{NO}_2]}$$

$$K_c = \frac{(9.67)(12.2)}{(1.31)(1.42)}$$

$$K_c = 63.4$$

**EXAMPLE 4.** The following reaction was allowed to come to equilibrium at 419 K.



The equilibrium concentrations were analyzed and found to be:

$$[\text{O}_2] = 0.768 \text{ M}, [\text{NO}_2] = 0.865 \text{ M}, [\text{NO}] = 0.871 \text{ M}.$$

What is the value of  $K_c$ ?

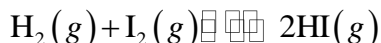
$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

$$K_c = \frac{(0.865)^2}{(0.871)^2(0.768)}$$

$$K_c = 1.28$$

**EXAMPLE 5.** A 6.00 L reaction vessel at 491 °C contained 0.488 mol  $\text{H}_2$ , 0.206 mol  $\text{I}_2$ , and 2.250 mol  $\text{HI}$ . Assuming that the substances are at equilibrium, find the value of  $K_c$  at 491 °C for the reaction of hydrogen and iodine to give hydrogen iodide.

The equation is



### SOLUTION

Calculate the concentration of the reactants and product

$$\text{Concentration (M)} = \frac{n}{V}$$

where  $n$  = number of mole

$V$  = volume

$$\begin{aligned} \text{Concentration of } \text{H}_2 &= \frac{0.488}{6.00} \text{ M} \\ &= 0.0813 \text{ M} \end{aligned}$$



$$\begin{aligned}\text{Concentration of I}_2 &= \frac{0.206}{6.00} M \\ &= 0.0343 M\end{aligned}$$

$$\begin{aligned}\text{Concentration of 2HI} &= \frac{2.250}{6.00} M \\ &= 0.375 M\end{aligned}$$

To calculate  $K_c$ :

Using 
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$K_c = \frac{(0.375)^2}{(0.0813)(0.0343)}$$

$$K_c = \frac{0.141}{(0.0028)}$$

$$\mathbf{K_c = 50.34}$$

**EXAMPLE 6.** The following reaction had  $K_c = 85.0$



At equilibrium,  $[\text{SO}_2] = 0.0112 \text{ M}$ ,  $[\text{NO}] = 0.869 \text{ M}$ , and  $[\text{NO}_2] = 0.277 \text{ M}$ . What is the concentration of  $\text{SO}_3$  in mol/L?

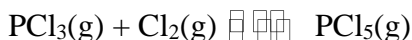
**SOLUTION**

$$K_c = \frac{[\text{NO}][\text{SO}_3]}{[\text{SO}_2][\text{NO}_2]}$$

$$85.0 = \frac{(0.89)[\text{SO}_3]}{(0.0112)(0.277)}$$

$$\mathbf{[\text{SO}_3] = 0.303 M}$$

**EXAMPLE 7.** For the following reaction



The partial pressures at equilibrium were:

$$P_{\text{PCl}_3} = 0.821 \text{ atm}, P_{\text{Cl}_2} = 0.821 \text{ atm}, P_{\text{PCl}_5} = 73.5 \text{ atm}$$

What is the value of  $K_p$ ?

$$K_p = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}$$

$$K_p = \frac{73.5}{0.821 \times 0.821}$$

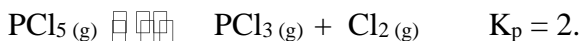
$$K_p = 109$$

**EXAMPLE 8.** Given the initial partial pressures of

$$\text{PCl}_5 = 0.0500 \text{ atm}, \text{PCl}_3 = 0.150 \text{ atm}, \text{Cl}_2 = 0.250 \text{ atm}, \text{ at}$$

50°C

for the following reaction, what must each equilibrium partial pressure be?



Make an ICE table.

	$\text{PCl}_5(\text{g})$	$\text{PCl}_3(\text{g})$	$\text{Cl}_2(\text{g})$
Initial	0.0500	0.150	0.250
Change	-x	+x	+x
After	0.0500 - x	0.150 + x	0.250 + x


Substitute into equilibrium expression and solve for x.

$$K_p = \frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

$$K_p = \frac{(0.150 + x)(0.250 + x)}{(0.0500 - x)}$$

So,  $x = 0.0272$

Determine Concentrations.

	$\text{PCl}_5 (\text{g})$ 	$\text{PCl}_3 (\text{g})$	$\text{Cl}_2 (\text{g})$
After	$0.0500 - x$	$0.150 + x$	$0.250 + x$
	<b>0.0228 M</b>	<b>0.177 M</b>	<b>0.277 M</b>

**EXAMPLE 9.** The following reaction has an equilibrium constant of 620 at a certain temperature. Calculate the equilibrium concentrations of all species if 4.5 mol of each component were added to a 3.0 L flask.



Determine molarity of solutions:

$$[4.5 \text{ mol} / 3.0 \text{ L}] = 1.5 \text{ M of all 3 solutions}$$

Make an ICE table

	$\text{H}_2 (\text{g})$	$\text{F}_2 (\text{g})$	$2 \text{HF} (\text{g})$
Initial	1.5 M	1.5 M	1.5 M
Change	-x	-x	+2x
After	$1.5 - x$	$1.5 - x$	$1.5 + 2x$

Substitute into equilibrium expression and solve for x.

$$K_c = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]}$$

$$620 = \frac{(1.5 + 2x)^2}{(1.5 - x)(1.5 - x)}$$

So,  $x = 1.33$

Determine concentrations.

After	$1.5 - x$	$1.5 - x$	$1.5 + 2x$
	$1.5 - 1.33$	$1.5 - 1.33$	$1.5 + 2(1.33)$
	<b>0.17M</b>	<b>0.17 M</b>	<b>4.13 M</b>

**EXAMPLE 10.** Ammonia undergoes hydrolysis according to the following reaction:



Calculate equilibrium  $[\text{NH}_3]$ ,  $[\text{NH}_4^+]$  and  $[\text{OH}^-]$  in a solution originally 0.200 M  $\text{NH}_3$  ( $K = 1.8 \times 10^{-5}$ )

	$\text{NH}_3(\text{aq})$	$\text{H}_2\text{O}$	$\text{NH}_4^+(\text{aq})$	$\text{OH}^-(\text{aq})$
Initial	0.200 M		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$0.200 - x$		$x$	$x$

Substitute into equilibrium expression and solve for x.

$$K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.2 - x)}$$

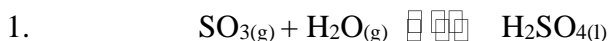
$$1.8 \times 10^{-5} = \frac{(x)^2}{(0.2 - x)}$$

So,  $x = 0.0018$

Determine concentrations.

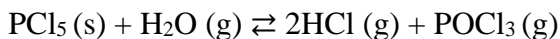
Change	$0.2 - x$	$x$	$x$
	<b>0.198 M</b>	<b>0.0018 M</b>	<b>0.0018M</b>

## EXERCISES

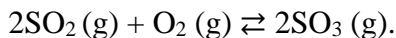


At equilibrium  $[\text{SO}_3] = 0.400\text{M}$ ,  $[\text{H}_2\text{O}] = 0.480\text{M}$ ,  $[\text{H}_2\text{SO}_4] = 0.600\text{M}$ . Calculate the value of the equilibrium constant.

2. At equilibrium at  $100^\circ\text{C}$ , a 2.0 L flask contains: 0.075 mol of  $\text{PCl}_5$ , 0.050 mol of  $\text{H}_2\text{O}$ , 0.750 mol of  $\text{HCl}$ , 0.500 mol of  $\text{POCl}_3$ . Calculate the equilibrium constant for the reaction:

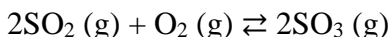


3.  $K_{\text{eq}} = 798$  at  $25^\circ\text{C}$  for the reaction:



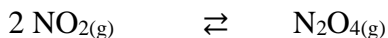
In a particular mixture at equilibrium,  $[\text{SO}_2] = 4.20 \text{ M}$  and  $[\text{SO}_3] = 11.0 \text{ M}$ . Calculate the equilibrium  $[\text{O}_2]$  in this mixture at  $25^\circ\text{C}$ .

4. Consider the following equilibrium:



0.600 moles of  $\text{SO}_2$  and 0.600 moles of  $\text{O}_2$  are present in a 4.00 L flask at equilibrium at  $100^\circ\text{C}$ . If the  $K_{\text{eq}} = 680$ , calculate the  $\text{SO}_3$  concentration at  $100^\circ\text{C}$ .

5. Consider the following equilibrium:

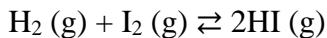


2.00 moles of  $\text{NO}_2$  and 1.60 moles of  $\text{N}_2\text{O}_4$  are present in a 4.00 L flask at equilibrium at  $20^\circ\text{C}$ . Calculate the  $K_{\text{eq}}$  at  $20^\circ\text{C}$ .

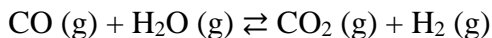
6.  $2\text{SO}_{3(\text{g})} \rightleftharpoons 2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})}$

4.00 moles of  $\text{SO}_2$  and 5.00 moles  $\text{O}_2$  are present in a 2.00 L container at  $100^\circ\text{C}$  and are at equilibrium. Calculate the equilibrium concentration of  $\text{SO}_3$  and the number of moles  $\text{SO}_3$  present if the  $K_{\text{eq}} = 1.47 \times 10^{-3}$ .

7. If at equilibrium  $[\text{H}_2] = 0.200 \text{ M}$  and  $[\text{I}_2] = 0.200 \text{ M}$  and  $K_{\text{eq}} = 55.6$  at  $250^\circ\text{C}$ , calculate the equilibrium concentration of  $\text{HI}$ .



8. 1.60 moles CO, 1.60 moles H<sub>2</sub>O, 4.00 moles CO<sub>2</sub>, 4.00 moles H<sub>2</sub> are found in a 8.00L container at 690 °C at equilibrium.



Calculate the value of the equilibrium constant.

9. 4.0 moles H<sub>2</sub> and 2.0 moles Br<sub>2</sub> are placed in a 1.0L container at 180 °C. If the [HBr] = 3.0 M at equilibrium, calculate the K<sub>eq</sub>.
10. At 2000C K<sub>eq</sub>= 11.6 for  $2\text{NO}_{(\text{g})} \rightleftharpoons \text{N}_{2(\text{g})} + \text{O}_{2(\text{g})}$ . If some NO is placed in a 2.0 L vessel and the equilibrium [N<sub>2</sub>] = 0.120 M, calculate all other equilibrium concentrations

## REFERENCES

- Atkins, P.W. (1996) *The Elements of Physical Chemistry*. 2nd edn, Oxford University Press, Oxford.
- Atkins, P.W. (1998) *Physical Chemistry*, 6th edn. Oxford University Press, Oxford.
- Barton, A.F.M. (1974) *The Dynamic Liquid State*. Longman, New York.
- Caldin, E.F. (1961) *Chemical Thermodynamics*. Clarendon Press, Oxford.
- Chang, R. (2000) *Physical Chemistry with Applications to Biological Systems*. Macmillan.
- Ebbing, D. D., & Gammon, S. D. (2007). *General Chemistry*. 9th Ed. Houghton Mifflin Company, Boston.
- Fletcher, P. (1993) *Chemical Thermodynamics for Earth Scientists*. Longman, Harlow.



- Hirschfelder, J.O. and Curtiss, C.F. (1992) *The Molecular Theory of Gases and Liquids*. Wiley, New York.
- Laidler, K.J. (1978) *Physical Chemistry with Biological Applications*. Benjamin/Cummings, London.
- Masterton, W. L., Hurley, C. N, Neth, E. J. (2012). *Chemistry: Principles and Reactions*. Brooks/Cole, Belmont.

## APPENDIX A

Standard Electrode (Reduction) Potentials in Aqueous Solution at 25°C*	
Cathode (Reduction) Half-Reaction	Standard Potential, $E^\circ$ (V)
$\text{Li}^+(aq) + e^- \rightleftharpoons \text{Li}(s)$	-3.04
$\text{Na}^+(aq) + e^- \rightleftharpoons \text{Na}(s)$	-2.71
$\text{Mg}^{2+}(aq) + 2e^- \rightleftharpoons \text{Mg}(s)$	-2.38
$\text{Al}^{3+}(aq) + 3e^- \rightleftharpoons \text{Al}(s)$	-1.66
$2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq)$	-0.83
$\text{Zn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Zn}(s)$	-0.76
$\text{Cr}^{3+}(aq) + 3e^- \rightleftharpoons \text{Cr}(s)$	-0.74
$\text{Fe}^{2+}(aq) + 2e^- \rightleftharpoons \text{Fe}(s)$	-0.41
$\text{Cd}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cd}(s)$	-0.40
$\text{Ni}^{2+}(aq) + 2e^- \rightleftharpoons \text{Ni}(s)$	-0.23
$\text{Sn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Sn}(s)$	-0.14
$\text{Pb}^{2+}(aq) + 2e^- \rightleftharpoons \text{Pb}(s)$	-0.13
$\text{Fe}^{3+}(aq) + 3e^- \rightleftharpoons \text{Fe}(s)$	-0.04
$2\text{H}^+(aq) + 2e^- \rightleftharpoons \text{H}_2(g)$	0.00
$\text{Sn}^{4+}(aq) + 2e^- \rightleftharpoons \text{Sn}^{2+}(aq)$	0.15
$\text{Cu}^{2+}(aq) + e^- \rightleftharpoons \text{Cu}^+(aq)$	0.16
$\text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s)$	0.34
$\text{IO}^-(aq) + \text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{I}^-(aq) + 2\text{OH}^-(aq)$	0.49
$\text{Cu}^+(aq) + e^- \rightleftharpoons \text{Cu}(s)$	0.52
$\text{I}_2(s) + 2e^- \rightleftharpoons 2\text{I}^-(aq)$	0.54
$\text{Fe}^{3+}(aq) + e^- \rightleftharpoons \text{Fe}^{2+}(aq)$	0.77
$\text{Hg}_2^{2+}(aq) + 2e^- \rightleftharpoons 2\text{Hg}(l)$	0.80
$\text{Ag}^+(aq) + e^- \rightleftharpoons \text{Ag}(s)$	0.80
$\text{Hg}^{2+}(aq) + 2e^- \rightleftharpoons \text{Hg}(l)$	0.85
$\text{ClO}^-(aq) + \text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{Cl}^-(aq) + 2\text{OH}^-(aq)$	0.90
$2\text{Hg}_2^{2+}(aq) + 2e^- \rightleftharpoons \text{Hg}_2^{2+}(aq)$	0.90
$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightleftharpoons \text{NO}(g) + 2\text{H}_2\text{O}(l)$	0.96
$\text{Br}_2(l) + 2e^- \rightleftharpoons 2\text{Br}^-(aq)$	1.07
$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(l)$	1.23
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \rightleftharpoons 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)$	1.33
$\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq)$	1.36
$\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \rightleftharpoons \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l)$	1.49
$\text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}(l)$	1.78
$\text{S}_2\text{O}_8^{2-}(aq) + 2e^- \rightleftharpoons 2\text{SO}_4^{2-}(aq)$	2.01
$\text{F}_2(g) + 2e^- \rightleftharpoons 2\text{F}^-(aq)$	2.87

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