

# Physical Chemistry: A practical approach

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# Preface

This book represents a collection of lectures given at Williams College on Physical Chemistry.

Now a days we continually use techniques that depend on thermodynamic principles. For example you may want to measure the molecular mass of a macromolecule by osmotic pressure measurements. All you observe is a pressure difference, but this difference can be quantitatively interpreted to yield an average molecular mass.

To use physical techniques intelligently you must understand their physical-chemical foundations.



# Chapter 1

## First Law of Thermodynamics

### 1.1 Definitions

#### 1.1.1 Introduction

Thermodynamics is based in three fundamental macroscopic laws. These laws, which are a consequence of experimental observations, deal with energy conservation, transformation and/or the possibility of a process to happen. Before we discuss the laws of thermodynamics and its implications, we are going to define a number of concepts widely used in Physical Chemistry.

#### 1.1.2 Basic Concepts

For a physical chemist, the precise object of study is called the System. It may be a gas in a piston, a liquid, a solid, a chemical reaction, or any combination of these. As a condition, the System has to be composed of a large number of individual microscopic components. One could say that a system is a particular segment of the Universe, which is the object of interest. The remaining of the Universe is defined as the Surroundings. In other words

$$\textit{System} + \textit{Surroundings} = \textit{Universe} . \quad (1.1)$$

A system is characterized by different macroscopic properties. For example the most common are: volume, pressure and temperature. One of the easiest to measure is the volume of the system. Next, the pressure is calculated by measuring the force applied to the system per unit area. For instance we use a manometer.

In the case of temperature we recall the Zeroth Law of Thermodynamics: If systems A and B are in thermal equilibrium and systems B and C are in thermal equilibrium then systems A and C are in thermal equilibrium. This law is independent of the composition of the systems and implies the existence of a property called temperature. The concept of temperature is derived from our feeling of hot and cold and whose gradient indicate the direction of heat flow in the case of thermal contact.

The Zeroth Law allow us to select from any material and property which is monitored and assure us that the same reading will be obtained for any system with the same temperature. But, the numerical value of a temperature to a selected property is arbitrary. Thus we have to adopt a scale. For example the Celsius scale, where we select  $0\text{ }^{\circ}\text{C}$  to the freezing point of water and  $100\text{ }^{\circ}\text{C}$  to the boiling point. In the case of liquid thermometers we observe a different expansion behavior and as a consequence, different thermometers show different numerical value of the temperature.

Nevertheless, any system with a measurable property that varies monotonically with temperature and that gives reproducible values of the measured property when the temperature is cycled (i.e. the property does not exhibit hysteresis) can be used as a thermometer. Therefore, our approach to temperature will be described by how temperature is measured. Thus, we have introduced the temperature concept in operational terms. although the fundamental basis of the temperature concept is subtle, the measurement of temperature is simple and straight forward.

1.2. *WORK*

3

## **1.2 Work**

## 1.3 Thermodynamic Relations

### 1.3.1 Basic Relations

{r1} Consider the temperature as a function of volume and pressure, i.e.  $T(V,P)$ . Thus, the differential in  $T$  is given by

$$dT = \left( \frac{\partial T}{\partial V} \right)_P dV + \left( \frac{\partial T}{\partial P} \right)_V dP . \quad (1.2)$$

{r2} On the other hand, one could measure the volume and the temperature. These measurements will yield the pressure as a function of volume and temperature i.e.  $P(V,T)$ . Hence, the differential change in pressure is given by:

$$dP = \left( \frac{\partial P}{\partial V} \right)_T dV + \left( \frac{\partial P}{\partial T} \right)_V dT . \quad (1.3)$$

{r3} From Eq.(1.3), we obtain an expression for  $dT$  given by:

$$dT = - \frac{\left( \frac{\partial P}{\partial V} \right)_T}{\left( \frac{\partial P}{\partial T} \right)_V} dV + \frac{1}{\left( \frac{\partial P}{\partial T} \right)_V} dP . \quad (1.4)$$

{r4} If now we compare Eqs. (1.2) and (1.4), we find

$$\left( \frac{\partial T}{\partial P} \right)_V = \frac{1}{\left( \frac{\partial P}{\partial T} \right)_V} \quad (1.5)$$

{r5}

$$\left( \frac{\partial T}{\partial V} \right)_P = - \frac{\left( \frac{\partial P}{\partial V} \right)_T}{\left( \frac{\partial P}{\partial T} \right)_V} . \quad (1.6)$$

{r6}

From Eq. (1.6) we get

$$\left( \frac{\partial T}{\partial V} \right)_P \left( \frac{\partial P}{\partial T} \right)_V \frac{1}{\left( \frac{\partial P}{\partial V} \right)_T} = -1 , \quad (1.7)$$

{r7}

but

$$\frac{1}{\left(\frac{\partial P}{\partial V}\right)_T} = \left(\frac{\partial V}{\partial P}\right)_T . \quad (1.8)$$

Therefore, Eq. (1.7) reduces to: {r8}

$$\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T = -1 . \quad (1.9)$$

Equation (1.8) can be related to the constant pressure coefficient of thermal expansion  $\alpha$ , {r9}

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P , \quad (1.10)$$

and the isothermal compressibility  $\kappa$ , {r10}

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T . \quad (1.11)$$

From Eq. (1.7) a relation is obtained if we first solve for  $(\partial P/\partial T)_V$  and use the following relation: {r11}

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_P} . \quad (1.12)$$

Therefore {r12}

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \quad (1.13)$$

and using  $\alpha$  and  $\kappa$ , we get {r13}

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa} . \quad (1.14)$$

Equation (1.14) relates a partial derivative with experiemntally measurable quantities.

### 1.3.2 $C_P - C_V$

In previous discussion, we intuitively predict that  $C_P$  should be greater than  $C_V$ . Now with the help of partial derivatives, we can obtain a general expression involving the specific heat capacities. We start with an expression of  $C_P$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad (1.15)$$

But we know that

$$H = U + PV \quad (1.16)$$

thus, Eq. (3.23) reduces to

$$C_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P . \quad (1.17)$$

From previous discussion we know

$$\left( \frac{\partial U}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \quad (1.18)$$

Since

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (1.19)$$

we can reduce Eq.(3.25) to

$$\left( \frac{\partial U}{\partial T} \right)_P = C_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \quad (1.20)$$

Sustitution of Eq. (3.31) in Eq. (3.25) yields

$$C_P - C_V = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P . \quad (1.21)$$

Also, we could prove

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P . \quad (1.22)$$

{cv9} With the help of Eq.(3.33), we get

$$C_P - C_V = T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_V. \quad (1.23)$$

Now, we use Eq.(1.10) and (1.14) to obtain a relation among measurable quantities

{cv10}

$$C_P - C_V = \frac{TV \alpha^2}{\kappa}. \quad (1.24)$$

Notice that this relation is general and no assumption were made. Therefore, any thermodynamic system will satisfy it. In particular, gases show  $\kappa > 0$ . Therefore

{cv11}

$$C_P - C_V > 0 \quad (1.25)$$

for gases.

## 1.4 Processes with Ideal Gases

### 1.4.1 Isothermal reversible expansion

{p1} For an isothermal reversible expansion, we found the the work done is given by the following expression:

$$W_{rev} = - RT \ln \left( \frac{V_f}{V_i} \right) . \quad (1.26)$$

If we consider the following conditions:

$$\begin{aligned} V_i &= 2.46L \\ P_i &= 10 \text{ atm} \\ T_i &= 300 \text{ K} \end{aligned}$$

{pp} with  $P_f = 1 \text{ atm}$  and  $V_f = 24.6 \text{ L}$  , the isothermal reversible work is equal to

$$W_{rev} = - 56.7L \text{ atm} . \quad (1.27)$$

{p2} We also know that for an ideal gas

$$\Delta U = n C_V \Delta T \quad (1.28)$$

{p3a}

$$\Delta H = n C_P \Delta T . \quad (1.29)$$

{p3b} This means that for an isothermal process

$$\Delta U = 0 \quad (1.30)$$

{p3c}

$$\Delta H = 0 , \quad (1.31)$$

{p4} but from the First Law, we know

$$\Delta U = q + W . \quad (1.32)$$

{p5} This means that for an isothermal process

$$q = - W . \quad (1.33)$$

### 1.4.2 Adiabatic reversible expansion

An adiabatic process is defined as a process where

{p6}

$$dq = 0 \quad (1.34)$$

which means no exchange of heat with the Surroundings. Let us consider the same initial conditions

$$\begin{aligned} V_i &= 2.46\text{L} \\ P_i &= 10 \text{ atm} \\ T_i &= 300 \text{ K} \end{aligned}$$

with  $P_f = 1 \text{ atm}$ . For an adiabatic proces we have

{p7}

$$dU = - P_{ext} dV, \quad (1.35)$$

where we have assume only P-V work. If we further consider a reversible process

{p8}

$$dU = - P dV, \quad (1.36)$$

where P stands for the systems pressure i.e  $P_{sys} = P = P_{ext}$ . which is a function of temperature. On the other hand, we know that

{p9}

$$dU = n C_V dT \quad (1.37)$$

Thus

{p10}

$$n C_V dT = - P dV \quad (1.38)$$

Foe an ideal gas

{p11}

$$n C_V dT = - n \frac{RT}{V} dV, \quad (1.39)$$

or

{p12}

$$\int_{T_i}^{T_f} C_V \frac{dT}{T} = - R \int_{V_i}^{V_f} \frac{dV}{V} \quad (1.40)$$

Integration of Eq.(1.40) yields

{p13}

$$C_V \ln \left( \frac{T_f}{T_i} \right) = - R \ln \left( \frac{V_f}{V_i} \right) . \quad (1.41)$$

{p14} For an ideal gas  $C_P - C_V = R$ , therefore we get

$$\ln \left( \frac{T_f}{T_i} \right) = - \left( \frac{C_P}{C_V} - 1 \right) \ln \left( \frac{V_f}{V_i} \right) . \quad (1.42)$$

{p15} If we define  $\gamma$  as

$$\gamma \equiv \frac{C_P}{C_V} \quad (1.43)$$

{p16} we can reduce Eq.(1.42) to

$$\ln \left( \frac{T_f}{T_i} \right) = \ln \left[ \left( \frac{V_f}{V_i} \right)^{(1-\gamma)} \right] \quad (1.44)$$

{p17} If now we apply in exponential function, we get from Eq. (1.44)

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^\gamma \frac{V_f}{V_i} \quad (1.45)$$

{p18} Finally using the ideal gas equation in Eq. (1.45) we get

$$P_f V_f^\gamma = P_i V_i^\gamma . \quad (1.46)$$

{p19} For an ideal gas  $C_P = 5 R/2$  and  $C_V = 3 R/2$ , therefore  $\gamma = 5/3$ . Using this value for the previous initial condition we get

$$P_i V_i^{\frac{5}{3}} = 10 \text{ atm} (2.46 \text{ L})^{\frac{5}{3}} = 1 \text{ atm} V_f^{\frac{5}{3}} , \quad (1.47)$$

{p20} or

$$V_f = (10)^{\frac{3}{5}} 2.46 \text{ L} = 9.79 \text{ L} . \quad (1.48)$$

{21} Therefore the final temperature is

$$T_f = 119 \text{ K} . \quad (1.49)$$

{22} Thus for an adiabatic process the change in internal energy is given by:

$$\Delta U = W = C_V = C_V (T_f - T_i) = - 22.2 \text{ L atm} . \quad (1.50)$$

### 1.4.3 Adiabatic irreversible expansion

Using the same initial condition as in the previous subsections, a sudden change from  $P_{ext} = 10 \text{ atm}$  to  $P_{ext} = 1 \text{ atm}$  will correspond to an irreversible adiabatic process. In this case the external pressure is held constant at the system's final temperature. Since the process is adiabatic the following relation is satisfied: {23}

$$dU = dW = - P_{ext} dV \quad (1.51)$$

or, since  $P_{ext}$  is constant, {24}

$$\Delta U = - P_{ext} \Delta V. \quad (1.52)$$

On the other hand, {25}

$$\Delta U = n C_V \Delta T. \quad (1.53)$$

Thus {26}

$$n C_V (T_f - T_i) = - P_{ext} (V_f - V_i). \quad (1.54)$$

Using the ideal gas equation in the left hand side and solving for  $T_f$ , we get {27}

$$T_f = \frac{C_V + R \left( \frac{P_{ext}}{P_i} \right)}{C_V + R} T_i. \quad (1.55)$$

Using the previous values, we find the final temperature and volume

$$\begin{aligned} T_f &= 192 \text{ K} \\ V_i &= 15.8 \text{ L} . \end{aligned}$$

Using these values, we get {28}

$$\Delta U = C_V (T_f - T_i) = w_{irrev} = - 13.3 \text{ L atm}. \quad (1.56)$$

We notice that for an adiabatic expansion the work satisfy the following relation {29}

$$- W_{rev} > - W_{irrev}. \quad (1.57)$$

### 1.4.4 Joule's experiment

In 1845 Joule published the results of an experiment that was designed to determine whether

$$\left(\frac{\partial U}{\partial V}\right)_T \quad (1.58) \quad \{1\}$$

is zero for real gases. In Joule's experiment, gas is allowed to expand in to a vacuumed container. The gas container was submerged in a water bath, and the change in temperature was monitored. Joule found no detectable change in temperature i.e.

{j2}

$$\delta T \approx 0, \quad (1.59)$$

which meant that no exchange of heat between the gas and the surroundings took place since

{j3}

$$q = C_V \Delta T \approx 0. \quad (1.60)$$

Therefore the gas expanded adiabatically. Also the work done

{j4}

$$W = - \int P_{ext} dV = 0, \quad (1.61)$$

since the external pressure opposing the expansion is zero,  $P_{ext} = 0$ . From this two observations, the change in internal energy is zero

{j5}

$$\Delta U = 0. \quad (1.62)$$

Using the differential expression of Eq. 1.62,  $dU = 0$ , we get

{j6}

$$du = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = 0. \quad (1.63)$$

Since Joule concluded that the experiment occurred at constant temperature,  $dT = 0$ , Eq. 1.63 can be reduced to

{j7}

$$0 = \left(\frac{\partial U}{\partial V}\right)_T dV. \quad (1.64)$$

But, the change in volume is not zero, therefore we conclude

{j8}

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad (1.65)$$

In general the following relation holds:

$$\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U \left(\frac{\partial T}{\partial U}\right)_V = -1. \quad (1.66)$$

Moreover we can rearrange Eq. 1.66 into

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V} = \frac{\left(\frac{\partial U}{\partial V}\right)_T}{C_V}. \quad (1.67)$$

Using Joule's conclusion, expressed by Eq. 1.65, in Eq. 1.67 we obtain the following result:

$$\left(\frac{\partial T}{\partial V}\right)_U = 0. \quad (1.68)$$

Equation (1.68) states the independence of the temperature on the volume when the internal energy is held constant. In terms of intermolecular forces, Eq. (1.68) implies the lack of any distance dependent potential energy store in the intermolecular interactions among particles. In the case of an Ideal gas the lack of any long range interaction implies that at constant internal energy the temperature of the system will be the same independent of its size. A condition that does not hold for real gases, i.e. the internal energy may not be the same for two systems with similar composition, temperature but different volume. Although the temperature is a macroscopic measure of the kinetic energy, a potential energy term is distance dependent and therefore volume dependent.

Due to large differences in specific heat capacity between air and water, Joule's apparatus was unable to detect small changes in temperature. Modern reproduction of Joule's experiment have detected temperature changes,

$$\Delta T_{\text{Joule's experiment}} < 2 \times 10^{-5} \text{ K}. \quad (1.69)$$

Therefore the relations in Eqs. (1.65) and 1.68 do not hold in general but only for ideal gases. In other words for real gases

$$\left(\frac{\partial T}{\partial V}\right)_U \equiv 0 . \quad (1.70)$$

The actual consequences of Joule's experiment applies only to Ideal gases. In the next subsection we will discuss some of the result obtained for ideal gases.

### 1.4.5 Joule's experiment and Ideal gases

{ig1} One of the most important implications of Joule's experiment is the relation of between the specific heat capacities. From previous results Eq. (3.32) we have

$$C_P - C_V = \left[ \left(\frac{\partial U}{\partial V}\right)_T + P \right] \left(\frac{\partial V}{\partial T}\right)_P \quad (1.71)$$

{ig2} Using one of Joule's results, Eq. (1.69), we can simplify Eq. 1.71 into

$$C_P - C_V = P \left(\frac{\partial V}{\partial T}\right)_P . \quad (1.72)$$

{ig3} Thus Eq. 1.72 yields the following result for Ideal gases:

$$C_P - C_V = n R , \quad (1.73)$$

where n is the number of moles of ideal gas.

{ig4} Another consequence of Eq. (1.69) can be derived from the differential expression if the internal energy  $U(T, V)$ , i.e.,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT . \quad (1.74)$$

{ig5} Therefore the change in internal energy for an ideal gas is given by:

$$\Delta U = \int_{U_i}^{U_f} dU = \int_{T_i}^{T_f} C_V dT = C_V \Delta T , \quad (1.75)$$

where we have assumed that  $C_V$  is a constant independent of the temperature. Equation (1.75) states that as long as the ideal gas maintains its temperature, its internal energy does not change.

Now let us consider enthalpy and study the consequence of Joule's experiment. For example we want to calculate

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial(U + PV)}{\partial P}\right)_T. \quad (1.76)$$

Since the partial derivative is taken at constant  $T$ , for an ideal gas  $PV = nRT$  is a constant. Therefore

$$\left(\frac{\partial PV}{\partial P}\right)_T = 0 \quad (1.77)$$

Using this result we can simplify Eq. (1.76)

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T = - \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T. \quad (1.78)$$

From Eq. (1.65) we conclude

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \quad (1.79)$$

for an ideal gas. The consequence of this result can be obtained by expressing  $H$  as a function of  $T$  and  $P$ . In this case the total differential of  $H$  is given by

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = \left(\frac{\partial H}{\partial T}\right)_P dT, \quad (1.80)$$

where we have used Eq. (1.79). From this result we can calculate the change of enthalpy for an ideal gas

$$\Delta H = \int dH = \int C_P dT = C_P \Delta T \quad (1.81)$$

## 1.5 Real gases

The Van der Waals equation is given by {rg1}

$$P = \frac{R T}{V_m - b} - \frac{a}{V_m^2}, \quad (1.82)$$

where  $V_m$  stands for the molar volume i.e.,  $V_m = \frac{V}{n}$ . Equation (1.82) can be rewritten as {rg2}

$$P = \frac{R T}{V_m} \left\{ \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{R T V_m} \right\}. \quad (1.83)$$

Assuming  $\frac{b}{V_m} \ll 1$  and using the expansion {rg3}

$$\frac{1}{1 - x} = \sum_{n=0}^{\infty} x^n, \quad (1.84)$$

we find that Eq. (1.83) reduces to the following Virial expansion: {rg4}

$$P = \frac{R T}{V_m} \left\{ 1 + \left( b - \frac{a}{R T} \right) \left( \frac{1}{V_m} \right) + b^2 \left( \frac{1}{V_m} \right)^2 + \dots \right\} \quad (1.85)$$

Notice that up to first order in  $1/V_m$ , the gas will behave ideally at {rg5}

$$T_B = \frac{a}{b} \frac{1}{R}, \quad (1.86)$$

where  $T_B$  is defined as the Boyle temperature.

Finally we can express Eq. (1.85) using the Boyle temperature as {rg6}

$$P = \frac{R T}{V_m} \left\{ 1 + b \left( 1 - \frac{T_B}{T} \right) \left( \frac{1}{V_m} \right) + b^2 \left( \frac{1}{V_m} \right)^2 + \dots \right\} \quad (1.87)$$

## 1.6 Thermochemistry

Chemical reactions are associated to a transfer of heat between a System defined as the reactants and products and its Surroundings. The heat evolved or absorbed at constant pressure is called heat of reaction and equal to the change of enthalpy due to the chemical reaction, i. e. {11}

$$\Delta H_{rxn} = q_p . \quad (1.88)$$

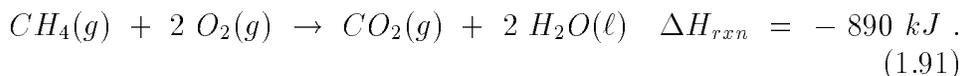
In the case of chemical reactions, we classify them in endothermic if the system gains heat i.e. {12}

$$q_P > 0 \rightarrow \text{endothermic reaction} , \quad (1.89)$$

or exothermic if the system losses heat, i. e. {13}

$$q_P < 0 \rightarrow \text{exothermic reaction} . \quad (1.90)$$

For example during the combustion of one mole of methane at 1 atm pressure and 25 °C the system will lose 890 kJ, i.e. {14}



The heat of a reaction is measured with a calorimeter. The Dewar Flask is an example of calorimeter at constant pressure, where we can study ammonium nitrate at 1 atm pressure and 25 °C {15}



The bomb calorimeter measures the heat of a process at constant volume. Thus,  $\Delta U_{rxn}$  is measured in a bomb calorimeter, where we are able to burn organic compounds. In this case, we still want to calculate the enthalpy change of the reaction. In order to do so, we use the general expression of enthalpy {16}

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta(PV) . \quad (1.93)$$

For liquids and solids  $\Delta(PV) \approx 0$ , thus {17}

$$\Delta H_{rx} \approx \Delta U_{rxn} . \quad (1.94)$$

{t8} For gases we have

$$\Delta(PV) = \Delta(n R T) = n_f R T_f - n_i R T_i , \quad (1.95)$$

{t9} where  $n_f$  and  $n_i$  are the number of moles of the gaseous species.  
But we also know

$$T_f = T_i + \Delta T . \quad (1.96)$$

{t10} Consequently we can rewrite Eq. (1.95)

$$\Delta(PV) = \Delta n_{gas} R T_f + n_i R \Delta T , \quad (1.97)$$

{t11} or

$$\Delta(PV) = \Delta n_{gas} R T_i + n_f R \Delta T . \quad (1.98)$$

{t12} Since

$$n R \Delta T \ll \Delta n R T \quad (1.99)$$

{t13} or

$$1 \text{ kJ} \approx n R \Delta T , \quad (1.100)$$

{t14} we can approximate the change of enthalpy by

$$\Delta H_{rxn} = \Delta U_{rxn} + \Delta n_{gas} R T_f . \quad (1.101)$$

## 1.7 Problems

i) Using Eq. (1.87) calculate the work done on a reversible isothermal expansion.

ii) Consider only the first two terms in the Virial expansion and the following three case: a)  $T > T_B$ , b)  $T = T_B$ , c)  $T < T_B$ . As in i), calculate the the amount of work.



# Chapter 2

## Second Law of Thermodynamics

In this chapter we develop the concept of entropy. First, we analyze Carnot cycle. This analysis will suggest a new state variable known as entropy. The general definition of entropy takes us to postulate the Second Law of thermodynamics. We follow with the operational definition of the absolute entropy, which enable us to postulate the Third Law. Finally, we discuss the application of the new state variable to different systems.

### 2.1 Carnot cycle

The Carnot cycle is defined as a sequence reversible expansion and compression. In particular, it is defined by an isothermal expansion at  $T_{hot}$  followed by an adiabatic expansion ending at  $T_{cold}$ . Next an isothermal compression at  $T_{cold}$  is performed and followed by an adiabatic compression that will take the system back to  $T_{hot}$ . Figure 2.1 depicts a Carnot cycle for a minimum volume of 0.5 L and a maximum volume of 5.0 L. The temperatures for this cycle are  $T_{hot} = 750K$  and  $T_{cold} = 370$

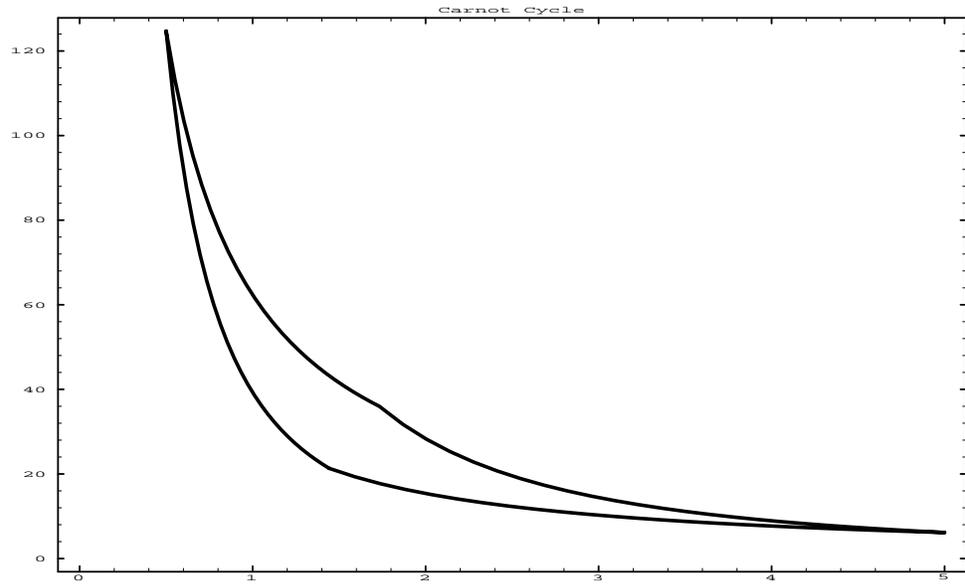


Figure 2.1: Carnot cycle for a volume range of 0.5L to 5.0L.

## 2.2 Entropy and the Second Law

## 2.3 Operational definition of Entropy

## 2.4 Physical interpretation of Entropy

## 2.5 Entropy relations

In this section we consider the entropy as a function of temperature and volume,  $S(T,V)$ . Also we consider a reversible path which allows us to write a differential relation for the entropy

$$T dS = dq^{rev} . \quad (2.1)$$

Using the differential form of the first law,

$$dU = dq^{rev} - P dV , \quad (2.2)$$

where we have assumed only PV work, we get for Eq. (2.1) the following expression:

$$T dS = dq^{rev} = dU + P dV . \quad (2.3)$$

Furthermore, using the general expression for the differential of the internal energy  $U(T,V)$ , we get

$$T dS = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV + P dV \quad (2.4)$$

or

$$T dS = C_V dT + \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] dV . \quad (2.5)$$

Now solving for the entropy differential yields

$$dS = C_V \frac{dT}{T} + \left[ 1 + \frac{1}{P} \left( \frac{\partial U}{\partial V} \right)_T \right] \frac{P}{T} dV . \quad (2.6)$$

On the other hand we also know that the differential for the entropy as a function of  $T$  and  $V$  is given by:

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV . \quad (2.7)$$

Comparing the last two equations, we get

$$\left( \frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T} \quad (2.8)$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \left[1 + \frac{1}{P} \left(\frac{\partial U}{\partial V}\right)_T\right] \frac{P}{T} . \quad \text{(2.9)} \quad \text{{er7}}$$

For an ideal gas we have

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{(2.10)} \quad \text{{er8}}$$

{{er9}}

and

$$P V = R T , \quad \text{(2.11)}$$

{{er10}}

where we have set  $n = 1 \text{ mole}$ . Consequently, Eq. (2.7) reduces to

$$dS = C_V \frac{dT}{T} + R \frac{dV}{V} . \quad \text{(2.12)}$$

{{er11}}

Finally, integrating Eq. (2.12), we get the change of entropy for an ideal gas when the entropy depends on T and V,

$$\Delta S = C_V \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i} . \quad \text{(2.13)}$$

## 2.6 Second Law and Gibbs free energy

In this section we will consider the transition between super cooled water at  $-10\text{ }^\circ\text{C}$  to ice at  $-10\text{ }^\circ\text{C}$ . Since the transition is irreversible at  $-10\text{ }^\circ\text{C}$ , we have to follow a reversible path if we want to calculate the change in entropy, i.e.,  $\Delta S_{\ell \rightarrow s}^\circ [-10\text{ }^\circ\text{C}]$ . First we can reversibly warm the liquid sample at constant pressure up to  $0\text{ }^\circ\text{C}$ . The change in entropy for this process is given by

{sc1}

$$\begin{aligned}
 \Delta S_1^\circ &= \int_{T_c}^{T_{fus}} \frac{dq^{rev}}{T} \\
 &= \int_{263\text{ K}}^{273\text{ K}} \frac{C_P^\ell dT}{T} \\
 &= C_P^\ell \ln \frac{T_{fus}}{T_c} \\
 &= C_P^\ell \ln \frac{273}{263},
 \end{aligned} \tag{2.14}$$

where we have assumed that  $C_P^\ell$  is independent of temperature. Now we allow the liquid sample to change to ice by removing heat. Since the process occurred at constant temperature, the change in entropy for this step is equal to

{sc2}

$$\begin{aligned}
 \Delta S_2^\circ &= \int \frac{dq^{rev}}{T_{fus}} \\
 &= \frac{q^{rev}}{T_{fus}} \\
 &= \frac{\Delta H_{\ell \rightarrow s}^\circ}{T_{fus}} \\
 &= \frac{-\Delta H_{fus}^\circ}{T_{fus}} \\
 &= \frac{-6.01\text{ kJ mol}^{-1}}{273\text{ K}} \\
 &= -22.01\text{ J K}^{-1}\text{ mol}^{-1}.
 \end{aligned} \tag{2.16}$$

Finally, we can cool isobarically and reversibly the ice sample to  $-10\text{ }^\circ\text{C}$ ; the change of entropy for this process is given by:

{sc3}

$$\begin{aligned}
\Delta S_3^\circ &= \int_{T_{fus}}^{T_c} \frac{dq^{rev}}{T} \\
&= \int \frac{C_P^s dT}{T} \\
&= C_P^s \ln \frac{T_c}{T_f} \\
&= C_P^s \ln \frac{263}{273},
\end{aligned} \tag{2.17}$$

{sc4} where we have assumed that  $C_P^s$  is independent of temperature. Therefore the total change of entropy is given by

$$\Delta S_{\ell \rightarrow s}^\circ [-10^\circ C] = \Delta S_1^\circ + \Delta S_2^\circ + \Delta S_3^\circ. \tag{2.18}$$

{sc4b} Now using Eqs. (2.14)-(2.17) in Eq. (2.18), we get that the total change in entropy for the freezing of water at 263 K is given by the following expression:

$$\begin{aligned}
\Delta S_{\ell \rightarrow s}^\circ [-10^\circ C] &= [C_P^\ell - C_P^s] \ln \frac{273}{263} + \frac{-\Delta H_{fus}^\circ}{273 K} \\
&= 37.8 JK^{-1}mol^{-1} \ln \frac{273}{263} - 22.01 JK^{-1}mol^{-1} \\
&= -20.6 JK^{-1}mol^{-1},
\end{aligned} \tag{2.19}$$

where we have used the following values:

$$\begin{aligned}
C_P^\ell &= 75.5 JK^{-1}mol^{-1} \\
C_P^s &= 37.75 JK^{-1}mol^{-1}.
\end{aligned}$$

{sc5} Notice that the change of entropy for the irreversible crystallization of water at 263 K is less than the change of entropy for the reversible crystallization at 273 K,

$$\Delta S_{\ell \rightarrow s}^\circ [0^\circ C] = \frac{\Delta H_{\ell \rightarrow s}^\circ [0^\circ C]}{T_{fus}} = -22.0 JK^{-1}mol^{-1}. \tag{2.20}$$

If the entropy is going to be used as the criterion of spontaneity, we have to consider not only the change of entropy of the system but also the change of entropy of the surroundings. Thus we are required to

measure changes of the surroundings. If the surroundings are large enough, changes in the system do not perturb the surroundings state. In other words the surroundings are always at equilibrium. In particular the temperature of the surroundings does not change. Therefore the change of entropy for the surroundings is given by {sc6}

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q_{sys}}{T} \quad (2.21)$$

where we have used the relation between the heat exchanges  $q_{surr} = -q_{sys}$  and temperature relation  $T_{surr} = T_{sys} \equiv T$ . For the irreversible freezing of water at 263 K the proces occurs at constant pressure therefore the amount of heat exchanged between the system and the surroundings is independent of the path. For the reversible path discussed earlier the amount of heat exchange is given by the following expression: {sc7}

$$q_P^{sys} = \Delta H_{\ell \rightarrow s}^{\circ} [-10^{\circ}C] \quad (2.22)$$

$$= [C_P^{\ell} - C_P^S] \Delta T + \Delta H_{\ell \rightarrow s}^{\circ} [0^{\circ}C] \quad (2.23)$$

$$= 37.7 J K^{-1} mol^{-1} 10 K - 6020 J mol^{-1} \\ = -5644 J mol^{-1} . \quad (2.24)$$

Once we know the amount of heat exchange by the system, the surroundings entropy change is given by: {sc8}

$$\Delta S_{\ell \rightarrow s}^{\circ} [-10^{\circ}C] = \frac{-q_P^{sys}}{T_c} \quad (2.25)$$

$$= \frac{-\Delta H_{\ell \rightarrow s}^{\circ} [-10^{\circ}C]}{T} \quad (2.26)$$

$$= \frac{5644 J mol^{-1}}{263 K} \\ = 21.45 J K^{-1} mol^{-1} .$$

Finally the total change of entropy of the universe when supercooled water freezes is given by {sc9}

$$\Delta S_{\ell \rightarrow s}^{\circ} [-10^{\circ}C] + \Delta S_{\ell \rightarrow s}^{\circ} [-10^{\circ}C] = 0.81 JK^{-1} mol^{-1} > 0 . \quad (2.27)$$

Notice that Eq. (2.27) can be rewritten using Eq. (2.25) to yield an expression entirely in term of system's quantities, {sc10}

$$\Delta S_{\ell \rightarrow s}^{\circ \text{sys}} [-10 \text{ }^\circ\text{C}] + \Delta S_{\ell \rightarrow s}^{\circ \text{surr}} [-10 \text{ }^\circ\text{C}] = \quad (2.28)$$

$$\Delta S_{\ell \rightarrow s}^{\circ \text{sys}} [-10 \text{ }^\circ\text{C}] - \frac{\Delta H_{\ell \rightarrow s}^{\circ \text{sys}} [-10 \text{ }^\circ\text{C}]}{T} > 0 . \quad (2.29)$$

{sc11} Or rewriting Eq. (2.28)

$$\Delta H_{\ell \rightarrow s}^{\circ \text{sys}} [-10 \text{ }^\circ\text{C}] - T \Delta S_{\ell \rightarrow s}^{\circ \text{sys}} [-10 \text{ }^\circ\text{C}] < 0 . \quad (2.30)$$

{sc12} Let reconsider the freezing of water at 273 K, at this temperature the process occurs reversibly thus

$$\Delta S_{\ell \rightarrow s}^{\circ \text{sys}} [0 \text{ }^\circ\text{C}] + \Delta S_{\ell \rightarrow s}^{\circ \text{surr}} [0 \text{ }^\circ\text{C}] = 0 , \quad (2.31)$$

{sc13} or

$$\Delta H_{\ell \rightarrow s}^{\circ \text{sys}} [0 \text{ }^\circ\text{C}] - T \Delta S_{\ell \rightarrow s}^{\circ \text{sys}} [0 \text{ }^\circ\text{C}] = 0 . \quad (2.32)$$

{sc14} After this analysis we can define a new state function. This state function is the Gibbs free energy,  $G$ , and is define as

$$G = H - T S. \quad (2.33)$$

{sc15} At constant pressure and temperature the change in Gibbs free energy is given by

$$\Delta G = \Delta H - T \Delta S . \quad (2.34)$$

{sc16b} Combining this definition with the second law of thermodynamics we get that a proceses will occur spontaneously only if  $\Delta G < 0$ . In other words

$$\Delta G^{\text{sys}} \rightarrow \begin{cases} < 0 & \text{process occurs spontaneously} \\ = 0 & \text{Equilibrium process} \\ > 0 & \text{process will never occur spontaneously} . \end{cases} \quad (2.35)$$

In this section we have define a new state variable that will serve as a criteria of spontaneity. Namely, Gibbs energy allows us to restate the second law in terms only of the properties of the system.

# Chapter 3

## Gibbs free energy

### 3.1 General properties

In the previous section we define the Gibbs free energy as {g1}

$$G = H - T S . \quad (3.1)$$

Thus {g2}

$$dG = dH - T dS - S dT . \quad (3.2)$$

On the other hand we know that {g3}

$$dH = dU + P dV + V dP , \quad (3.3)$$

and {g4}

$$dU = dq - P dV + dW_{nonPV} , \quad (3.4)$$

where we have considered PV work and non PV work. Using these two equations in Eq. 3.2 yields {g5}

$$dG = dq - T dS + V dP - S dT + dW_{nonPV} . \quad (3.5)$$

Equation (3.5) represent the most general expression for the differential change of the Gibbs energy.

For a process occuring at constant P and T, Eq. (3.5) reduces to {g6}

$$dG = dq - T dS + dW_{nonPV} . \quad (3.6)$$

Since

$$T dS \geq dq , \quad (3.7) \quad \text{\{g7\}}$$

$$dG \leq dW_{nonPV} . \quad (3.8) \quad \text{\{g8\}}$$

In the case of constant temperature and pressure  $dG$  is less than  $dW_{nonPV}$  for a spontaneous irreversible process or equal to  $dW_{nonPV}$  for a reversible process at equilibrium with its surroundings.

\{g9\} For a reversible process  $dq = T dS$ . Thus Eq. (3.5) reduces to

$$dG = V dP - S dT + dW_{nonPV} . \quad (3.9)$$

\{g10\} In the case of constant temperature and pressure Eq. 3.9 reduces to

$$dG = dW_{nonPV} . \quad (3.10)$$

This equation means that  $dG$  is the maximum work that can be obtained from a spontaneous process or the minimum work that is required to make a non spontaneous process to occur.

\{g11\} Finally in the absence of non-PV work Eq. (3.8) reduces to

$$dG \leq 0 , \quad (3.11)$$

at constant pressure and temperature, which is the criterium for spontaneity derived in the previous section.

### 3.1.1 General relations

\{g11b\} In this section we are going to consider process with only PV work. Therefore from Eq. (3.9) we get that the differential change of Gibbs free energy for a reversible process is equal to

$$dG = V dP - S dT . \quad (3.12)$$

\{g12\} If we use the general definition for the differential change of  $G(P,T)$  i.e.,

$$dG = \left( \frac{\partial G}{\partial P} \right)_T dP + \left( \frac{\partial G}{\partial T} \right)_P dT, \quad (3.13)$$

\{g13\} we obtain the following relations:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (3.14)$$

{g14}

$$\left(\frac{\partial G}{\partial P}\right)_T = V. \quad (3.15)$$

As a consequence of  $G$  being a state function and exact differential e.g,

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P, \quad (3.16)$$

{g15}

we obtain the following relation:

{g16}

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T. \quad (3.17)$$

This relation connects the entropy with the equation of state. In other words, if we have an equation of state we can calculate the left hand side of Eq. (3.17) and gain information on the entropy dependence on pressure at constant temperature.

### 3.1.2 Process at constant temperature

For a reversible process at constant temperature Eq. 3.6 reduces to

{g17}

$$dG = V dP. \quad (3.18)$$

Now we can integrate Eq. 3.18

{g18}

$$\Delta G = \int_{P_i}^{P_f} V dP. \quad (3.19)$$

#### Ideal gases

For an ideal gas, and since  $T$  is a constant, the change in Gibbs energy is

$$\Delta G = R T \ln\left(\frac{P_f}{P_i}\right). \quad (3.20)$$

{g19}

{g20}

$$G(P_f) = G(P_i) + R T \ln\left(\frac{P_f}{P_i}\right). \quad (3.21)$$

{g21} Now we can choose a reference pressure. For example 1 atm or 1 bar pressure. In this case we get

$$G(P_f) = G^\circ + R T \ln\left(\frac{P_f}{atm}\right), \quad (3.22)$$

where  $G^\circ$  is the Gibbs energy of one mole of ideal gas at standard state. Therefore  $G(P_f)$  is the Gibbs free energy of one mole of ideal gas at pressure  $P_f$ .

### Carbon as an example

In the case of carbon we know that its planar structure is the stable form at standard conditions and  $25^\circ C$ . This form of carbon is known as graphite. Another possibility is the tetrahedral structure of carbon. This form is known as diamond. Therefore graphite and diamond are two possible phases of solid carbon. The transition from graphite to diamond,



{c1} is not a spontaneous process. For this transition the change of enthalpy is positive,

$$\Delta H^\circ = 1895 \text{ J mol}^{-1}. \quad (3.24)$$

The entropies for graphite and diamond are

$$\begin{aligned} S_{diamond}^\circ &= 2.377 \text{ J K}^{-1} \text{ mol}^{-1} \\ S_{graphite}^\circ &= 5.740 \text{ J K}^{-1} \text{ mol}^{-1}. \end{aligned}$$

{c2} Therefore the change in Gibbs energy for the transition of one mole of graphite into one mole of diamond is equal to

$$\begin{aligned} \Delta G^\circ &= 1 \text{ mole } \Delta H^\circ - T 1 \text{ mole } \Delta S^\circ \\ &= 1895 \text{ J} - T (-3.363 \text{ J K}^{-1}) \\ &= 2898 \text{ J}. \end{aligned}$$

{c3} where we have considered  $T = 298.15 \text{ K}$ . Since  $\Delta G^\circ > 0$  the process can not occur spontaneously at the standard condition of 1 atm. But it

may be spontaneous under different conditions. For example we could fix the temperature and change the pressure. To find the pressure dependence of the Gibbs energy we can use Eq. (3.18). In particular we consider the differential change of the change of Gibbs energy {c4}

$$d\Delta G \equiv dG_{diamond} - dG_{graphite} \quad (3.25)$$

$$= V_{diamond} dP - V_{graphite} dP \quad (3.26)$$

$$= \Delta V dP \quad (3.27)$$

where the molar volumes in this case are

$$\begin{aligned} V_{diamond} &= 3.42 \text{ cc mol}^{-1} \\ V_{graphite} &= 5.33 \text{ cc mol}^{-1} . \end{aligned}$$

Assuming that the molar volumes do not vary significantly with pressure, Eq. (3.25) can be integrated {c5}

$$\int_{\Delta G^\circ}^{\Delta G(P)} d\Delta G = \Delta G(P) - \Delta G^\circ \quad (3.28)$$

$$= \Delta V \int_{1 \text{ atm}}^P dP \quad (3.29)$$

$$= \Delta V (P - 1 \text{ atm}) \quad (3.30)$$

We want  $P$  such that  $\Delta G(P) = 0$ , which means {c6}

$$\begin{aligned} P &= 1 \text{ atm} - \frac{\Delta G^\circ}{\Delta V} \quad (3.31) \\ &= 1 \text{ atm} + \frac{2866.1 \text{ J} \frac{9.869 \text{ cm}^3 \text{ atm}}{\text{J}}}{1.91 \text{ x cm}^3} \\ &= 14,810 \text{ atm} . \end{aligned}$$

Thus at 14,810 atm and 298 K, graphite will spontaneously transform into diamond.

### 3.1.3 Process at constant pressure

For a reversible process at constant pressure Eq. (3.6) reduces to {c7}

$$dG = -S dT = \left( \frac{\partial G}{\partial T} \right)_P . \quad (3.32)$$

Now we can the definition of Gibbs energy,  $G = H - TS$ , in Eq. 3.32 {c8}

$$\left(\frac{\partial G}{\partial T}\right)_P = -S = \frac{G - H}{T}. \quad (3.33)$$

{c9} Now we divide by  $T$  both sides of Eq. (3.33),

$$\frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = -\frac{H}{T^2}. \quad (3.34)$$

{c10} Equation (3.34) can be reduce to the so-called Gibbs-Helmholtz equation

$$\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_P = -\frac{H}{T^2}. \quad (3.35)$$

{c11} Using the chain rule we can reexpress Eq. (3.35) as

$$\left(\frac{\partial \frac{1}{T}}{\partial T} \frac{\partial G}{\partial \frac{1}{T}}\right)_P = -\frac{H}{T^2}. \quad (3.36)$$

{c12} or

$$-\frac{1}{T^2} \left(\frac{\partial G}{\partial \frac{1}{T}}\right)_P = -\frac{H}{T^2}. \quad (3.37)$$

{c13} Finally, we get

$$\left(\frac{\partial G}{\partial \frac{1}{T}}\right)_P = H. \quad (3.38)$$

{c14} Therefore in the case of a change in Gibbs energy, we have the following differential relation at constant pressure:

$$d\left(\frac{\Delta G}{T}\right) = \Delta H d\left(\frac{1}{T}\right), \quad (3.39)$$

{c15} In particularl we consider  $P = 1 \text{ atm}$  and a variable temperature. Thus the change in Gibbs energy at standard state at two different temperatures is given by

$$\int_{\frac{\Delta G^\circ}{T_1}}^{\frac{\Delta G^\circ}{T_2}} d\left(\frac{\Delta G}{T}\right) = \int_{\frac{1}{T_1}}^{\frac{1}{T_2}} \Delta H^\circ d\left(\frac{1}{T}\right). \quad (3.40)$$

{c16} In general enthalpy is a function of temperature,

$$\Delta H^\circ(T) = \Delta H^\circ(T_1) + \int_{T_1}^T \Delta C_P dT' , \quad (3.41)$$

where  $\Delta C_P$  is the difference in specific heats of the system's final and initial states. Moreover, in general, this quantity depends on the temperature as {c17}

$$\Delta C_P = A + B T - \frac{C}{T^2} . \quad (3.42)$$

For simplicity we will assume that  $\Delta C_P$  is a constant independent of the temperature. Thus Eq. (3.41) reduces to {c18}

$$\begin{aligned} \Delta H^\circ(T) &= \Delta H^\circ(T_1) + \Delta C_P (T - T_1) \\ &= \Delta H^\circ(T_1) - T_1 \Delta C_P + T \Delta C_P . \end{aligned} \quad (3.43)$$

Now we can use this expression in the integral of Eq. (3.40). After integration we get {c19}

$$\begin{aligned} \frac{\Delta G^\circ(T)}{T} - \frac{\Delta G^\circ(T_1)}{T_1} &= \{\Delta H^\circ(T_1) - T_1 \Delta C_P\} \left( \frac{1}{T} - \frac{1}{T_1} \right) \\ &+ \Delta C_P \int_{\frac{1}{T_1}}^{\frac{1}{T}} \frac{1}{\frac{1}{T}} d\left(\frac{1}{T}\right) . \end{aligned} \quad (3.44)$$

After performing the second integral we get {c20}

$$\begin{aligned} \frac{\Delta G^\circ(T)}{T} - \frac{\Delta G^\circ(T_1)}{T_1} &= \{\Delta H^\circ(T_1) - T_1 \Delta C_P\} \left( \frac{1}{T} - \frac{1}{T_1} \right) \\ &+ \Delta C_P \ln \left( \frac{T_1}{T} \right) . \end{aligned} \quad (3.45)$$

Equation (3.45) can be rearranged as {c21}

$$\begin{aligned} \Delta G^\circ(T) &= \Delta H^\circ(T_1) + \frac{T}{T_1} [\Delta G^\circ(T_1) - T_1 \Delta H^\circ(T_1)] \\ &+ \Delta C_P \Delta T - T \Delta C_P \ln \left( \frac{T}{T_1} \right) , \end{aligned} \quad (3.46)$$

where  $\Delta T = T - T_1$ . Equation (3.46) can be used if we know  $\Delta G^\circ(T_1)$ ,  $\Delta H^\circ(T_1)$  and  $\Delta C_P(T)$ . But sometimes we know  $\Delta S^\circ(T_1)$  instead of

the change of Gibbs energy. In this case we can reexpress Eq. (3.46) as

$$\Delta G^\circ(T) = \Delta H^\circ(T) - T \Delta S^\circ(T), \quad (3.47) \quad \{c22\}$$

{c23}

where we have used the following relations:

$$\Delta H^\circ(T) = \Delta H^\circ(T_1) + \Delta C_P \Delta T \quad (3.48)$$

$$\Delta S^\circ(T) = \Delta S^\circ(T_1) + \Delta C_P \ln\left(\frac{T}{T_1}\right). \quad (3.49)$$

{c24}

Notice that Eq. (3.47) is a general relation, and, depending on the temperature behavior of enthalpy and specific heats, Eqs. (3.48)- (3.49) are going to have different temperature dependences since

$$\Delta H^\circ(T) = \Delta H^\circ(T_1) + \int_{T_1}^T \Delta C_P(T') dT' \quad (3.50)$$

$$\Delta S^\circ(T) = \Delta S^\circ(T_1) + \int_{T_1}^T \Delta C_P(T') \frac{dT'}{T'}. \quad (3.51)$$

Therefore Eq. (3.47) gives the change of Gibbs energy at temperature  $T$ , with Eqs. (3.50) - (3.51) giving the temperature behavior for the changes in enthalpy and entropy.

## 3.2 The Gibbs energy for chemical reactions

In the case of general gas phase reaction {rxg1}



the change in Gibbs free energy is given by {rxg2}

$$\Delta G_{rxn} = x G[X] + y G[Y] - a G[A] - b G[B] . \quad (3.53)$$

where the units of the the stoichiometric coefficient are mole Thus using Eq. (3.21) in Eq. (3.53) {rxg3}

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + mole R T \ln \left[ \frac{\left(\frac{P_X}{atm}\right)^x \left(\frac{P_Y}{atm}\right)^y}{\left(\frac{P_A}{atm}\right)^a \left(\frac{P_B}{atm}\right)^b} \right] \quad (3.54)$$

If we define the quotient as {rxg4}

$$Q \equiv \frac{\left(\frac{P_X}{atm}\right)^x \left(\frac{P_Y}{atm}\right)^y}{\left(\frac{P_A}{atm}\right)^a \left(\frac{P_B}{atm}\right)^b} , \quad (3.55)$$

Eq. (3.54) reduces to {rxg5}

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + R' T \ln Q , \quad (3.56)$$

where we have defined {rxg6a}

$$R' \equiv mol R = 8.314 J K^{-1} . \quad (3.57)$$

At equilibrium the change in Gibbs energy is zero, {rxg6b}

$$\Delta G_{rxn} = 0 , \quad (3.58)$$

and the quotient, at equilibrium, is known as the equilibrium constat, K. Therefore from Eq. (3.56) we get {rxg7}

$$\Delta G_{rxn}^{\circ} = - R' T \ln K . \quad (3.59)$$

Using this result in Eq. (3.56), we get

{rxg8}

$$\Delta G_{rxn} = R' T \ln \left( \frac{Q}{K} \right) . \quad (3.60)$$

From Eq. (3.60) we can infer that changes from equilibrium will imply spontaneous changes in the forward or backwards direction , i.e.,

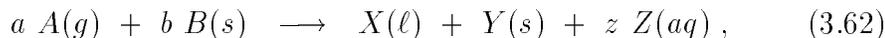
{rxg9}

$$\frac{Q}{K} \rightarrow \begin{cases} < 1 & \Delta G_{rxn} < 0 & \rightarrow \\ = 0 & \Delta G_{rxn} = 0 & \rightleftharpoons \\ > 1 & \Delta G_{rxn} > 0 & \leftarrow . \end{cases} \quad (3.61)$$

Equation (3.61) represents Le Châtelier principle.

In the case of reaction involving solids, pure liquids and aqueous solution,

{rxg10}



the quotient only includes gases and aqueous phases solids and pure liquids do not appear.. For Eq. (3.62) the quotient is given by:

{rxg11}

$$Q = \frac{\left( \frac{[Z]}{M} \right)^z}{\left( \frac{P_A}{atm} \right)^a} . \quad (3.63)$$

### 3.2.1 van't Hoff's equation

Considering Eq. (3.59) at temperature  $T_1$ , we can write the following expression:

{rxg12}

$$\ln K(T_1) = - \frac{\Delta G_{rxn}^\circ(T_1)}{R' T_1} = - \frac{\Delta H_{rxn}^\circ(T_1)}{R' T_1} + \frac{\Delta S_{rxn}^\circ(T_1)}{R'} \quad (3.64)$$

{rxg13}

also at  $T_2$  e have a similar relation, e.g.,

$$\ln K(T_2) = - \frac{\Delta G_{rxn}^\circ(T_2)}{R' T_2} = - \frac{\Delta H_{rxn}^\circ(T_2)}{R' T_2} + \frac{\Delta S_{rxn}^\circ(T_2)}{R'} . \quad (3.65)$$

If we consider small temperature changes,  $\Delta H_{rxn}^\circ$  and  $\Delta S_{rxn}^\circ$  are almost temperature independent, .e.g.,

{rxg14}

$$\Delta H_{rxn}^{\circ}(T_1) \approx \Delta H_{rxn}^{\circ}(T_2) \quad (3.66)$$

and

$$\Delta S_{rxn}^{\circ}(T_1) \approx \Delta S_{rxn}^{\circ}(T_2) . \quad (3.67)$$

Under these conditions we can subtract Eq. (3.64) from Eq. (3.65) and obtain the following relation:

$$\ln \frac{K(T_1)}{K(T_2)} = - \frac{\Delta H_{rxn}^{\circ}(T_1)}{R'} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] . \quad (3.68)$$

Equation (3.68) is known as the van't Hoff's equation, which relates the value of the equilibrium constant at  $T_2$  with the value of the equilibrium constant and the change of enthalpy at  $T_1$ .

### 3.2.2 Gibbs free energy of formation

For a given reaction,



we can calculate  $\Delta H_{rxn}^{\circ}$  from tables of enthalpies of formation, e.g.

$$\begin{aligned} \Delta H_{rxn}^{\circ} &= x \text{ mol } \Delta H_f^{\circ}[X] + y \text{ mol } \Delta H_f^{\circ}[Y] \\ &- a \text{ mol } \Delta H_f^{\circ}[A] - b \text{ mol } \Delta H_f^{\circ}[B] . \end{aligned} \quad (3.70)$$

Also from literature values of absolute entropy we can calculate  $\Delta S_{rxn}^{\circ}$ , i.e.,

$$\Delta S_{rxn}^{\circ} = x \text{ mol } S^{\circ}[X] + y \text{ mol } S^{\circ}[Y] - a \text{ mol } S^{\circ}[A] - b \text{ mol } S^{\circ}[B] . \quad (3.71)$$

Equation (3.71) can be applied to formation reactions and calculate the change in entropy,  $\Delta S_f^{\circ}$ . Therefore we can construct a table of changes in Gibbs energy for formation reactions,

$$\Delta G_f^{\circ} = \Delta H_f^{\circ} - T \Delta S_f^{\circ} . \quad (3.72)$$

In building such a table we have assumed that the Gibbs energy of formation is zero for the element at their most stable phase at 1 bar pressure,

$$\Delta G_f^\circ[\textit{element}] = 0. \quad (3.73)$$

With the help of table of Gibbs energy of formation, we calculate the change in Gibbs energy for any reaction as {rxg21}

$$\begin{aligned} \Delta G_{rxn}^\circ &= x \textit{ mol } \Delta G_f^\circ[X] + y \textit{ mol } \Delta G_f^\circ[Y] \\ &- a \textit{ mol } \Delta G_f^\circ[A] - b \textit{ mol } \Delta G_f^\circ[B]. \end{aligned} \quad (3.74)$$

### 3.3 Helmholtz free energy

In previous discussion we introduced the Gibbs function which is linked to the second law and give us a condition for spontaneity at constant P and T. In this section we consider a parallel analysis for processes occurring at constant T and V.

In general we have

$$T dS \geq dq , \quad (3.75) \quad \text{\small {he1}}$$

where the equality only holds for reversible processes. On the other hand at constant volume, V, we have

$$T dS \geq dq_V = dU . \quad (3.76) \quad \text{\small {he2}}$$

At constant temperature we can integrate easily Eq. (3.76) and get

$$\Delta A \equiv \Delta U - T \Delta S \leq 0 , \quad (3.77) \quad \text{\small {he3}}$$

where we have defined the Helmholtz energy as

$$A \equiv U - T S . \quad (3.78) \quad \text{\small {he4}}$$

Equation (3.77) is similar to the equation satisfied by the Gibbs energy at constant temperature and pressure.

The total differential of the Helmholtz energy is given by

$$dA = dU - T dS - S dT , \quad (3.79) \quad \text{\small {he5}}$$

but

$$dU = dq + dW . \quad (3.80) \quad \text{\small {he6}}$$

Using the previous relation, Eq. (3.79) reduces to

$$dA = dq + dW - T dS - S dT . \quad (3.81) \quad \text{\small {he7}}$$

For reversible processes heat transfer satisfies the following relation:

$$dq^{rev} = T dS . \quad (3.82) \quad \text{\small {he8}}$$

Thus for reversible processes the differential change in Helmholtz energy is given by:

\small {he9}

$$dA = -P dV - S dT + dW_{nonPV} . \quad (3.83)$$

For a reversible process at constant temperature the change in Helmholtz energy is equal to the work done, e.g., {he10}

$$dA = -P dV + dW_{nonPV} . \quad (3.84)$$

{he11} If the volume is constant we have

$$dA = dW_{nonPV} . \quad (3.85)$$

{he12} Therefore for reversible processes at constant temperature and volume and only PV work the differential change in Helmholtz energy is equal to zero,

$$dA = 0 . \quad (3.86)$$

{he13} In general for isothermal and isocoric processes and only PV work the following relation is satisfied by the Helmholtz energy

$$dA \leq 0 . \quad (3.87)$$

Notice that Helmholtz free energy is the counterpart of Gibbs energy for isothermal and isobaric processes.

### 3.4 Maxwell relations

In previous section we have discuss the basic relations and definitions in Thermodynamics. For example we know that the two fundamental differential relations are given by the First law, {max1}

$$dU = dq + dW , \quad (3.88)$$

and the Second law, {max2}

$$T dS \geq dq . \quad (3.89)$$

In Eq. (3.89) the equality holds for reversible processes, {max3}

$$T dS = dq^{rev} . \quad (3.90)$$

Thus for process with only PV-work, Eq. (3.88) reduces to {max4}

$$dU = T dS - P dV . \quad (3.91)$$

Now if we compare the mathematical expression for the differential of U function of entropy and temperature, U(S,V), {max5}

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV , \quad (3.92)$$

we find the following relations: {max6}

$$T = \left( \frac{\partial U}{\partial S} \right)_V \quad (3.93)$$

$$- P = \left( \frac{\partial U}{\partial V} \right)_S . \quad (3.94)$$

Applying the property of cross second partial derivatives satisfied by exact differentials, {max8}

$$\left[ \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right)_V \right]_S = \left[ \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)_S \right]_V , \quad (3.95)$$

we get the following Maxwell relation: {max9}

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V . \quad (3.96)$$

**Enthalpy, H**

For the differential change in enthalpy we have

{max10}

$$\begin{aligned}
 dH &= dU + d(PV) \\
 &= T dS - P dV + P dV + V dP \\
 &= T dS + V dP \\
 &= \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP .
 \end{aligned} \tag{3.97}$$

{max11}

Therefore we get the following relations:

$$T = \left(\frac{\partial H}{\partial S}\right)_P \tag{3.98}$$

{max12}

$$V = \left(\frac{\partial H}{\partial P}\right)_S . \tag{3.99}$$

{max13}

Finally using the property of cross partial derivatives,

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S}\right)_P\right]_S = \left[\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P}\right)_S\right]_P , \tag{3.100}$$

{max14}

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P , \tag{3.101}$$

which is another of the Maxwell relations.

**Gibbs free energy, G**

{max15}

For the differential change in Gibbs free energy we have

$$\begin{aligned}
 dG &= dH - d(TS) \\
 &= dH - T dS - S dT \\
 &= -S dT + V dP \\
 &= \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP .
 \end{aligned} \tag{3.102}$$

{max16}

Therefore we get the following relations:

$$- S = \left( \frac{\partial G}{\partial T} \right)_P \quad (3.103)$$

$$V = \left( \frac{\partial G}{\partial P} \right)_T . \quad (3.104)$$

Finally using the property of cross partial derivatives,

$$\left[ \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial T} \right)_P \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial P} \right)_T \right]_P , \quad (3.105)$$

$$- \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P , \quad (3.106)$$

which is another of the Maxwell relations.

### Hemholtz free energy, $A$

For the differential change in Hemholtz free energy we have

$$\begin{aligned} dA &= dU - d(T S) \\ &= T dS - P dV - T dS - S dT \\ &= - S dT - P dV \\ &= \left( \frac{\partial A}{\partial T} \right)_V dT + \left( \frac{\partial A}{\partial V} \right)_T dV . \end{aligned} \quad (3.107)$$

Therefore we get the following relations:

$$- S = \left( \frac{\partial A}{\partial T} \right)_V \quad (3.108)$$

$$- P = \left( \frac{\partial A}{\partial V} \right)_T . \quad (3.109)$$

Finally using the property of cross partial derivatives,

$$\left[ \frac{\partial}{\partial V} \left( \frac{\partial A}{\partial T} \right)_V \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial A}{\partial V} \right)_T \right]_V , \quad (3.110)$$

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V , \quad (3.111)$$

which is another of the Maxwell relations.

**Entropy S(P,T)**

{en1} The differential change of the entropy when it is a function pressure and temperature is given by;

$$dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP . \quad (3.112)$$

{en2} We also know that at constant pressure the amount of heat exchanged during a reversible process is related with the change in entropy, i.e.,

$$q_P^{rev} = C_P dT = T dS . \quad (3.113)$$

{en3} Equation (3.113) can be reexpress as a partial derivative

$$\left( \frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T} . \quad (3.114)$$

{en4} Using a Maxwell relation,

$$- \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P , \quad (3.115)$$

{en5} we obtain general relation for the differential change in entropy when the entropy is a function of temperature and pressure

$$dS = C_P \frac{dT}{T} - \left( \frac{\partial V}{\partial T} \right)_P dP \quad (3.116)$$

$$= C_P \frac{dT}{T} - \alpha V dP . \quad (3.117)$$

{en6} For an ideal gas Eq. (3.116) reduces to

$$dS = C_P \frac{dT}{T} - n R \frac{dP}{P} . \quad (3.118)$$

{en7} Finally we can integrate Eq. (3.116) and get the change in entropy

$$\Delta S = C_P \ln \left( \frac{T_f}{T_i} \right) - n R \ln \left( \frac{P_f}{P_i} \right) . \quad (3.119)$$

In the case of real gases we can integrate Eq. (3.116) and get

$$\Delta S = \int_{T_i}^{T_f} C_P(T) \frac{dT}{T} - \int_{P_i}^{P_f} \left( \frac{\partial V}{\partial T} \right)_P dP . \quad (3.120)$$

Now we can use the expression of the temperature dependent heat capacities and the equation of state in Eq. (3.120).

For example consider a process where at the initial pressure,  $P_i$ , an expression of the entropy as a function of temperature is given. Namely we know  $S(P_i, T)$ . We want to calculate the change of Gibbs free energy when the system changes from the initial pressure and temperature to a final pressure and temperature. This calculation can be done in two different ways. First we can maintain the pressure constant and change the temperature up to the final temperature. Second we can maintain the final temperature fixed and change the pressure. Another possibility will be to fix the initial temperature first and change the pressure. Second, fix the pressure and change the temperature.

For the first path we use Eq. (3.12) to calculate the change in Gibbs energy at constant pressure  $P_i$ ,

$$\Delta G_1 = - \int_{T_i}^{T_f} S(P_i, T) dT. \quad (3.121)$$

Next, the change in Gibbs energy for fixed temperature,  $T_f$ , is given by:

$$\Delta G_2 = \int_{V_i}^{V_f} V dP = nRT_f \ln \left( \frac{P_f}{P_i} \right) . \quad (3.122)$$

Thus the total change in Gibbs energy is equal to

$$\Delta G(\text{Path 1}) = - \int_{T_i}^{T_f} S(P_i, T) dT + nRT_f \ln \left( \frac{P_f}{P_i} \right) . \quad (3.123)$$

For the second path, we fix the temperature at  $T_i$  and change the pressure. In this case the change in Gibbs energy is given by:

$$\Delta G_3 = \int_{V_i}^{V_f} V dP = nRT_i \ln \left( \frac{P_f}{P_i} \right) . \quad (3.124)$$

For the second part in this path, we get a similar relation as in Eq. (3.121) but with entropy at the final pressure  $P_f$ , i.e.,

{en13}

$$\Delta G_4 = - \int_{T_i}^{T_f} S(P_f, T) dT. \quad (3.125)$$

Since we need the entropy at  $P_f$ , we have to calculate it using a Maxwell relation. Eq. recmax19 relates the change of entropy with respect to changes in the pressure at constant temperature with changes in the volume with respect to changes in temperature at constant pressure,

{en14}

$$\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P = - \frac{nR}{P}, \quad (3.126)$$

where we have used the ideal equation of state. Thus from Eq. (3.126) we get the following differential relation at constant temperature:

{en15}

$$dS = - nR \frac{dP}{P}. \quad (3.127)$$

Now we can integrate Eq. (3.127) from the initial pressure,  $P_i$ , to the final pressure,  $P_f$ ,

{en16}

$$\begin{aligned} \Delta S &= \int_{S(P_i, T)}^{S(P_f, T)} dS \\ &= S(P_f, T) - S(P_i, T) \\ &= - nR \int_{P_i}^{P_f} \frac{dP}{P} \\ &= - nR \ln \left( \frac{P_f}{P_i} \right). \end{aligned} \quad (3.128)$$

From this calculation we get that the entropy at the final pressure is given by:

{en17}

$$S(P_f, T) = S(P_i, T) - nR \ln \left( \frac{P_f}{P_i} \right). \quad (3.129)$$

Finally, we use Eq. (3.129) in Eq. (3.125) to get the change in Gibbs energy, i.e.,

{en18}

$$\begin{aligned}
\Delta G_4 &= - \int_{T_i}^{T_f} S(P_f, T) dT \\
&= - \int_{T_i}^{T_f} S(P_i, T) dT \\
&\quad + nR (T_f - T_i) \ln \left(\frac{P_f}{P_i}\right) . \quad (3.130)
\end{aligned}$$

Using Eqs. (3.124) and (3.130), the total change in Gibbs energy for the second path is equal to the total change in Gibbs energy for the first path, {en19}

$$\Delta G_3 + \Delta G_4 = \Delta G(\text{Patha 2}) = \Delta G(\text{Path 1}) . \quad (3.131)$$

### 3.5 Calculation of $\left(\frac{\partial U}{\partial V}\right)_P$

In Chapter 1 we used a relation linking  $\left(\frac{\partial U}{\partial V}\right)_P$  with the equation of state. In this section we will derive it with the help of the Maxwell relations. First we will consider the internal energy as function of volume and temperature,  $U(V, T)$ . In this case the differential of  $U$  is given in general by: {utv1}

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT . \quad (3.132)$$

But from the First law for a reversible process we also have {utv2}

$$dU = T dS - P dV . \quad (3.133)$$

Now we can express the entropy differential as: {utv3}

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT . \quad (3.134)$$

Using Eq. (3.134) in Eq. (3.133) we get {utv4}

$$dU = \left[ T \left(\frac{\partial S}{\partial V}\right)_T - P \right] dV + \left(\frac{\partial S}{\partial T}\right)_V dT . \quad (3.135)$$

If now we compare Eq. (3.135) with Eq. (3.132) we find the following relation:

$$\left(\frac{\partial U}{\partial V}\right)_T = \left[T \left(\frac{\partial S}{\partial V}\right)_T - P\right]. \quad (3.136) \tag{utv5}$$

{utv6}

Finally using a Maxwell relation, Eq. (3.111), we get Eq. (1.22)

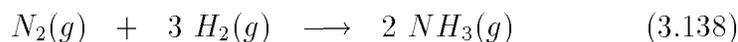
$$\left(\frac{\partial U}{\partial V}\right)_T = \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right]. \quad (3.137)$$

## 3.6 Problems

### Problem 3.1.1

Consider the following reaction:

{c1p1}



and calculate  $\Delta G^\circ$  at 500K and 100K assuming first that  $\Delta H^\circ$  is independent of temperature and for a temperature dependent  $\Delta H^\circ$ .

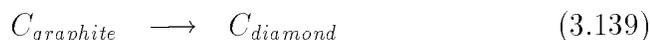
At  $T_1 = 298.15K$  we have the following values for the change in Gibbs energy and enthalpy:

$$\begin{aligned} \Delta G^\circ &= -62.0 \text{ kJ mol}^{-1} \\ \Delta H^\circ &= -184.4 \text{ kJ mol}^{-1} . \end{aligned}$$

### Problem 3.1.2

Is there a temperature at which the transition

{p1}



becomes spontaneous?

$$\begin{aligned} C_P(\text{graphite}) &= 8.527 \text{ J K}^{-1} \text{ mol}^{-1} \\ C_P(\text{diamond}) &= 6.113 \text{ J K}^{-1} \text{ mol}^{-1} . \end{aligned}$$

### Problem 3.2.1

Will the reaction

{rxg22}

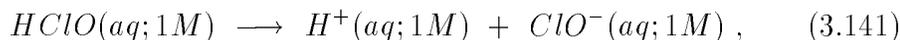


occurs spontaneously at  $25^\circ C$  ?

### Problem 3.2.2

Consider hypochlorous acid

{rxg23}



with equilibrium constant at  $25^\circ C$  equal to

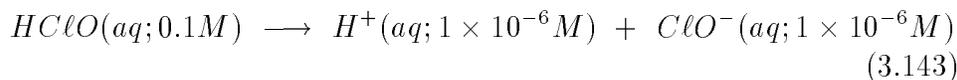
{rxg24}

$$K_a = 3.0 \times 10^{-8} . \quad (3.142)$$

a) Calculate  $\Delta G_{rxn}^\circ$  for Eq. (3.141).

b) Consider the same reaction at different concentrations

{rxg25}



Calculate  $\Delta G_{rxn}$  for Eq. (3.143).

**Problem 3.2.3**

Calculate the equilibrium constant for the dissociation of bromine:

{rxn26}



at 500K and 1000K.

i) Assume no temperature dependence for  $\Delta H_{rxn}^\circ$  and  $\Delta S_{rxn}^\circ$ .

ii) Assume that  $\Delta H_{rxn}^\circ$  and  $\Delta S_{rxn}^\circ$  depend on temperature but the specific heats are independent of temperature.

iii) Use the following temperature dependence for the heat capacity of  $Br_2(g)$ :

{rxn27}

$$\bar{C}_P[Br_2(g)] = a + bT + \frac{c}{T^2}, \quad (3.145)$$

with

$$\begin{aligned} a &= 37.32 \text{ J K}^{-1} \text{ mol}^{-1} \\ b &= 0.50 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1} \\ c &= -1.26 \times 10^5 \text{ J mol}^{-1} \end{aligned}$$

For  $Br(g)$  use the ideal gas value for  $\bar{C}_P$ . By the way this last approximation breaks down above 1000K.

iv) Compare your values with the literature values

$$\begin{aligned} K_a(500K) &= 2.21 \times 10^{-15} \\ K_a(1000K) &= 3.27 \times 10^{-5} \end{aligned}$$

# Chapter 4

## Phase equilibria

In general we know that a phase transition occurs at constant temperature and pressure with total change in Gibbs energy equal to zero. For example if we consider the vaporization of water at  $P = 1\text{bar}$ , the total change in Gibbs energy is equal to

$$\Delta G_{vap}^{\circ} = \Delta H_{vap}^{\circ} - T \Delta S_{vap}^{\circ} . \quad (4.1)$$

Thus at the boiling temperature,  $T_b$ , we have

$$0 = \Delta H_{vap}^{\circ} - T_b \Delta S_{vap}^{\circ} . \quad (4.2)$$

from this equation we get

$$T_b = \frac{\Delta H_{vap}^{\circ}}{\Delta S_{vap}^{\circ}} . \quad (4.3)$$

Finally since enthalpy and entropy are state functions, the net changes of these state functions for sublimation can be expressed in terms of the changes for vaporization and fusion, i.e.,

$$\Delta H_{sub}^{\circ} = \Delta H_{fus}^{\circ} + \Delta H_{vap}^{\circ} \quad (4.4)$$

$$\Delta S_{sub}^{\circ} = \Delta S_{fus}^{\circ} + \Delta S_{vap}^{\circ} . \quad (4.5)$$

## 4.1 One component systems

In this section we will consider a closed one component two phase system. In this case,



{ph2} the Gibbs energy is given by

$$G = n_\alpha \mu_\alpha + n_\beta \mu_\beta . \tag{4.7}$$

{ph3} At constant temperature and pressure the differential change of the Gibbs energy is given by:

$$dG = \mu_\alpha dn_\alpha + \mu_\beta dn_\beta \tag{4.8}$$

{ph4} For closed systems mass conservation implies

$$dn_\alpha + dn_\beta = 0 . \tag{4.9}$$

{ph5} Thus the differential change in Gibbs energy is given by:

$$dG = (\mu_\alpha - \mu_\beta) dn_\alpha \tag{4.10}$$

{ph6} Since we are considering the coexistence of the two phases, any differential change in the Gibbs energy has to be equal to zero,  $dG = 0$ . Therefore the equilibrium condition for the coexistence of two phases at constant T and P is given by the equality among their chemical potentials, i.e.,

$$\mu_\alpha = \mu_\beta . \tag{4.11}$$

{ph7} Now consider differential changes in temperature or pressure or both. These changes will affect the value of the chemical potentials, but they will not affect the equilibrium condition. In other words, after the changes have been made the new chemical potentials will satisfy the following equality:

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta . \tag{4.12}$$

{ph8} If we use Eq. (4.11) we a relation between differential changes of the chemical potential,

$$d\mu_\alpha = d\mu_\beta . \quad (4.13)$$

Equation (4.13) gives us a relation between the differential changes of the chemical potential of two phases of the same component at equilibrium with each other when the temperature and pressure change.

Since the chemical potentials are independent of the number of moles of substance present its differential changes are given by {ph9}

$$d\mu_\alpha = -\bar{S}_\alpha dT + \bar{V}_\alpha dP \quad (4.14)$$

$$d\mu_\beta = -\bar{S}_\beta dT + \bar{V}_\beta dP , \quad (4.15) \quad \text{{ph9}}$$

where the over bar stand for molar quantities. Using Eq. (4.13), we get the following relation: {ph10}

$$-\bar{S}_\alpha dT + \bar{V}_\alpha dP = -\bar{S}_\beta dT + \bar{V}_\beta dP . \quad (4.16)$$

This relation can be rearrange to yield {ph11}

$$(\bar{V}_\beta - \bar{V}_\alpha) dP = (\bar{S}_\beta - \bar{S}_\alpha) dT . \quad (4.17)$$

Finally Eq. (4.17) allows us to get the a relation between the change in pressure and the change in temperature. This relation is given by the following relation: {ph12}

$$\frac{dP}{dT} = \frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} = \frac{\Delta\bar{S}_{\alpha\rightarrow\beta}}{\Delta\bar{V}_{\alpha\rightarrow\beta}} . \quad (4.18)$$

Recalling that for two pahses at equilibrium we have {ph13}

$$\Delta\bar{S}_{\alpha\rightarrow\beta} = \frac{\Delta\bar{H}_{\alpha\rightarrow\beta}}{T} , \quad (4.19)$$

Eq. (4.18) reduces to {ph14}

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{\alpha\rightarrow\beta}}{T \Delta\bar{V}_{\alpha\rightarrow\beta}} . \quad (4.20)$$



# Chapter 5

## Mixtures

### 5.1 Mixture of volatile liquids

In an ideal solution of two liquids the vapor pressure of the components are related to the composition in the condensed phase by Raoult's Law,

{mv1}

$$P_A = X_A P_A^\circ \quad (5.1)$$

$$P_B = X_B P_B^\circ . \quad (5.2)$$

Using Dalton's law, the total vapor pressure is

{mv2}

$$\begin{aligned} P_{total} &= P_A + P_B \\ &= X_A P_A^\circ + X_B P_B^\circ \\ &= P_B^\circ + (P_A^\circ - P_B^\circ) X_A . \end{aligned} \quad (5.3)$$

Now we will consider the composition of the vapor. For an ideal mixture we recall Dalton's law, i.e.,

{mv3}

$$P_A = Y_A P_{total} \quad (5.4)$$

$$P_B = Y_B P_{total} , \quad (5.5)$$

where  $Y_i$  is the mole fraction in the gas phase. In other words we have

{mv4}

$$Y_A = \frac{n_A(g)}{n_A(g) + n_B(g)} . \quad (5.6)$$

Therefore the mole fraction in gas phase is equal to

{mv5}

$$Y_A = \frac{P_A}{P_{total}} \quad (5.7)$$

{mv6}

Now if we use Eqs. (5.1) and (5.3) we get

$$Y_A = \frac{X_A P_A^\circ}{P_B^\circ + (P_A^\circ - P_B^\circ) X_A} \quad (5.8)$$

If A is the more volatile component,  $P_A^\circ > P_B^\circ$ , its mole fraction in the vapor,  $Y_A$ , is greater than its mole fraction in the liquid,  $X_A$ .

{mv7}

Next, we can solve for  $X_A$  as a function of  $Y_A$  using Eq. (5.8). This calculation yields

$$X_A = \frac{Y_A P_B^\circ}{P_A^\circ + (P_B^\circ - P_A^\circ) Y_A} \quad (5.9)$$

{mv8}

Finally we use Eq. (5.9) in Eq. (5.3) to get an expression of the total pressure as a function of A's mole fraction in gas phase,

$$\begin{aligned} P_{total} &= P_B^\circ + \frac{(P_A^\circ - P_B^\circ) Y_A P_B^\circ}{P_A^\circ + (P_B^\circ - P_A^\circ) Y_A} \\ &= \frac{P_A^\circ P_B^\circ}{P_A^\circ + (P_B^\circ - P_A^\circ) Y_A} \end{aligned} \quad (5.10)$$

From Eq. (5.10) we can see that when  $Y_A = 0$  there is no A in gas phase thus the total pressure is equal to  $P_B^\circ$ . The same way if  $Y_A = 1$ , which means pure A, the total pressure is equal to  $P_A^\circ$ .

Figure 5.1 depicts the diagram P vs. X for the Benzene+ Toluene ideal mixture.

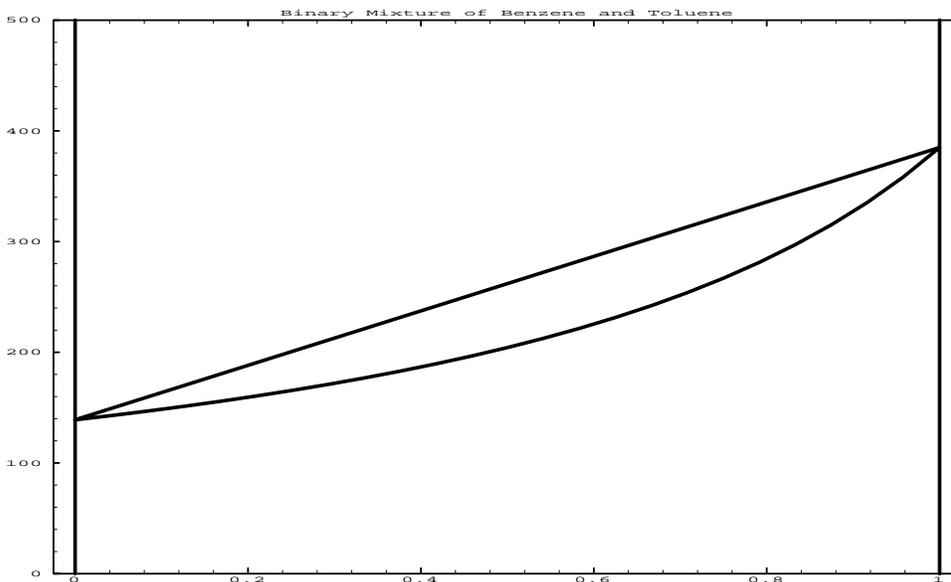


Figure 5.1: Ideal mixture P vs X diagram.

## 5.2 Chemical potential and reference states

The general expression for the differential change of the Gibbs energy,  $G$ , is given by:

$$dG = -S dT + V dP, \quad (5.11)$$

where  $S$  is the entropy,  $V$  the volume,  $P$  is the pressure, and  $T$  is the absolute temperature. From Eq/ (5.11) we have a relation between the change of  $G$  with respect to a change of pressure at constant temperature, i.e.,

$$\left(\frac{\partial G}{\partial P}\right)_T = V. \quad (5.12)$$

If we rewrite Eq. (5.12) as a differential relation, we can calculate the Gibbs free energy as a function of pressure, namely

$$\int_{G^\circ}^G dG = G - G^\circ = \int_{P_{ref}}^P V(P') dP', \quad (5.13)$$

where the temperature is held constant.

### 5.2.1 Chemical potential for gases

{cps4} Since  $PV = nRT$  for an ideal gas, with  $R$  the gas constant and  $n$  the number of moles, we find

$$G - G^\circ = nRT \int_{P_{ref}}^P \frac{dP'}{P'} = nRT \ln \left( \frac{P}{P_{ref}} \right). \quad (5.14)$$

{cps5} In Eq. (5.14) an arbitrary pressure reference,  $P_{ref}$ , corresponds to the pressure where Gibbs free energy is equal to  $G^\circ$ . Thus, the Gibbs free energy of an ideal gas at constant  $T$  is given by:

$$G = G^\circ + nRT \ln \left( \frac{P}{P_{ref}} \right). \quad (5.15)$$

In practice the values of  $P'_{ref}$ s defined a set of conditions called standard state. Usually one atmosphere or one bar is chosen for all gases; in the present discussion we will leave  $P_{ref}$  as a value to be defined. In this case the molar Gibbs free energy or chemical potential,  $\mu$ , is given by:

{cps6}

$$\mu = \mu^\circ + RT \ln \left( \frac{P}{P_{ref}} \right). \quad (5.16)$$

According to Eq. (5.16), when  $P$  is equal to the reference pressure,  $P_{ref}$ , the molar Gibbs free energy is equal to the standard state molar Gibbs free energy  $\mu^\circ$ . If one considers interactions between particles, i.e., nonideal gases, one has to replace the argument of the natural logarithm by the fugacity,  $f$ . Thus we have

{cps7}

$$\mu = \mu^\circ + RT \ln \left( \frac{f}{P_{ref}} \right). \quad (5.17)$$

{cps8} where

$$f(P) = P \exp \left\{ \int_0^P \left[ \frac{P' V(P')}{RT} - 1 \right] dp' \right\} \quad (5.18)$$

{cps9} where

$$\lim_{P \rightarrow 0} \frac{f(P)}{P_{ref}} = \frac{P}{P_{ref}}. \quad (5.19)$$

Equation (5.18) is the chemical potential for an arbitrary standard state defined by the reference pressure,  $P_{ref}$ .

### 5.2.2 Chemical potential for solvents

In the case of solutions, where the solvent is at equilibrium with its vapor, we know that

$$\mu_{Solvent} = \mu_{Vapor} . \quad (5.20) \quad \{\text{cps10}\}$$

Since Eq. (5.20) applies to the chemical potential of an ideal vapor, we have

$$\mu_{Solvent} = \mu_{Vapor} = \mu^\circ + RT \ln \left( \frac{P}{P_{ref}} \right) . \quad (5.21) \quad \{\text{cps11}\}$$

For a pure solvent  $P$  is equal to the pure solvent vapor pressure,  $P^*$ . Thus the pure liquid chemical potential is given by:

$$\mu_{Solvent}^* \equiv \mu^\circ + RT \ln \left( \frac{P^*}{P_{ref}} \right) . \quad (5.22) \quad \{\text{cps12}\}$$

Solving for  $\mu^\circ$  and substituting in Eq. (5.21) we get

$$\mu_{Solvent} = \mu_{Solvent}^* + RT \ln \left( \frac{P}{P^*} \right) . \quad (5.23) \quad \{\text{cps13}\}$$

In the case of an ideal solution, Raoult's law is satisfied. Therefore, the following relation between the vapor pressure and composition is observed:

$$\frac{P}{P^*} = X_{Solvent} \quad (5.24) \quad \{\text{cps14}\}$$

where  $X$  is the mole fraction. Therefore for ideal solutions we have

$$\mu_{Solvent} = \mu_{Solvent}^* + RT \ln (X_{Solvent}) . \quad (5.25) \quad \{\text{cps15}\}$$

Notice that now the reference point is the pure solvent.

For a nonideal solution, the following relation is defined:

$$\frac{P}{P^*} \equiv a_{Solvent} \equiv \gamma_{Solvent} X_{Solvent} \quad (5.26) \quad \{\text{cps16}\}$$

where  $a_{Solvent}$  is defined as the activity and  $\gamma_{Solvent}$  as the activity coefficient. In this case the solvent chemical potential of a nonideal solution is given by:

$$\mu_{Solvent} = \mu_{Solvent}^* + RT \ln (a_{Solvent}) . \quad (5.27) \quad \{\text{cps17}\}$$

Equation (5.27) is the most general expression for the solvent's chemical potential where the nonideality is taken in consideration in the activity coefficient. Also notice that for pure solvent the activity and the activity coefficient are equal to unity

### 5.2.3 Chemical potential for solutes

In the case of the solute, Henry's law relates the solute's composition with the vapor pressure, i.e.,

$$P = K'[Solute] = Km_{Solute} , \quad (5.28)$$

where [...] represents the molar concentration and m the molal concentration. Therefore, for a solute we have

$$\mu_{Solute} = \mu^\circ + RT \ln \left( \frac{K' [Solute]}{P_{ref}} \right) . \quad (5.29)$$

Now, we can select a reference concentration,  $[Solute]_{ref}$ . Using this reference concentration, we define the reference chemical potential as:

$$\mu_{Solute}^\ominus = \mu^\circ + RT \ln \left( \frac{K' [Solute]_{ref}}{P_{ref}} \right) . \quad (5.30)$$

Again, we solve for  $\mu^\circ$  and substitute in Eq.(5.29). Thus we get for the solute the following chemical potential

$$\mu_{Solute} = \mu_{Solute}^\ominus + RT \ln \left( \frac{K' [Solute]}{[Solute]_{ref}} \right) . \quad (5.31)$$

For nonideal solutions, Henry's Law is expressed as a function of the activity

$$P \equiv K' a_{Solute}^M \equiv K' [Solute] \gamma_{Solute}^M \equiv K a_{Solute}^m . \quad (5.32)$$

where the M and the m represent for molar or molal based activity. Following the previous procedure, we get

$$\mu_{Solute} = \mu_{Solute}^\ominus + RT \ln \left( \frac{a_{Solute}^M}{a_{Solute_{ref}}^M} \right) . \quad (5.33)$$

{cps23b}

$$\mu_{Solute} = \mu_{Solute}^{\ominus} + RT \ln \left( \frac{a_{Solute}^m}{a_{Solute,ref}^m} \right) . \quad (5.34)$$

Usually the reference activity is defined as equal to one when the concentration is equal to one molar or one molal. This definition implies that the activity coefficient is equal to one when the concentration is equal to one molar or one molal. With these definitions of the reference activity Eqs. (5.33) and (5.34) can be written as

{cps23c}

$$\mu_{Solute} = \mu_{Solute}^{\ominus M} + RT \ln \left( \frac{a_{Solute}^M}{M} \right) . \quad (5.35)$$

{cps23d}

$$\mu_{Solute} = \mu_{Solute}^{\ominus m} + RT \ln \left( \frac{a_{Solute}^m}{1 \text{ molal}} \right) . \quad (5.36)$$

Physically, the definition of the reference activity means that at the reference concentration the solute particles behave ideally, e.g., they do not interact with each other. In general we can not find physical systems that behave ideally at such standard concentrations. Therefore these reference or standard states for solutes are hypothetical states.

### 5.2.4 Chemical potential for solids

For a solid, we first rewrite Eq.(5.13) in term of chemical potential and molar volume,  $\bar{V}$ , i.e.,

{cps24}

$$\begin{aligned} \mu(T, P) - \mu^{\circ}(T, P_{ref}) &= \int_{P_{ref}}^P \bar{V}(P') dP' \\ &\equiv RT \ln (a_{Solid}) . \end{aligned} \quad (5.37)$$

For pressure changes up to a couple of hundreds of atmospheres, solids, in general, experience negligible changes in molar volume. Thus, Eq.(5.37) can be approximate as

{cps25}

$$\begin{aligned} \mu(T, P) &= \mu^{\circ}(T, P_{ref}) + \bar{V}(P_{ref}) \Delta P \\ &\equiv \mu^{\circ}(T, P_{ref}) + RT \ln (a_{Solid}) , \end{aligned} \quad (5.38)$$

where  $\Delta P = P - P_{ref}$ ; the activity of a solid can be calculated by the following expression: {cps26}

$$a_{Solid} = \exp \left\{ \frac{\bar{V}(P_{ref}) \Delta P}{RT} \right\} . \quad (5.39)$$

Furthermore, in most typical chemical reactions the following condition is usually satisfied: {cps27}

$$\frac{\bar{V}(P_{ref}) \Delta P}{RT} \ll 1 . \quad (5.40)$$

Thus, the activity of a solid, under the previous assumption, is approximately equal to unity. Therefore the contribution to the chemical potential of a solid due to changes in pressure is approximately equal to zero.

In summary, we have calculated the most general expressions for the gas, solvent, solute, and solid chemical potentials in terms of an arbitrary set of reference conditions, which may define the so-called standard state.

### 5.2.5 Fugacity

The concept of fugacity is one that generally is not easy to learn and that causes confusion not only among students but among chemists as well. The source of confusion resides on how the fugacity is introduced.

{fu1} For an ideal gas, we have

$$\mu_{Ideal} = \mu_{Ideal}^{\circ'} + RT \ln \left( \frac{P}{P_{\circ}} \right) , \quad (5.41)$$

{fu2} where  $\mu_{Ideal}^{\circ'}$  is the value of the chemical potential for a particular pressure  $P_{\circ}$ . For a real gas, one defines the chemical potential as

$$\mu_{Real} = \mu_{Real}^{\circ'} + RT \ln \left( \frac{\bar{f}}{f_{\circ}} \right) , \quad (5.42)$$

{fu3} Now, the difference between the real and ideal chemical potential can be written as

$$\begin{aligned}
\Delta\mu_{Real} - \Delta\mu_{Ideal} &= RT \ln \left( \frac{P_o \bar{f}}{P \bar{f}_o} \right) \\
&= \int_{P_o}^P [\bar{V}_{Real} - \bar{V}_{Ideal}] dP' \\
&= RT \int_P^{P_{ref}} [Z(P') - 1] \frac{dP'}{P'} , \quad (5.43)
\end{aligned}$$

where we have used the compressibility,  $Z(P)=PV/nRT$ . From Eq. (5.43), we get the following relation {fu4}

$$\bar{f} = \frac{P \bar{f}_o}{P_o} \exp \left\{ \int_{P_o}^P [Z(P') - 1] \frac{dP'}{P'} \right\} \quad (5.44)$$

Since real gases at low pressures behave ideally, Eq. (5.43) reduces to {fu5}

$$\lim_{P \rightarrow 0} (\Delta\mu_{Real} - \Delta\mu_{Ideal}) = 0 . \quad (5.45)$$

Therefore we pick an  $\bar{f}$  and  $\bar{f}_o$  such that {fu6}

$$\lim_{P \rightarrow 0} \frac{\bar{f}}{\bar{f}_o} = \frac{P}{P_o} . \quad (5.46)$$

Equation (5.46) implies {fu7}

$$\mu'_{Real} = \mu'_{Ideal} , \quad (5.47)$$

where we have used Eq. (5.41) - (5.42).

On the other hand, the value of the chemical potential is independent of the reference pressure i.e., {fu8}

$$\mu_{Ideal} = \mu'_{Ideal} + RT \ln \left( \frac{P}{P_o} \right) = \mu^{\circ}_{Ideal} + RT \ln \left( \frac{P}{P_{ref}} \right) , \quad (5.48)$$

where  $P_{ref}$  is the reference pressure that defines the standard state. Hence, we find the following relation between reference chemical potential {fu9}

$$\mu^{\circ}_{Ideal} = \mu'_{Ideal} + RT \ln \left( \frac{P_o}{P_{ref}} \right) . \quad (5.49)$$

Using this relation in Eq. 5.42, we get {fu10}

$$\mu_{Real} = \mu_{Real}^{\circ} + RT \ln \left( \frac{\bar{f} P_{\circ}}{\bar{f}_{\circ} P_{ref}} \right) \quad (5.50)$$

But

{fu11}

$$\frac{\bar{f} P_{\circ}}{\bar{f}_{\circ} P_{ref}} = \frac{P}{P_{ref}} \exp \left\{ \int_{P_{\circ}}^P [Z(P') - 1] \frac{dp'}{P'} \right\} \quad (5.51)$$

{fu11b}

where the fugacity is defined by:

$$f = P \exp \left\{ \int_{P_{\circ}}^P [Z(P') - 1] \frac{dp'}{P'} \right\} . \quad (5.52)$$

{fu12}

The final expression for the chemical potential for a real gas is given by:

$$\mu_{Real} = \mu_{Ideal}^{\circ} + RT \ln \left( \frac{f}{P_{ref}} \right) . \quad (5.53)$$

{fu13}

Finally, we have to choose  $P_{\circ}$ . From Eq. (5.52), we notice that

$$\lim_{P \rightarrow P_{\circ}} \frac{f}{P_{\circ}} = \frac{P}{P_{\circ}} , \quad (5.54)$$

consequently we pick  $P_{\circ} = 0$ .

## 5.3 Colligative Properties

The properties of dilute solutions that depend only on the number of solute particles and not on the type of species present are called colligative properties. In the case of dilute solutions we have the boiling point elevation, the freezing point depression and osmotic pressure. These are cases where the lowering of the vapor pressure, due to the presence of a solid solute, triggers changes in the solvent properties.

The assumptions are as follows:

- a) Solid solutes do not appear in the gas phase. Therefore the gas phase is unchanged
- b) At freezing the solid phase contains only solid solvent. Therefore the solid phase of the solute is

As a consequence of assumptions a) and b), only the liquid phase of the solvent is changed, {col1}

$$\mu_{Solvent}^{\ell}(T, P, X_1) = \mu_{Solvent}^{\ell*}(T, P) + RT \ln(X_1) . \quad (5.55)$$

### 5.3.1 Freezing point depression

First we will consider a solution in equilibrium with its pure solvent's solid phase with  $\mu_{Solvent}^{Solid}(T, P) \equiv \mu_1^s(T, P)$ . In this case the following equality between the chemical potentials will hold: {col2}

$$\mu_1^s(T, P) = \mu_1^{\ell*}(T, P) + RT \ln(X_1) . \quad (5.56)$$

From this relation we can solve for  $\ln(X_1)$  and get {col3}

$$\begin{aligned} \ln(X_1) &= - \frac{[\mu_1^{\ell*}(T, P) - \mu_1^s(T, P)]}{R T} \\ &= - \frac{\Delta_{fus}\mu}{R T} , \end{aligned} \quad (5.57)$$

where fusion stands for the transition  $Solid \rightleftharpoons Liquid$  Now we take the derivative with respect to temperature at constant pressure, i.e., {col4b}

$$\frac{d \ln(x_1)}{dT} = - \frac{1}{R} \left( \frac{\partial (\Delta_{fus}\mu/T)}{\partial T} \right)_P , \quad (5.58)$$

where  $\Delta_{fus}H$  is the molar heat of fusion for the pure solvent and could be assumed independent of  $T$  over a moderate range of temperature. Using the the so-called Gibbs-Helmholtz equation,

$$\left( \frac{\partial(\Delta_{fus}\mu/T)}{\partial T} \right)_P = - \frac{\Delta_{fus}H}{T^2}, \quad (5.59)$$

Eq. (5.58) reduces to

$$\frac{d \ln(x_1)}{dT} = \frac{\Delta_{fus}H}{R T^2}, \quad (5.60)$$

Now we can integrate both sides of Eq. (5.59). The right hand side from mole fraction equal to unity  $X = 1$  (pure solvent) to the mixture with mole fraction equal to  $X_1$ . The right hand side from the normal pure solvent's freezing temperature to the new freezing temperature for the mixture,

$$\int_{X=1}^{X_1} d \ln X = \int_{T_F^*}^{T'_F} \frac{\Delta_{fus}H}{R} \frac{dT}{T^2}. \quad (5.61)$$

Assuming a temperature independent  $\Delta_{fus}H$ , we get

$$\ln(X_1) = \frac{\Delta_{fus}H}{R} \left[ \frac{1}{T_F^*} - \frac{1}{T'_F} \right]. \quad (5.62)$$

This expression is valid for ideal solution with an enthalpy of fusion independent of temperature. For non ideal solutions the mole fraction in Eq. (5.62) is replaced by the activity,  $a_1$ .

In the case of dilute solutions,  $X_2 \ll 1$ , we can expand the logarithm of the mole fractin in Eq. (5.62),

$$\ln(X_1) = \ln(1 - X_2) \approx - X_2. \quad (5.63)$$

Assuming  $T_F^* > T'_F$  and Eq. (5.63), Eq. (5.62) reduces to

$$X_2 = \frac{\Delta_{fus}H}{R} \frac{T_F^* - T'_F}{T_F^* T'_F}. \quad (5.64)$$

If we now solve for  $T'_F$ , we get

$$T'_F = \frac{T_F^*}{1 + X_2 \frac{RT_F^*}{\Delta_{fus}H}} . \quad (5.65)$$

Under the following condition:

$$X_2 \frac{R T^*}{\Delta_{fus}H} \ll 1, \quad (5.66)$$

the solvent's freezing temperature reduces to

$$T'_F = T_F^* \left[ 1 - X_2 \frac{R T_F^*}{\Delta_{fus}H} \right] . \quad (5.67)$$

In this case the change in freezing temperature is given by:

$$\begin{aligned} T_F^* - T'_F &\equiv \Delta_{fus}T \\ &= X_2 \left[ \frac{R T_F^{*2}}{\Delta_{fus}H} \right] . \end{aligned} \quad (5.68)$$

Equation (5.68) can be used to the determination of molar masses of dissolved macromolecules. For this purpose we will relate the solute's mole fraction,  $X_2$ , with its molal concentration. This relation is obtained first by noting that  $n_1 \gg n_2$  and second using the following relations:

$$\begin{aligned} X_2 &= \frac{n_2}{n_1 + n_2} \\ &\approx \frac{n_2}{n_1} \\ &= \frac{n_2}{W_1} \frac{W_1}{n_1} \\ &= m_2 M_1 , \end{aligned} \quad (5.69)$$

where  $W_1$  is the solvent's weight,  $M_1$  is the solvent's molecular mass, and  $m_2$  is the solute's molal concentration. Using this relation, Equation (5.68) reduces to

$$\Delta_{fus}T \approx \left[ \frac{M_1 R T_F^{*2}}{\Delta_{fus}H} \right] m_2 . \quad (5.70)$$

Defining the freezing point constant as

{col15}

$$K_f \equiv \frac{M_1 R T_F^{*2}}{\Delta_{fus} H}, \quad (5.71)$$

the following relation between the solute's molecular mass and the change in freezing temperature can be derived:

{col16}

$$m_2 = \frac{n_2}{W_1} = \frac{W_2}{M_2} \frac{1}{W_1} = \frac{\Delta_{fus} T}{K_f}. \quad (5.72)$$

Hence for dilute solution and small changes in the solution's freezing temperature, the solutes molecular mass is given by:

{col17}

$$M_2 = \frac{K_f W_2}{\Delta_{fus} T W_1}, \quad (5.73)$$

where the solvent's and solute's weights and change in freezing temperature are readily measurable.

The system could be viewed as a saturated solution of solid 1 in solvent 2. We can think that the solid solute is at equilibrium with its liquid phase inbeded in the solvent. In this case we are looking at the "freezing of the solute" at a new freezing,  $T'_F \rightarrow T$ , temperature interpreted as the temperature at which solubility is measured. Therefore Eq. (5.62) applies to the solute's solubility i.e.,

{col18}

$$\ln(X_2) = \frac{\Delta_{fus} H_2}{R} \left[ \frac{1}{T_{2F}^*} - \frac{1}{T} \right]. \quad (5.74)$$

Equation (5.74) represents a relation between solubility,  $X_2$ , and the temperature for and ideal system. Notice that the solubility is independent of the solvent.

### 5.3.2 Boiling point elevation

{col19}

$$\ln(X_1) = -\frac{\Delta_{vap}H_1}{R} \left[ \frac{1}{T_{1b}^*} - \frac{1}{T'_b} \right]. \quad (5.75)$$

For a dilute solution we have

$$T'_b - T_b = \Delta_{vap}T = K_b m_2 \quad (5.76)$$

$$K_b = \frac{M_1 RT_b^{*2}}{\Delta_{vap}H_1} \quad (5.77)$$

### 5.3.3 Osmotic pressure

In this case we consider the change in chemical potential as we change the pressure.

$$\mu(T, P + \pi, X_1) = \mu^*(T, P) \quad (5.78)$$

$$\mu^*(T, P + \pi) + RT \ln(X_1) = \mu^*(T, P) \quad (5.79)$$

Notice that we have assumed ideal slution behavior.

$$\left( \frac{\partial \mu^*}{\partial P} \right)_{T, n_i} = \bar{V}_1^* \quad (5.80)$$

$$\int_{\mu^*(P)}^{\mu^*(T, P + \pi)} d\mu^* = \int_P^{P + \pi} \bar{V}_1^* dP \quad (5.81)$$

$$\mu^*(T, P + \pi) \approx \mu^*(T, P) + \bar{V}_1^* \pi \quad (5.82)$$

Using this result in Eq. (5.79) we get

$$\pi = -\frac{RT}{\bar{V}_1^*} \ln(X_1) \quad (5.83)$$

Typically  $n_1 \gg n_2$  therefore the following approximation holds for dilute solutions:

$$\ln(X_1) = \ln(1 - X_2) \approx -X_2 \approx -\frac{n_2}{n_1} \quad (5.84)$$

$$\pi = \frac{n_2}{n_1 \bar{V}_1^*} RT = [2] R T , \quad (5.85)$$

where [2] is the solute's molar concentration. Equation (5.86) can be used to determine the molar masses of macromolecules. First recall {os9}

$$\frac{n_2}{n_1 \bar{V}_1^*} = \frac{W_2}{M_2 V} . \quad (5.86)$$

{os10}

second solve for  $M_2$

$$M_2 = \frac{RT}{\pi} \frac{W_2}{V} = RT C_2 , \quad (5.87)$$

where  $C_2$  is the solutes concentration in grams of solute per liter of solvent. Equation (5.86) is known as the Van't Hoff's equation.

{os11}

In practice solutions may not behave ideally. In this cases you have to plot  $\frac{\pi}{C_2}$  vs  $c_2$  and extrapolate the curves for  $C_2 = 0$ , i.e.,

$$M_2 = \lim_{C_2 \rightarrow 0} \frac{RT}{\frac{\pi}{C_2}} \quad (5.88)$$

## 5.4 Problems

Prove that by including the temperature behavior of  $\Delta_{melt}H$  and the non ideality of the solution through the activity coefficient, Eq. (5.62) gets changed into

{pcol1}

$$\begin{aligned} \ln(X_1) &= \frac{\Delta_{fus}H}{R} \left[ \frac{1}{T_F^*} - \frac{1}{T'_F} \right] \\ &- \Delta C_P T_F^* \left[ \frac{1}{T_F^*} - \frac{1}{T'_F} \right] \\ &+ \frac{\Delta C_P}{R} \ln \left( \frac{T'_F}{T_F^*} \right) - \ln(\gamma(X_1)). \end{aligned} \quad (5.89)$$

For dilute solutions and small chnges in freezing temperature, we can reduce the previous equation to

{pcol2}

$$X_2 = \frac{\Delta_{fus}H}{R} \frac{\Delta_{fus}T}{T_F^{*2}} \frac{1}{1 + \left( \frac{d\gamma(X_1)}{dX_1} \right)_{x_1=1}}. \quad (5.90)$$

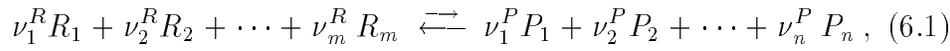


# Chapter 6

## Chemical equilibrium

In the case of chemical reactions, we can consider the following general notation:

{ml1}



where R stands for reactants, P for products and the  $\nu_i^{R,P}$  for the stoichiometric coefficients. For this reaction the Gibbs free energy is given by:

{ml1b}

$$G = \sum_{i=1}^m n_{R_i} \mu_i(R) + \sum_{i=1}^n n_{P_i} \mu_i(P). \quad (6.2)$$

For Eq. (6.2) the differential change reduces to

{ml1c}

$$dG = \sum_{i=1}^m dn_{R_i} \mu_i(R) + \sum_{i=1}^n dn_{P_i} \mu_i(P), \quad (6.3)$$

where we have used the chemical potential's independence on the number of moles.

In the case of differential changes in the number of moles of reagents the following relation is satisfied:

{ml2}

$$-\frac{dn_{R_1}}{\nu_1^R} = -\frac{dn_{R_2}}{\nu_2^R} = \cdots = \frac{dn_{R_m}}{\nu_m^R} = \frac{dn_{P_1}}{\nu_1^P} = \frac{dn_{P_2}}{\nu_2^P} = \cdots = \frac{dn_{P_n}}{\nu_n^P} \equiv d\xi, \quad (6.4)$$

where  $\xi$  is a variable called the extent of the reaction, and it is a measure of the number of reactive events. Using the extent of the reaction

variable the differential changes in the number of moles can be expressed as

$$dn_{R_i} = - \nu_i^R d\xi \quad (6.5) \quad \text{\{ml3\}}$$

\{ml4\}

$$dn_{P_i} = + \nu_i^P d\xi . \quad (6.6)$$

\{ml5\}

Using Eqs. (6.5) - (6.6) we can rewrite Eq. (6.3) as

$$dG = \left[ \sum_{i=1}^n \nu_i^P \mu_i(P) - \sum_{i=1}^m \nu_i^R \mu_i(R) \right] d\xi . \quad (6.7)$$

\{ml6\}

At equilibrium  $dG = 0$ , and since  $d\xi \neq 0$ , we get a generalization of the Law of Mass Action. The law of mass action was first postulated for ideal systems in 1867 by Goldberg and Weage.

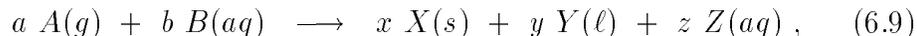
$$\sum_{i=1}^n \nu_i^P \mu_i(P) - \sum_{i=1}^m \nu_i^R \mu_i(R) = 0 . \quad (6.8)$$

Equation (6.8) not only can be applied to ideal systems but also to non ideal systems by the inclusion of the activities in the chemical potential.

Previously we have calculated the most general expressions for the chemical potentials for gases, solvents, solutes, and solids in terms of an arbitrary set of conditions, which defines a reference state or commonly called standard state.

\{kc1\}

Now we consider the following general chemical reaction:



where Eq. (6.9) represents a chemical reaction where a moles of A react with b moles of B yielding x moles of X, y moles of Y and z moles of Z. If we want to calculate the change in Gibbs free energy, we have to consider the difference in Gibbs free energy between the products and reactants. Since the chemical potential is the molar Gibbs free energy, we can obtain the total change in Gibbs free energy as a function of the chemical potential Notice that we have explicitly included the unit mole after each stoichiometric coefficient to obtain the contribution to the Gibbs energy of each reactant and product.

\{kc2\}

Now, if we use the expressions for the chemical potentials calculated in the previous chapter, we get

$$\begin{aligned}
\Delta G_{rxn} &= x \text{ mole } [\mu_X^\circ(T, P_{X \text{ ref}}) + RT \ln(a_{Solid})] \\
&+ y \text{ mole } [\mu_Y^*(T, P_{Y \text{ ref}}) + RT \ln(a_{Solvent})] \\
&+ z \text{ mole } \left[ \mu_Z^\ominus(T, P_{Z \text{ ref}}) + RT \ln\left(\frac{a_Z}{a_{Z \text{ ref}}}\right) \right] \\
&- a \text{ mole } \left[ \mu_A^\circ(T, P_{A \text{ ref}}) + RT \ln\left(\frac{a_{P_A}}{P_{A \text{ ref}}}\right) \right] \\
&- b \text{ mole } \left[ \mu_B^\ominus(T, P_{B \text{ ref}}) + RT \ln\left(\frac{a_B}{a_{B \text{ ref}}}\right) \right] \quad (6.10)
\end{aligned}$$

Using the following expressions:

{kc3}

$$\begin{aligned}
\Delta G_{rxn}^{\circ'} &= x \text{ mole } \mu_X^\circ(T, P_{X \text{ ref}}) + y \text{ mole } \mu_Y^*(T, P_{Y \text{ ref}}) \\
&+ z \text{ mole } \mu_Z^\ominus(T, P_{Z \text{ ref}}) - a \text{ mole } \mu_A^\circ(T, P_{A \text{ ref}}) \\
&- b \text{ mole } \mu_B^\ominus(T, P_{B \text{ ref}}) , \quad (6.11)
\end{aligned}$$

{kc4}

$$Q \equiv \left[ \frac{(a_{solid})^x (a_{Solvent})^y \left(\frac{a_Z}{a_{Z \text{ ref}}}\right)^z}{\left(\frac{a_A}{a_{A \text{ ref}}}\right)^a \left(\frac{a_B}{a_{B \text{ ref}}}\right)^b} \right] . \quad (6.12)$$

Eq. (6.12)w yields

{kc5}

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ'} + R' T \ln(Q) . \quad (6.13)$$

Notice that Eqs. (6.12) - (6.13) refer to an arbitrary set of conditions, which define a standard state. We have defined R' as the product of one mole times the gas constant, R.

For most chemical reaction involving solid phases, the solid phase involved will not contribute to the quotient i.e.,

{kc6}

$$a_{Solid} = \exp\left(\frac{\bar{V} \Delta P}{RT}\right) \approx 1 , \quad (6.14)$$

where  $\Delta P$  is the total pressure change with respect to the reference pressure on the solid. Thus

{kc7}

$$R' T \ln(Q) \equiv \left[ \frac{(a_{Solvent})^y \left(\frac{a_Z}{a_{Z\ ref}}\right)^z}{\left(\frac{a_A}{a_{A\ ref}}\right)^a \left(\frac{a_B}{a_{B\ ref}}\right)^b} \right] . \quad (6.15)$$

{kc8} For dilute solutions, the activity coefficients are approximately unity, which means that the reactants and products behave. Therefore for ideal behavior, Eq. (6.15) reduces to

$$R' T \ln(Q) \equiv \left[ \frac{(X_{Solvent})^y \left(\frac{[Z]}{[Z]_{ref}}\right)^z}{\left(\frac{P_A}{P_{A\ ref}}\right)^a \left(\frac{[B]}{[B]_{ref}}\right)^b} \right] , \quad (6.16)$$

{kc9} where we have intentionally left the solvent mole fraction,  $X_{Solvent}$ , which for dilute solutions is approximately equal to unity, i.e.,

$$X_{Solvent} \approx 1 . \quad (6.17)$$

{kc10} Finally using Eq.(6.17), we obtain a general expression for the quotient

$$Q = \left[ \frac{\left(\frac{[Z]}{[Z]_{ref}}\right)^z}{\left(\frac{P_A}{P_{A\ ref}}\right)^a \left(\frac{[B]}{[B]_{ref}}\right)^b} \right] . \quad (6.18)$$

{kc11} Notice that Eq. (6.18) allow us to define a set of reference pressures and concentrations. For example, if all reference pressures are set equal to one atmosphere and the concentrations set equal to one mole, the reference state is the standard state used in physical chemistry. In this case, Eq. (6.18) reduces to

$$Q = \left[ \frac{\left(\frac{[Z]}{M}\right)^z}{\left(\frac{P_A}{atm}\right)^a \left(\frac{[B]}{M}\right)^b} \right] , \quad (6.19)$$

{kc12} and Eq. (6.13) reduces to

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + R'T \ln \left[ \frac{\left(\frac{[Z]}{M}\right)^z}{\left(\frac{P_A}{atm}\right)^a \left(\frac{[B]}{M}\right)^b} \right] . \quad (6.20)$$

Notice that the choice of reference states affects  $\Delta G_{rxn}^{\circ}$  through the reference chemical potentials,  $\mu_i^{\circ}$ , of all the reactants and products

in their respective phases. The reference chemical potentials depend on the chosen reference conditions. And, only under the conditions expressed by Eqs. (6.14) and (6.17) the quotient,  $Q$ , depends on the reactants and products in gas and aqueous phases.

Since the choice of reference states is arbitrary, Eq. 6.18 allows us to write the quotient as a function of those conditions. For example, if we only change one reference concentration and select  $10^{-7} M$  to be the reference concentration for the hydrogen ion in aqueous form, we have the biochemical standard state. Notice that since we have modified the reference concentrations we have affected the corresponding reference chemical potential. Another possibility will be to change the gas pressures. For example we can select the physiological pressures of oxygen, nitrogen and carbon dioxide and define this as a physiological standard state.

Finally, if we consider Eqs. (6.20) and assume equilibrium, we get {kc13}

$$\Delta G_{rxn}^{\circ} = - R' T \ln \left[ \frac{\left( \frac{[Z]^{eq}}{[Z]_{ref}} \right)^z}{\left( \frac{P_A^{eq}}{P_{A ref}} \right)^a \left( \frac{[B]^{eq}}{[B]_{ref}} \right)^b} \right] \equiv - R' T \ln(K), \quad (6.21)$$

where  $K$  is the equilibrium constant defined by the reference states. Although we are free to select the reference states, the net change in Gibbs energy of any reaction is completely independent of the choice of reference states. In other words, the numerical value of  $\Delta G_{rxn}^{\circ}$  is independent of the standard state.

For non ideal behavior we obtain the following expression for the quotient: {kc14}

$$Q = \frac{\left( \frac{a_Z}{a_{Z ref}} \right)^z}{\left( \frac{a_A}{a_{A ref}} \right)^a \left( \frac{a_B}{a_{B ref}} \right)^b}, \quad (6.22)$$

where we have used the conditions  $a_{solid} = 1$  and  $a_{Solvent} = 1$  in Eq. (6.12). Usually, the reference activity is defined as unity for the reference concentration.

In the previous section, we have derived an explicit expression of the reference chemical potential which depends on the choice of reference concentrations, pressures and temperatures. We stress the fact

that such choice is completely arbitrary and in most cases this is made based on working conditions. Using these expressions, we have calculated the change in Gibbs free energy for a chemical reaction and shown that under general conditions the quotient depends on all the reactants and products in their respective phases. We use  $R' = \text{mole } R$  instead of the more commonly used  $R$  notation to clearly show that the constant multiplying the temperature in the net change of Gibbs energy for a chemical reaction does not have the units of mole as in the gas constant. We also emphasised the different approximations usually assumed and shown that under specific conditions we obtain a quotient which depends only on reactants and products in gas or aqueous phase as is typically taught in introductory chemistry. Therefore this particular form of the quotient will break down if the conditions of compressibility for the solids and dilution for the solvent are not met. In this case our Eq. (6.13) has to be used. Finally, Eq. (6.21) allows us in a to define in an easy and direct way the reference states for the standard state used in physical chemistry, biochemistry and physiology.

# Chapter 7

## Electrolyte solutions

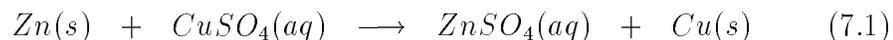
Among solutions, electrolyte solutions are found in a variety of phenomena ranging from simple chemical reaction to energy transduction at the cellular level. Since electrolyte solutions are characterized by the presence of ions and these ions show a long range interaction due to the ionic charge. This long range interaction motivates us to consider the non ideality of these class of solutions.

### 7.1 Electrochemical cell

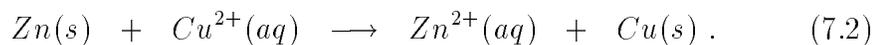
One of the most important are the electron transfer reactions. In this section we will consider this type of reactions. First we will discuss some general aspects and definitions. Second we will consider the thermodynamic aspects of electrochemical cells.

#### 7.1.1 General aspects

In this section we will start our discussion on electrochemical cell by considering the following spontaneous reaction:



or

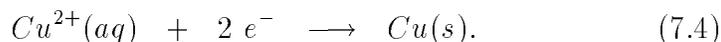


Notice that spontaneously electrons were transferred from Zn to Cu. In this case we can think in modifying the set up in such a way to obtain a current which will be able to do some work. First we consider the following oxidation and reduction reactions:

{cel3}



{cel4}



Now we can separate the Zn(s) and the Cu(s) by building an oxidation half-reaction and a reduction half-reaction. In this way electrons flow from the zinc electrode to the copper electrode. The current in the solution and the salt bridge is carried by ions. For example  $\text{Cl}^{-}$  ions from the salt bridge flow in to the zinc side, and  $\text{K}^{+}$  ions, also from the salt bridge, flow to the copper side. Note that  $\text{Cl}^{-}$  moves towards the negative electrode and  $\text{K}^{+}$  moves towards the positive electrode. The salt bridge conducts electricity but does not allow bulk mixing of the two solutions. Typical salt bridges are made of an strong electrolyte in a agar gel. Also porous partitions are used, but it sets up a small emf

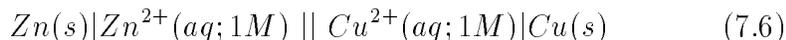
The cell notation is expressed in a condensed form by listing in sequence the various phases in contact. We start with the anode on the left and ending with the cathode on the right. The concentrations or pressures of all participating ions or gases are given in parenthesis. A single solid vertical line shows the presence of a phase boundary, and a double solid lines represents a salt bridge between the two half-cell reactions. For example

{cel5}



{cel6}

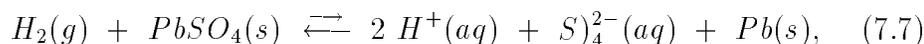
or



The difference in electrical potential between the anode and the cathode of a cell is called the cell electromotive force (emf), cell potential or cell voltage, and which is designated by the symbol E or  $E$ . This cell voltage is a measure of a driving force of the cell reaction.

For electrochemical cells the voltage generated depends upon the cell reaction and the concentrations and pressures of the various components. But it is independent of the size of the electrodes and the

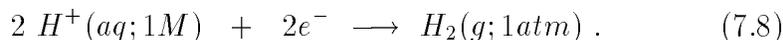
volumes of the various solutions involved. For example in the case of the following reaction:



we find the following behavior:

Change to experiental conditions	Change to cell voltage
a) Increase in $P_{H_2}$	↑
b) Increase size of Pb(s) electrode	no change
c) Decrease pH ( $[H^+] \uparrow$ )	↓
d) Dilute cell ( $[SO_4^{2-}] \downarrow$ )	↑
e) Dissolution of $Na_2SO_4(s)$ ( $[SO_4^{2-}] \uparrow$ )	↓
f) Decrease amount of $PbSO_4(s)$	no change
g) Dissolution of some NaOH(s) ( $[H^+] \downarrow$ )	↑

Since oxidation and reduction always occur together, the voltage of a single electrode cannot be measured. Only differences in voltage are measurable. Therefore a particular electrode can be chosen as a reference electrode. We can assign a voltage to a given half-cell reaction or electrode and then refer all measured voltages relative to it. The standard hydrogen electrode has been chosen to be a reference electrode



where the temperature is 25 °C. By convention

$$E_{red}^\circ(H^+/H_2) = 0. \quad (7.9)$$

Now we can set up a table of standard reduction potentials. For example



In general a complete electrochemical cell reaction consists of two half-reactions, i.e.,

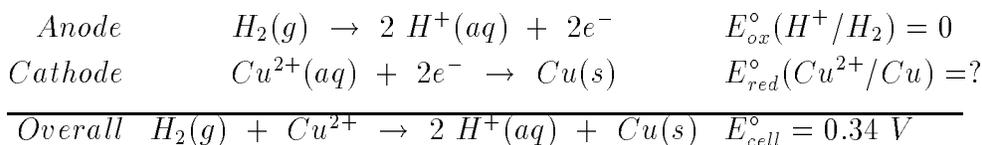
$$E_{cell}^\circ = E_{red}^\circ(cathode) + E_{ox}^\circ(anode), \quad (7.11)$$

where

$$E_{ox}^{\circ}(anode) = - E_{red}^{\circ}(anode) . \quad (7.12)$$

Therefore for Eq. (7.10) we have

{cel12}



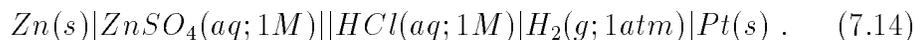
{cel13}

But from Eq. (7.11)

$$\begin{aligned} E_{cell}^{\circ} &= 0.34 V \\ &= E_{red}^{\circ}(Cu^{2+}/Cu) + E_{ox}^{\circ}(H^+/H_2) \\ &= E_{red}^{\circ}(Cu^{2+}/Cu) , \end{aligned} \quad (7.13)$$

where we have used Eq. (7.9). In a similar fashion we can analyze the following half-reaction:

{cel14}



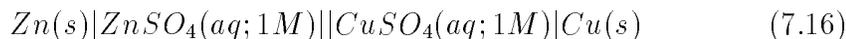
{cel15}

For this redox couple we find

$$\begin{aligned} E_{cell}^{\circ} &= 0.76 V \\ &= E_{ox}^{\circ}(Zn^{2+}/Zn) + E_{red}^{\circ}(H^+/H_2) \\ &= - E_{red}^{\circ}(Zn^{2+}/Zn) . \end{aligned} \quad (7.15)$$

In a similar way we can continue for other half-reactions and construct a table of Standard Reduction Potentials at 298.15K. From such a table we can consider other electrochemical cell reactions. For instance for the following cell:

{cel16}



{cel17}

the cell potential is given by:

$$\begin{aligned} E_{cell}^{\circ} &= E_{ox}^{\circ}(Zn^{2+}/Zn) + E_{red}^{\circ}(Cu^{2+}/Cu) \\ &= - E_{red}^{\circ}(Zn^{2+}/Zn) + E_{red}^{\circ}(Cu^{2+}/Cu) \\ &= 0.76V + 0.34V \\ &= 1.10V . \end{aligned} \quad (7.17)$$

An external potential or counter potential could change the flow of electrons. For example if the counter potential is less than the cell potential, electrons will flow from left to right; Zn(s) gets oxidized. But if the counter potential is greater than the cell potential, electrons will flow from right to left;  $Zn^{2+}(aq)$  gets reduced. Consequently we can set up a reversible chemical cell with the help of an counter potential

### 7.1.2 Electrodes

A redox couple consist of the oxidized and reduced forms of the same species undergoing oxidation or reduction. The electrodes are reduced states of a redox couple. For example the Zn and Cu electrodes are reduced forms of the  $Zn^{2+}/Zn$  and  $Cu^{2+}/Cu$  redox couples.

Inert electrodes are use in solutions when both the oxidized and reduced states of species are ions. For example platinum and graphite are chemical inert and conducting materials. The sole function of this electrodes are to provide a surface at which ions in solution can donate or accept electrons from the external circuit. In this group the redox couples  $Fe^{3+}/Fe^{2+}$  and  $Ce^{4+}/Ce^{3+}$  are commonly used.

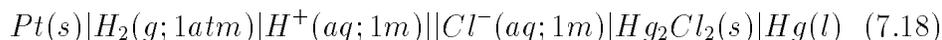
When one of the reactants or products of a redox reaction is a gas, we use a gas electrode wher electrons are transfered between the gaseous phase and the external circuit. For these electrodes a platinum electrode where the surface has been increased is typically used. The redox couples  $H^+/H_2$  and  $Cl_2/Cl^-$  are examples of gas electrodes.

Finally a metal/insoluble salt electrode is an electrode where the metal, which is the reduced form, is coated with the insoluble salt. For example Ag coated with AgCl. This electrode is inmerse in a solution containing the ion of the salt. The concentration of the  $Ag^+$  ion is fixed by the concentration of  $Cl^-$  and the value of the solubility product.

Other standard electrodes are:

**Calomel electrode** A mercury/mercurous chloride (calomel) electrode has a half-reaction potential of 0.3338V,

{cel18}



**Glass electrode** A glass electrode uses a glass membrane to selectively permeable to hydrogen ions,  $H^+$ . At present we can find more

that 50 selective ion glass and membrane electrodes. These electrodes are highly selective to a particular ion. For example, a sodium electrode is  $10^4$  times more responsive to  $Na^+$  than to  $K^+$ .

### 7.1.3 Thermodynamics

The electrical work done by an electrochemical cell is given by the product of the total charge delivered ( $nF$ ) by the cell times the cell potential ( $E$ ). In its differential form we have

$$dW_e = -E dq , \quad (7.19)$$

where  $dq$  stands for the infinitesimal amount of charge. If we integrate both sides and recalling that  $E$  is independent of the charge delivered, we get

$$W_e = -nF E , \quad (7.20)$$

where  $n$  is the number of moles of electrons transferred from the anode to the cathode and  $F$  is the Faraday constant, which is defined as the charge of one mole of electrons ( $96,485 C mol^{-1}$ ). Therefore

$$\Delta G = W_{nonPV} = -nF E . \quad (7.21)$$

Under standard conditions

$$\Delta G^\circ = -nF E^\circ , \quad (7.22)$$

where  $E^\circ$  is the standard cell potential (emf). From Eq. (7.22) we get an expression for the equilibrium constant i.e.,

$$K^{equ} = \exp \left\{ \frac{nF}{RT} E^\circ \right\} . \quad (7.23)$$

Also for non standard conditions we have a relation between the cell voltage and concentrations and/or pressures of the species involved in the electrochemical cell reaction,

$$\begin{aligned} \Delta G &= \Delta G^\circ + R'T \ln Q \\ &= -nF E^\circ + R'T \ln Q \\ &= -nF E . \end{aligned} \quad (7.24)$$

From Eq. (7.24) we get

$$E = E^\circ - \frac{R'T}{nF} \ln Q, \quad (7.25)$$

which is called the Nernst equation and expresses the relation between the cell voltage and the standard cell potential and the quotient. For example if we consider Eq. (7.2) the equation for the cell potential as a function of the concentrations is given by:

$$\begin{aligned} E &= E^\circ - \frac{R'T}{2F} \ln \left[ \frac{[Zn^{2+}]}{[Cu^{2+}]} \right] \\ &= 1.10V - 0.0128V \ln \left[ \frac{[Zn^{2+}]}{[Cu^{2+}]} \right], \end{aligned} \quad (7.26)$$

where we have considered  $T = 298.15K$ . Notice that the modification to the standard cell potential are in the order of millivolts. Also notice that Eq. (7.26) assumes ideal behavior.

In order to include real behavior the quotient in Eq. (7.25) has to include the activities i.e.,

$$E = E^\circ - \frac{R'T}{nF} \ln \left( \frac{a_{Products}}{a_{Reactants}} \right). \quad (7.27)$$

Finally from the previous discussions the following thermodynamic relations apply the cell potential E:

$$\Delta S = - \left( \frac{\partial \Delta G}{\partial T} \right)_P = nZ F \left( \frac{\partial E}{\partial T} \right)_P, \quad (7.28)$$

$$\Delta H = -n Z F \left[ E - T \left( \frac{\partial E}{\partial T} \right)_P \right]. \quad (7.29)$$

Therefore if we know the cell potential at constant pressure as a function of the temperature, we know the change in Gibbs energy and we can calculate the changes in entropy and enthalpy.

**Electrochemical potential**

The differential form of Eq. (7.24) is given by:

$$dG = -ZF E dn , \quad (7.30)$$

where  $Z$  is the ionic charge. But

$$\begin{aligned} dG + ZF E dn &= \mu dn + ZF E dn = 0 \\ &= (\mu + ZF E) dn \\ &\equiv \tilde{\mu} dn, \end{aligned} \quad (7.31)$$

where we have defined the electrochemical potential as

$$\tilde{\mu}_i \equiv \mu_i^\ominus + RT \ln Q + ZF E . \quad (7.32)$$

The electrochemical potential is the molar Gibbs energy of a system with PV work and electrical work.

**7.2 Mean activity coefficient**

In general the chemical potential of an ion in solution is given by:

$$\mu_i = \mu_i^\ominus + RT \ln(m_i \gamma_i) , \quad (7.33)$$

where  $\gamma_i$  is the activity coefficient. The term  $RT \ln(\gamma_i)$  represents the correction to the ideal behavior. Namely it is the contribution due to the interaction between the ions. This contribution is given by the non PV work,

$$\mu_i - \mu_{i \text{ Ideal}} = \ln(\gamma_i) = W_{nonPV} , \quad (7.34)$$

where

$$\mu_{i \text{ Ideal}} = \mu_i^\ominus + RT \ln(m_i) . \quad (7.35)$$

Since we can not measure individual activity coefficients we have to define a salt chemical potential. For example consider a solid compound,  $AC(s)$ , which dissolves producing  $\nu_-$  anions,  $A^{Z-}$ , with ionic charge equal to  $Z_-$  and  $\nu_+$  cations,  $C^{Z+}$ , with ionic charge equal to  $Z_+$ ,



In this case we define the salt chemical potential as

$$\mu_{Salt} \equiv \frac{\nu_+ \mu_+ + \nu_- \mu_-}{\nu_+ + \nu_-} \quad (7.37)$$

$$\equiv \frac{\mu_{\pm}}{\nu_+ + \nu_-} . \quad (7.38)$$

In general the chemical potential have the general form given in Eq. (7.33). Using this functional form, we find that  $\mu_{\pm}$  is given by:

$$\begin{aligned} \mu_{\pm} &= \nu_+ \mu_+ + \nu_- \mu_- \\ &= \nu_+ \mu_+^{\ominus} + \nu_+ \mu_+^{\nu} + RT \nu_+ \ln(a_+) + RT \nu_- \ln(a_-) \\ &= \mu_{\pm}^{\ominus} + RT \ln[a_+^{\nu_+} a_-^{\nu_-}] \\ &= \mu_{\pm}^{\ominus} + RT \ln(m_+^{\nu_+} m_-^{\nu_-}) + RT \ln(\gamma_+^{\nu_+} \gamma_-^{\nu_-}) , \end{aligned} \quad (7.39)$$

where

$$\mu_{\pm}^{\ominus} \equiv \nu_+ \mu_+^{\ominus} + \nu_- \mu_-^{\ominus} . \quad (7.40)$$

Now we define the mean activity,  $a_{\pm}$ , as

$$\begin{aligned} a_{\pm}^{(\nu_+ + \nu_-)} &\equiv m_{\pm}^{(\nu_+ + \nu_-)} \gamma_{\pm}^{(\nu_+ + \nu_-)} \\ &\equiv a_+^{\nu_+} a_-^{\nu_-} \\ &= m_+^{\nu_+} m_-^{\nu_-} \gamma_+^{\nu_+} \gamma_-^{\nu_-} . \end{aligned} \quad (7.41)$$

From Eq. (7.41) we define the mean concentration,  $m_{\pm}$ , and the mean activity coefficient,  $\gamma_{\pm}$ , as

$$m_{\pm}^{(\nu_+ + \nu_-)} \equiv m_+^{\nu_+} m_-^{\nu_-} , \quad (7.42)$$

$$\gamma_{\pm}^{(\nu_+ + \nu_-)} \equiv \gamma_+^{\nu_+} \gamma_-^{\nu_-} . \quad (7.43)$$

Therefore we get

$$\mu_{Salt} = \mu_{Salt}^{\ominus} + RT \ln(m_{\pm}) + RT \ln(\gamma_{\pm}) , \quad (7.44)$$

where we have defined the salt reference chemical potential by the following expression:

$$\mu_{Salt}^{\ominus} \equiv \frac{\nu_+ \mu_+^{\ominus} + \nu_- \mu_-^{\ominus}}{\nu_+ + \nu_-} . \quad (7.45)$$

Notice that if know the total molality,  $m$ , we can calculate the mean molality using the following relations: {mac13}

$$m_+ = \nu_+ m \quad (7.46)$$

$$m_- = \nu_- m \quad (7.47)$$

$$m_{\pm} = m [\nu_+^{\nu_+} \nu_-^{\nu_-}]^{\frac{1}{\nu_+ + \nu_-}} . \quad (7.48)$$

{mac14} From Eq. (7.44) we get

$$\begin{aligned} \ln(\gamma_{\pm}) &= \frac{1}{\nu_+ + \nu_-} \ln[\gamma_+^{\nu_+} \gamma_-^{\nu_-}] \\ &= \frac{1}{\nu_+ + \nu_-} \{\nu_+ \ln(\gamma_+) + \nu_- \ln(\gamma_-)\} . \end{aligned} \quad (7.49)$$

{mac15} From the Debye-Hückel theory we recall the value of  $\ln(\gamma_i)$  for an ion in solution,

$$\ln(\gamma_i) = - \frac{Z_i^2 |e|^2 N_o \kappa}{8\pi \epsilon_o \epsilon RT} , \quad (7.50)$$

{mac16} where  $Z_i$  is the ionic charge of the  $i^{th}$  ion,  $|e|$  the absolute value of the electronic charge,  $\epsilon_o$  and  $\epsilon$  the vacuum and solvent permittivities. A measure of the ionic shell is given by the Debye length defined by  $\kappa^{-1}$ , with

$$\kappa = \left( \frac{2N_o^2 |e|^2 \rho_{Solvent} I}{\epsilon_o \epsilon RT} \right)^{\frac{1}{2}} , \quad (7.51)$$

{mac17} where  $\rho_{Solvent}$  is the solvents density and  $I$  the molality ionic strength defined as

$$I = \frac{1}{2} \sum_i m_i Z_i^2 , \quad (7.52)$$

{mac18} where the sum considers all the different ionic species in solution.

Using Eq. (7.50) in Eq. (7.49) we get

$$\ln(\gamma_{\pm}) = \frac{1}{\nu_+ + \nu_-} \left( \frac{(-1) |e|^2 N_o \kappa}{8\pi \epsilon_o \epsilon RT} \right) [\nu_+ Z_+^2 + \nu_- Z_-^2] . \quad (7.53)$$

{mac19} From the solution's electroneutrality we have the following relation:

$$\nu_+ Z_+ + \nu_- Z_- = 0 , \quad (7.54)$$

but in the case of the anion the ionic charge is a negative number,  $Z_- = -|Z_-|$ . With relation Eq. (7.54) reduces to {mac20}

$$Z_+ \nu_+ = |Z_-| \nu_- . \quad (7.55)$$

Using Eq. (7.55) we get {mac21}

$$\ln(\gamma_{\pm}) = -|Z_+| |Z_-| B_{Solvent}(T) \sqrt{I} , \quad (7.56)$$

with {mac22}

$$B_{Solvent}(T) = \frac{|e|^2 N_o}{8\pi \epsilon_o \epsilon R} \sqrt{\frac{2 |e|^2 N_o^2}{\epsilon_o \epsilon R} \frac{\sqrt{\rho_{Solvent}(T)}}{T^{\frac{3}{2}}}} . \quad (7.57)$$

For water at 298 K, Eq. (7.56) reduces to {mac23}

$$\begin{aligned} \epsilon &= 78.54 \\ \rho_{H_2O(\ell)} &= 0.997 \text{ Kg } dm^{-3} \\ \log(\gamma_{\pm}) &= -0.509 |Z_+| |Z_-| \sqrt{I} . \end{aligned} \quad (7.58)$$

### 7.3 Debye-Hückel theory

In the Debye-Hückel theory we consider the solute-solute interactions (ion-ion). For example we consider a one to one electrolyte i.e., NaCl,. Next we add one ion of charge  $Z_i e$  where  $e$  represents the electronic charge i.e.,  $Na^+$ . Now we look at the changes in the electrolyte solution. for example we look at a small volume away from the ion. In the presence of a dynamical active solventt we can ask for the time average of the positive and negative ions inside a differential volume  $dV$ . The number of ions inside  $dV$  is given by the Boltzman principe,

{elec1}

$$n \sim \exp \left\{ \frac{E}{RT} \right\} \quad (7.59)$$

{elec2}

where the energy  $E$  is given by the following relation:

$$E = - Z_i N_o |e| \phi . \quad (7.60)$$

In Eq. (7.60)  $Z_+ |e|$  ( $- |Z_-| |e|$ ) is the charge of the positive (negative) ion and  $\phi$  the electrostatic potential. Next we consider the total average charge inside of  $dV$  if we know the number of ions per unit volume of solution. Namely  $N_+$  and  $N_-$ . In this case we have

{elec3}

$$dN_+ = N_+ \exp \left\{ - \frac{Z_+ |e| \phi}{kT} \right\} dV , \quad (7.61)$$

{elec4}

$$dN_+ = N_- \exp \left\{ + \frac{|Z_-| |e| \phi}{kT} \right\} dV , \quad (7.62)$$

where  $N_+$  and  $N_-$  represent the total number of ions per unit volume of solution and  $k_B$  the Boltzman constant and  $R = k_B N_o$ . From electromagnetism we know that

{elec5}

$$\phi \sim \frac{1}{r} . \quad (7.63)$$

{elec6}

From this behavior we have the following asymptotics

$$\lim_{r \rightarrow 0} dN_+ = 0 \quad (7.64)$$

{elec7}

$$\lim_{r \rightarrow 0} dN_- = \infty . \quad (7.65)$$

These limit behaviors are unphysical and are the result of assuming point particles while actual ions have size. since we want to include the size of the ions, we have to recalculate  $\phi$  from the Maxwell equation. for this purpose we first find an expresion for the charge density, {elec8}

$$\begin{aligned} \rho &= \frac{|e|Z_+dN_+ - |e||Z_-|dN_-}{dV} \\ &= |e| [N_+Z_+ \exp\{-Z_+|e|\phi\beta\} \\ &\quad - N_-|Z_-| \exp\{+|Z_-||e|\phi\beta\}] , \end{aligned} \quad (7.66)$$

where we have used the notation  $\beta \equiv (k_B T)^{-1}$ . Notice that the electroneutrality condition implies  $Z_+N_+ = |Z_-|N_-$ , and we have not included the size of the ion .

If  $Z_i|e|\phi\beta$  is small we can approximate the exponential function {elec9}

$$\exp\{\mp Z_{\pm}|e|\phi\beta\} \approx 1 \mp |Z_{\pm}||e|\phi\beta . \quad (7.67)$$

With this approximation Eq. (7.66) reduces to {elec10}

$$\begin{aligned} \rho &= |e| [N_+ Z_+ - N_- |Z_-| - |e| (N_+ Z_+^2 + N_- |Z_-|^2) \phi \beta] \\ &= - \frac{|e|^2 N_o \phi}{RT} [N_+ Z_+^2 + N_- |Z_-|^2] . \end{aligned} \quad (7.68)$$

In the general case where we have several electrolytes we get for the charge density {elec11}

$$\rho = - \frac{2 |e|^2 \phi N_o}{RT} \left\{ \frac{1}{2} \sum_{i=1} N_i Z_i^2 \right\} \quad (7.69)$$

$$= - \frac{2 |e|^2 \phi N_o^2}{RT} \left\{ \frac{1}{2} \sum_{i=1} C_i Z_i^2 \right\} \quad (7.70)$$

$$= - \frac{2 |e|^2 \phi N_o^2}{RT} \left\{ \frac{\rho_{Solvent}(T)}{2} \sum_{i=1} m_i Z_i^2 \right\} , \quad (7.71)$$

where  $\rho_{Solvent}$  is the solvent's mass density,  $N_i$  the number density,  $C_i$  the molar density and  $m_i$  the molality. Notice that Eq. (7.69) is

a relation between the charge density and the electrostatic potential. But we do not know the exact nature of both the charge density and electrostatic potential. Thus we need another relation between these two functions. From the theory of electromagnetism we find a second relation between the charge density and electrostatic potential in the Maxwell's equations. In particular we will consider the first Maxwell equation,

{elec12}

$$\begin{aligned}\vec{\nabla} \cdot \vec{E} &= \left[ \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} \right] \\ &= \frac{\rho}{\epsilon_0 \epsilon},\end{aligned}\tag{7.72}$$

where  $E$  is the electric field associated to the charge density  $\rho$ . Also from electromagnetism we know that the electrostatic potential and the electric field are related by

{elec13}

$$\begin{aligned}\vec{E} &= (E_x, E_y, E_z,) \\ &= -\nabla\phi \\ &= -\left( \frac{\partial\phi}{\partial x}, \frac{\partial\phi}{\partial y}, \frac{\partial\phi}{\partial z} \right).\end{aligned}\tag{7.73}$$

{elec14}

After combining Eqs. (7.72) - (7.72) we get

$$\begin{aligned}\nabla^2\phi &= -\frac{\rho}{\epsilon_0 \epsilon} \\ &= -\left( \frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2} \right).\end{aligned}\tag{7.74}$$

Equation (7.74) relates the Laplacian of the electrostatic potential and the charge density, which can be combined with Eq. (7.69) to get a partial differential equation for the the electrostatic potential. In most cases of interest  $\rho$  and  $\phi$  will only depend on the distance away from the central charge; no angular dependance is foreseen. In other words the analysis of electrolytes is expected to have radial symmetry. Assuming radial symmetry, we get from Eq. (7.74) the following differential equation:

{elec15}

$$\begin{aligned}\nabla^2\phi &= \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d\phi(r)}{dr} \right] \\ &= \kappa^2 \phi ,\end{aligned}\tag{7.75}$$

where we have defined the following constants:

{elec16}

$$\kappa^2 \equiv \frac{2 N_o^2 |\epsilon|^2 \rho_{Solvent}(T) I}{\epsilon_o \epsilon RT} ,\tag{7.76}$$

where we have defined the ionic strength as:

{elec17}

$$I \equiv \left\{ \frac{1}{2} \sum_{i=1} m_i Z_i^2 \right\} .\tag{7.77}$$

Equation (7.75) is called the linear Poisson-Boltzman equation. It assumes no solute-solvent interactions and point ions. The general solution to Eq. (7.75) is given by:

{elec18}

$$\phi(r) = A \frac{\exp \{-\kappa r\}}{r} + B \frac{\exp \{+\kappa r\}}{r} .\tag{7.78}$$

Recalling the boundary conditions, we know that

{elec19}

$$\lim_{r \rightarrow \infty} \phi(r) = 0 ,\tag{7.79}$$

which means that  $B = 0$  or

{elec19b}

$$\phi(r) = A \frac{\exp \{-\kappa r\}}{r} .\tag{7.80}$$

Also, for point particles

{elec20}

$$\lim_{\kappa \rightarrow 0} \phi(r) = \frac{Z_i |e|}{4\pi \epsilon_o \epsilon r} ,\tag{7.81}$$

which means

{elec21}

$$A = \frac{Z_i |e|}{4\pi \epsilon_o \epsilon} .\tag{7.82}$$

Therefore the particular solution to Eq. (7.75) for the  $i^{th}$  point central ion is given by:

{elec22}

$$\phi(r) = \frac{Z_i |e|}{4\pi \epsilon_o \epsilon} \frac{\exp\{-\kappa r\}}{r}. \quad (7.83)$$

The electrostatic potential has the form of a screened potential due to the ionic atmosphere around the  $i^{th}$  central ion.

For finite size ions we use Eq. (7.83) in Eq. (7.69) we get the charge density of the ionic atmosphere as a function of distance from the central ion,

{elec23}

$$\rho(r) = - \frac{2 N_o^2 |\epsilon|^2 \rho_{Solvent}(T) I}{RT} A \frac{\exp\{-\kappa r\}}{r}. \quad (7.84)$$

The net charge of the ionic atmosphere has to be equal to the negative central ion's charge,

{elec24}

$$\begin{aligned} - Z_i |e| &= \int_{r_a}^{\infty} 4\pi r^2 \rho(r) dr \\ &= - A \kappa^2 4\pi \epsilon_o \epsilon \int_{r_a}^{\infty} r \exp\{-\kappa r\} dr \\ &= A \kappa^2 4\pi \epsilon_o \epsilon (1 + \kappa r_a) \exp\{-\kappa r_a\}, \end{aligned} \quad (7.85)$$

where  $r_a = R_+ + R_-$  is the central ion's radius plus the counter ion's radius. Solving for A and using it in Eq. (7.83) we get

{elec25}

$$\phi(r) = \frac{Z_i |e|}{4\pi \epsilon \epsilon_o} \frac{\exp(\kappa r_a)}{1 + \kappa r_a} \frac{\exp(-\kappa r)}{r}. \quad (7.86)$$

## 7.4 Debye-Hückel limiting law

From the Debye-Hückel theory we know that the electric potential,  $\phi$ , at a distance  $r$  from a central ion is given by Eq. (7.86). In order to calculate the non-PV work involved in bringing the central ion from an infinite large distance to its position in the center of the ionic atmosphere we need to know the electrostatic potential produced by the ionic atmosphere. Thus we will assume dilute solutions. This condition implies

$$\kappa r_a \ll 1, \quad (7.87) \quad \{\text{dH1}\}$$

$$\kappa r \ll 1. \quad (7.88) \quad \{\text{dH2}\}$$

These conditions imply the following approximation for Eq. (7.86):

$$\phi(r) \approx \frac{Z_i |e|}{4\pi\epsilon\epsilon_0} \left[ \frac{1}{r} - \kappa \right]. \quad (7.89) \quad \{\text{dH3}\}$$

This electrostatic potential can be separated into two contributions. One from the central ion,  $\phi_{\text{Centralion}}$ , and one from the ionic atmosphere,  $\phi_{\text{Ionicatmosphere}}$ , i.e.,

$$\phi(r)_{\text{Centralion}} \approx \frac{Z_i |e|}{4\pi\epsilon\epsilon_0} \frac{1}{r}, \quad (7.90) \quad \{\text{dH4}\}$$

$$\phi(r) - \phi_{\text{Centralion}} \approx - \frac{Z_i |e|}{4\pi\epsilon\epsilon_0} \kappa. \quad (7.91) \quad \{\text{dH5}\}$$



# Chapter 8

## Quantum chemistry

The early XX century saw the birth of the theory of relativity. This theory was developed after the 1887 Michelson and Morley's experiment which was designed to reveal the earth's motion relative to the ether. In an effort to explain the experimental facts, Poincare and Einstein altered the ideas and concept of space, time and astronomical distances. Most of the development of the theory of relativity was carried out by the latter scientists. In contrast Quantum chemistry took several decades and many contributors to be developed. This theory can be seen as an extension of classical mechanics to the subatomic, atomic and molecular sizes and distances.

In this chapter we will study the fundamental theory of electrons, atoms and molecules known as Quantum Chemistry. In our approach we will follow the historical development of Quantum Chemistry. In this approach we will see how Quantum Chemistry gradually evolves from confusion and dilemma into a formal theory.

### 8.1 Introduction

As we have seen in previous chapters, the world we experience with our senses is a world described by Thermodynamics, Classical Mechanics and Classical Electromagnetism. It is a macroscopic world based in macroscopic laws. But scientist have long recognized experimentally the existence of small particles which are the components of matter.

Therefore it is natural to look first for microscopic laws that explain the particle's behavior, and second we have to look for a theoretical approach that will link the microscopic laws with the macroscopic laws.

Towards the end of the XIX century, many physicist felt that all the principles of physics had been discovered and little remained to be understood except for few minor problems. At that time our world was understood using Classical Mechanics, Thermodynamics and Classical Electromagnetism. For example in Classical Mechanics or Newtonian Mechanics we needed to find the dynamical variables of the system under study. Once done this, we needed to construct the equation of motion which predicted the system's evolution in time. The predicted behavior was finally compared with the experimental observations.

At the time the Universe was divided into matter and radiation. Matter was ruled by Newtonian mechanics and thermodynamics, and radiation obeyed Maxwell's laws of Electromagnetism. A controversy whether light was wave-like or corpuscular-like existed since Newton's days, who proposed the corpuscular theory of light. The wave-like theory was developed by Huggens based in the constructive and destructive interference of light; a property which is characteristic of waves.

The interaction between matter and radiation was not well understood. For example, Earnshaw's theorem states that a system of charged particles can not remain at rest in stable equilibrium under the influence of purely electrostatic forces. Moreover, according to Electromagnetism an accelerated charged particles radiate energy in the form of electromagnetic waves. Thus how is that molecules are stable? From this minor problems the theory of Quantum chemistry was developed.

### 8.1.1 Black-body radiation

Experimentally we observe that when a metallic object is heated it would change its color. As the temperature is increased, first the object changes its color into a dull red and, progressively, becomes more and more red. Eventually it changes from red to blue. As it is well established experimentally, the radiated energy is associated with a color which is associated to a frequency or wavelength. To understand this phenomenon, we will consider a so-called black-body

An ideal object that absorbs and emits all frequencies is defined as a black-body. It is a theoretical model invented by theorist to study the emission and absorption of radiation. Its experimental counterparts consist of an insulated box which can be heated. On one of its faces a small pinhole allows radiation to enter or leave. This radiation is equivalent to that of a perfect black-body.

One of the “minor” problems mentioned earlier relates to the density of radiated energy per unit volume per unit frequency interval  $d\nu$  at temperature  $T$ ,  $\rho(\nu, T)$ . The search for an expression for  $\rho(\nu, T)$  backs to 1860 when Gustav Kirchhoff recognized the need of a theoretical approach to blackbody radiation. Also the relation between  $\rho(\nu, T)$  with certain empirical equations was not well understood. In 1899 Wien noticed that the product of temperature  $T$ , and maximum wavelength,  $\lambda_{max}$  was always a constant,

{qm1a}

$$T \lambda_{max} = \text{constant}. \quad (8.1)$$

Equation (8.1) is called the displacement law. Also the total energy radiated per unit area per unit time,  $R$ , from a blackbody followed Stefan-Boltzmann law,

{qm1b}

$$R = \sigma T^4, \quad (8.2)$$

where  $\sigma$  is a constant. These two empirical laws needed to be explained from first principles.

In 1896 Wilhelm Wien derived the following expression for  $\rho$ :

{qm0}

$$\rho(\nu, T) = C \nu^3 \exp\left\{-a \frac{\nu}{T}\right\}, \quad (8.3)$$

where  $C$  and  $a$  are constants. Wien's result was experimentally confirmed for high frequencies by Frederick Paschen in 1897. But in 1900, Otto Lummer and Ernest Pringsheim found that Wien's expression failed in the low frequency regime.

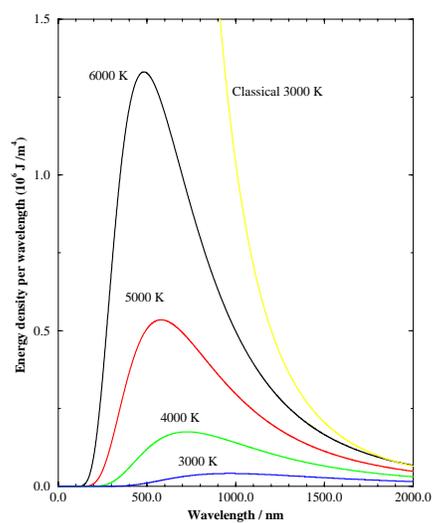


Figure 8.1: Planck's radiation density for a blackbody.

The first attempts to explain the previous empirical laws from first principles used the classical knowledge at the time. For example in 1900 Rayleigh assumed that the radiation trapped in the box interacted with the walls. On the walls small oscillators which in turn vibrate emitting radiation. Finally the equilibrium between the “oscillators” and the radiation trapped in the box is responsible of the properties of black-body radiation. Under these assumptions, the density of radiated energy per unit volume per unit frequency at temperature  $T$  is given by the following equation:

$$\rho(\nu, T) d\nu = N_\nu d\nu \bar{\epsilon}(\nu, T), \quad (8.4)$$

where  $N_\nu d\nu$  represents the number of oscillators between  $\nu$  and  $\nu + d\nu$ , and  $\bar{\epsilon}(\nu, T)$  is the average energy radiated by the “electronic oscillator” at frequency  $\nu$  and temperature  $T$ . The number density was widely accepted to be

$$N_\nu = \frac{8\pi \nu^2}{c^3} \quad (8.5)$$

where  $c$  is the speed of light.

In the calculation of  $\bar{\epsilon}(\nu, T)$  Rayleigh assumed that the “oscillators” could achieve any possible energy and the equipartition theorem. In other words Rayleigh assumed a continuous energy spectrum for the oscillators and

$$\bar{\epsilon}(\nu, T) = k_B T, \quad (8.6)$$

where  $k_B$  is Boltzman constant. With these assumptions, Rayleigh obtained the following expression for the amount of radiative energy between  $\nu$  and  $\nu + d\nu$ :

$$\rho(\nu, T) d\nu = \frac{8\pi \nu^2}{c^3} k_B T d\nu. \quad (8.7)$$

If we express Eq. (8.7) as radiated energy per unit volume per unit wavelength we get

$$\rho'(\lambda, T) d\lambda = \frac{8\pi}{\lambda^4} k_B T d\lambda, \quad (8.8)$$

where we have used the relation  $c = \lambda\nu$ . This latter result agreed with the low frequency observation but did not fit the experimental observations at high frequencies.

From the low and high frequency expressions,

{iqlim1}

$$\bar{\epsilon}(\nu, T) \approx \begin{cases} k_B T & \text{for low } \nu \\ \nu \exp\left\{-a \frac{\nu}{T}\right\} & \text{for high } \nu \end{cases}, \quad (8.9)$$

{iqlim2}

Planck derived an expression consistent with both limiting behaviors,

$$\bar{\epsilon}(\nu, T) = \frac{h \nu}{\exp\left\{\frac{h\nu}{k_B T}\right\} - 1}. \quad (8.10)$$

This expression required only one constant,  $h$ , which Plank determined by fitting the expression to the experimental data. Equation (8.10) is called the Plank distribution law. Plank obtained an excellent agreement with experiments using

{iqm10}

$$h = 6.626 \times 10^{-34} \text{ J s}. \quad (8.11)$$

Although Eq. (8.10) fitted the experimental data extraordinary well, Plank wanted to understand why Eq. (8.10) worked so well. First Plank calculated the entropy of the system from (8.10). Second, he calculated the entropy using Boltzman mechanistic approach. When these two independent expressions for the entropy were compared, Plank concluded that the oscillators spectrum had to be discrete. In other words the “oscillators” could only achieve the following energy values:

{iqm4b}

$$\epsilon_n = n h \nu, \quad (8.12)$$

where  $n$  is a positive integer and  $h$  is Plank’s constant. Thus both of Plank’s entropy expressions were consistent if energy was quantized.

From Max Planck’s underlying assumption that the energies of the “electronic oscillators” could have only a discrete set of values we can derive the semiempirical Plank’s distribution using statistical methods. In this approach we assumed that only jumps of  $\Delta n = \pm 1$  can occur, so the change of energy is given by:

{iqm5}

$$\Delta\epsilon = h \nu. \quad (8.13)$$

This means that energy is absorbed or emitted only in packets.

In order to obtain an expression for the density of radiative energy between  $\nu$  and  $\nu + d\nu$  we have to calculate the average energy,  $\bar{\epsilon}(\nu)$ , at frequency  $\nu$ . First we consider the Boltzman probability for the energy level of each oscillator at frequency  $\nu$ , i.e.,

$$P_n(\nu) \approx \exp \left\{ \frac{n h\nu}{k_B T} \right\} . \quad (8.14)$$

Using Eq. (8.14) we get for the average oscillator's energy

$$\begin{aligned} \bar{\epsilon}(\nu) &= \frac{\sum_{n=1}^{\infty} n h\nu \exp \left\{ \frac{n h\nu}{k_B T} \right\}}{\sum_{n=1}^{\infty} \exp \left\{ \frac{n h\nu}{k_B T} \right\}} \\ &= \frac{\sum_{n=1}^{\infty} n h\nu X^n}{\sum_{n=1}^{\infty} X^n} \\ &= \frac{h\nu \frac{X}{(1-X)^2}}{\frac{1}{1-X}} \\ &= \frac{h\nu X}{1-X} \\ &= \frac{h\nu}{\exp \left\{ \frac{h\nu}{k_B T} \right\} - 1} . \end{aligned} \quad (8.15)$$

Finally using Eqs. (8.4) and (8.5) the Plank's expression for the radiative energy density is equal to

$$\rho(\nu, T) d\nu = \frac{8\pi \nu^2}{c^3} \frac{h\nu}{\exp \left\{ \frac{h\nu}{k_B T} \right\} - 1} d\nu . \quad (8.16)$$

Also as a function of wavelength we get

$$\rho'(\lambda, T) d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp \left\{ \frac{hc}{k_B T \lambda} \right\} - 1} d\lambda . \quad (8.17)$$

From Eq. (8.17) we can obtain the Wien displacement law and the Stefan-Boltzman law.

### 8.1.2 Photoelectric effect

Late in the 19<sup>th</sup> century a series of experiments revealed that electrons are emitted from a metal surface when light of sufficient high frequency falls upon it. This is known as the photoelectric effect. Classical theory predicted that the energy of the ejected electron is proportional to the intensity of the light; electrons are ejected for any frequency radiated. Both prediction are not support by the experients.

The experiemnts show the existance of a threshold frequency,  $\nu_0$ . Einstein in 1905 assumed that radiation consists of little packets of energy  $\epsilon = h\nu$ . If this is true the kinetic energy of the ejected electron is given by the following equation:

{pe1}

$$KE = \frac{1}{2} mv^2 = h\nu - \phi \quad (8.18)$$

where  $\phi$  is the work function which is usually expressed in electron volts, eV. Note that the threshhold frequency,  $\nu_0$ , implies no kinetic energy. Thus

{pe2}

$$h\nu_0 = \phi, \quad (8.19)$$

and the photoelectric effect is observed only if  $h\nu \geq \phi$ . Equation (8.18) represents a straight line with slope h. Actually in an experiment one measures the stopping potential,  $V_S$ , such that

{pe3}

$$KE = -e V_S = \frac{1}{2}mv^2 . \quad (8.20)$$

## 8.2 Wave equation

In this section we discuss the wave equation for a string attached at both ends. In this case we consider a string along the x-axis with displacement in the y-direction. The string's displacement will be denoted as  $u(x,t)$ . Finally if we consider a string of length  $\ell$  the displacement satisfies the following equation:

{we1}

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} , \quad (8.21)$$

where  $v$  is the magnitud of the velocity of the wave along the string. Next we consider the boundary conditions (BC). These are the vaues

of  $u$  at the ends of the string. Since the ends are attached to say a wall, these points do not displace from its position, {we2}

$$u(0, t) = 0 = u(\ell, t) . \quad (8.22)$$

Notice that these values are valid for any time  $t$ . Thus we have a partial differential equation and its boundary conditions for a string. This equation is commonly referred as a 1-dimensional wave equation.

Of the different methods of solution of partial differential equations, we will consider the method of separation of variables. In this method we consider the the solution to Eq. (8.21) can be written as a product of a function of time and function of space, i.e., {we3}

$$u(x, t) = X(x) T(t) . \quad (8.23)$$

If we substitute Eq. (8.23) in Eq. (8.21) we get {we4}

$$T(t) \frac{d^2 X(x)}{d x^2} = \frac{1}{v^2} X(x) \frac{d^2 T(t)}{d t^2} . \quad (8.24)$$

Notice that the partial derivatives have transformed to regular derivatives since they are applied to single variable function. Now if we divide both sides of Eq. (8.24) by Eq. (8.23) we get {we5}

$$\frac{1}{X(x)} \frac{d^2 X(x)}{d x^2} = \frac{1}{v^2 T(t)} \frac{d^2 T(t)}{d t^2} . \quad (8.25)$$

In Eq. (8.25) the left hand side is a function only of position  $x$ ; the right hand side is a function only of time. Since position and time are independent variables the only possibility that satisfies Eq. (8.25) is {we6}

$$\frac{1}{X(x)} \frac{d^2 X(x)}{d x^2} = \alpha , \quad (8.26)$$

$$\frac{1}{T(t)} \frac{d^2 T(t)}{d t^2} = \alpha , \quad (8.27)$$

where  $\alpha$  is a constant.

For the spatial function  $X(x)$  we have now the following equation: {we8}

$$\frac{d^2 X(x)}{d x^2} = \alpha X(x) \quad (8.28)$$

From Eq. (8.22) the boundary conditions for  $X(x)$  are

{we9a}

$$X(0) = X(\ell) = 0 . \quad (8.29)$$

Thus we are looking for a function that satisfies Eq. (8.28) and vanishes at  $x = 0$  and  $x = \ell$ . After some thinking we find that the function  $\sin(x)$  and  $\cos(x)$  satisfy the differential equation but only  $\sin(x)$  satisfies the boundary condition at  $x = 0$ . In other words, if

{we9}

$$X(x) = A \sin(\kappa x) , \quad (8.30)$$

{we10}

Eq. (8.28) reduces to

$$\begin{aligned} \frac{d^2 A \sin(\kappa x)}{d x^2} &= - A \kappa^2 \sin(\kappa x) \\ &= - \kappa^2 X(x) \\ &= \alpha X(x) . \end{aligned} \quad (8.31)$$

{we11}

Therefore

$$\alpha = - \kappa^2 . \quad (8.32)$$

{we12}

Next we consider the boundary condition

$$\sin(\kappa \ell) = 0 . \quad (8.33)$$

{we13}

Equation (8.33) is satisfied if the argument of the sine function is an integer multiple of  $\pi$ ,

$$\kappa \ell = n \pi . \quad (8.34)$$

{we14}

Solving for  $\kappa$  we find that the spatial solution of Eq. (8.21) to be

$$X(x) = A_n \sin\left(\frac{\pi}{\ell} n x\right) . \quad (8.35)$$

{we15}

And the displacement  $u(x, t)$  can be written as

$$u_n(x, t) = T(t) A_n \sin\left(\frac{\pi}{\ell} n x\right) . \quad (8.36)$$

Equation (8.35) represents standing waves, and the wavelength of these standing waves,  $\lambda_n$  satisfy the following relation:

$$\frac{\pi}{\ell} n \lambda_n = 2\pi . \quad (8.37)$$

Thus  $\lambda_n$  is equal to

$$\lambda_n = \frac{2 \ell}{n} , \quad (8.38)$$

where  $n$  is an integer greater than one. Using this result we can express  $\kappa$  in terms of  $\lambda_n$ ,

$$\kappa = \frac{2 \pi}{\lambda} , \quad (8.39)$$

and plugg it in Eq. (8.26) to get the following equation:

$$\frac{d^2 X(x)}{d x^2} = - \left( \frac{2\pi}{\lambda_n} \right)^2 X(x) . \quad (8.40)$$

Equation (8.40) represents the wave equation satisfied by the spatial part of the amplitud,  $u(x, t)$ .

### 8.2.1 Particle's wave equation

Since particles behave as waves we need a wave equation for a particle. A simple approach is to use de Broglie's assumption in Eq. (8.40). Namely we substitute the value of the wavelength associated to a particle with momentum  $p$ ,

$$\lambda = \frac{h}{p} , \quad (8.41)$$

in the right hand side of Eq. (8.40). This substitution yields the following equation:

$$\frac{d^2 \psi(x)}{d x^2} = - \left( \frac{p}{\hbar} \right)^2 \psi(x) , \quad (8.42)$$

where  $\psi$  is the wave associated to a particle with momentum  $p$  and  $\hbar \equiv h/2\pi$ . Now if we recall the expression for the mechanical energy of a particle with momentum  $p$  in a potential  $V(x)$ ,

$$E = \frac{p^2}{2 m} + V(x) , \quad (8.43)$$

and solve for  $p^2$  we get

$$p^2 = 2 m [E - V(x)] . \quad (8.44)$$

Equation (8.44) can be used in Eq. (8.42) and get

$$\frac{d^2 \psi(x)}{d x^2} = - \frac{2m}{\hbar^2} [E - V(x)] \psi(x) . \quad (8.45)$$

Finally we can rewrite Eq. (8.45) as

$$- \frac{\hbar^2}{2 m} \frac{d^2 \psi(x)}{d x^2} + V(x) \psi(x) = E \psi(x) . \quad (8.46)$$

Equation (8.46) is the time-independent Schrödinger equation. Although this derivation is not formal, nor Schrödinger “official” derivation, it obtains the quantization of the energy, in the case of the hydrogen atom, as a consequence of the properties of the wave function  $\psi(x)$ . Schrödinger success attracted the attention of scientist and change the world.

### 8.2.2 Schrödinger equation

$$- \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Phi(x, t) + V(x) \Phi(x, t) = i \hbar \frac{\partial}{\partial t} \Phi(x, t) . \quad (8.47)$$

Separation of variables

$$\Phi(x, t) = \phi(t) \psi(x) \quad (8.48)$$

$$- \frac{1}{\psi(x)} \frac{\hbar^2}{2m} \frac{d^2}{d x^2} \psi(x) + V(x) = \frac{i \hbar}{\phi} \frac{d}{dt} \phi(t) = \text{constant} = E \quad (8.49)$$

$$\frac{d \phi(t)}{dt} = - \frac{i E}{\hbar} \phi(t) \quad (8.50)$$

$$\phi(t) = \exp \left\{ - \frac{i E}{\hbar} t \right\} \quad (8.51)$$

$$- \frac{\hbar^2}{2m} \frac{d^2}{d x^2} \psi(x) + V(x) \psi(x) = E \psi(x) \quad (8.52)$$

## 8.3 Axiomatic quantum mechanics

Classical mechanics deals with position ( $\vec{r}$ ), momentum ( $\vec{p}$ ), angular momentum ( $L \equiv mvr$ ) and energy. These quantities are called dynamical variables. A measurable dynamical variable is called an observable.

Time evolution of the system's observables is governed by Newton's equations, which yield the system's trajectory. In Quantum mechanics the Uncertainty Principle forbids the concept of trajectory. Thus we need another approach to study the microscopic world of the atom. In this section we consider an axiomatic approach. Namely we will state a number of axioms or postulates which define the foundation of quantum mechanics. The postulates are justified only by their ability to predict and correlate experimental facts and their general applicability.

### Postulate 1

The state of a quantum-mechanical system is completely specified by a function  $\Psi(\vec{r}, t)$ . This function is called the wave function or the state function.

The probability of finding the particle in a volume element  $dV$  around  $\vec{r}$  at time  $t$  is given by:

$$P(\vec{r}, t) = |\Psi(\vec{r}, t)|^2 dV = \Psi^*(\vec{r}, t) \Psi(\vec{r}, t) dV , \quad (8.53)$$

{aq1}

where the star,  $\Psi^*$  represents the complex conjugate of the wave function  $\Psi$ . As a consequence of the probabilistic interpretation, the probability of finding the particle some place in the space is equal to unity or

$$\int_{Space} |\Psi(\vec{r}, t)|^2 dV = 1 . \quad (8.54)$$

{aq2}

This condition puts some requirements on the kind of state function that we can consider. For example  $\Psi$  and  $d\Psi/d\vec{r}$  have to be continuous, finite and single-valued (for each position  $\vec{r}$  only one value of  $\Psi(\vec{r}, t)$ ).

### Postulate 2

For any observable in classical mechanics, we can find a corresponding quantum mechanical operator. For example momentum in the  $x$  direction:

{aq2b}

$$p_x = m v_x \longleftrightarrow \hat{p} = -i \hbar \frac{d}{dx}, \quad (8.55)$$

{a93} angular momentum in the x direction:

$$L_x = y p_z - z p_y \longleftrightarrow \hat{L}_x = -i \hbar \left\{ y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right\}, \quad (8.56)$$

{a94} energy:

$$E = \frac{p^2}{2m} + V(x) \longleftrightarrow \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \quad (8.57)$$

### Postulate 3

{a95} When an observable, corresponding to  $\hat{A}$ , is measured, the only values observed are given by:

$$\hat{A} \Psi_n = a_n \Psi_n, \quad (8.58)$$

where  $a_n$  is a set of eigenvalues called the spectrum of  $\hat{A}$ . What if the system is in some arbitrary state,  $\Psi$ , which is not the eigenfunction of  $\hat{A}$ ?

### Postulate 4

{a96} The expected value of  $\hat{A}$  when  $\Psi$  is not an eigenfunction of  $\hat{A}$  is given by:

$$\langle \hat{A} \rangle \equiv \int_{Space} \Psi^* \hat{A} \Psi dV. \quad (8.59)$$

### Postulate 5

{a97} The time dependence of  $\Psi(\vec{r}, t)$  is given by the time-dependent Schrödinger equation,

$$\hat{H} \Psi(\vec{r}, t) = i \hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t). \quad (8.60)$$

{a98} If the the hamiltonian,  $\hat{H}$ , does not include time explicitly, the wave function can be written as a product of two functions,

$$\Psi(\vec{r}, t) = \psi(\vec{r}) f(t) . \quad (8.61)$$

As we have mentioned earlier this separation of variables leads to the time independent Schrödinger equation

$$\hat{H} \psi(\vec{r}) = E \psi(\vec{r}) . \quad (8.62)$$

The solution of Eq. (8.62) implies a set of energies  $\{E_n\}$  i.e.,

$$\hat{H} \psi_n(\vec{r}) = E_n \psi_n(\vec{r}) , \quad (8.63)$$

where  $\psi_n$ 's are called the stationary states, and each state is characterized by an energy  $E_n$ . In this sense we say that the energy is quantized.

Also we can solve the time dependent differential equation and find

$$f(t) = \exp \left\{ -i \frac{E_n}{\hbar} t \right\} , \quad (8.64)$$

which means that the time dependent wave function is given by the following expression:

$$\Psi(\vec{r}, t) = \psi(\vec{r}, t) \exp \left\{ -i \frac{E_n}{\hbar} t \right\} . \quad (8.65)$$

Since the energy is quantized, we represent an atom or molecule by a set of stationary energy states. The spectroscopic properties of the system will be understood in terms of transitions from one stationary state to another. The energy associated with the transition is equal to:

$$\Delta E_{n \rightarrow m} = E_m - E_n = h\nu , \quad (8.66)$$

where  $\nu$  is the frequency of the photon either emitted or absorbed.

In general the system is not going to be in a stationary state  $\psi_n$ . In this case we can ask How many atoms are in each stationary state  $\psi_n$ ? Since the system is not in a stationary state we can construct a wave function for the system as a linear combination of the stationary states  $\psi_n$ . In other words the system's wave function is given by:

$$\Phi(\vec{r}, t) = \sum_{n=1}^{\infty} C_n \psi_n(\vec{r}) \exp \left\{ -i \frac{E_n}{\hbar} t \right\} . \quad (8.67)$$

Therefore the probability of measuring a particular  $E_n$  value in a series of observations is proportional to the square of its coefficient  $C_n$ , i.e.,  $C^*C = |C|^2$ .



# Chapter 9

## Three dimensional systems

In the case of three dimensions the momentum operator has three components

{3d1}

$$\hat{p}_x = -i \hbar \frac{\partial}{\partial x} \quad (9.1)$$

$$\hat{p}_y = -i \hbar \frac{\partial}{\partial y} \quad (9.2)$$

$$\hat{p}_z = -i \hbar \frac{\partial}{\partial z} . \quad (9.3)$$

Using these expression we can construct the momentum square operator in cartesian coordinates as

{3d2}

$$\begin{aligned} \hat{\vec{p}}^2 &= \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 \\ &= -\hbar^2 \left\{ \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right\} \end{aligned} \quad (9.4)$$

$$= -\hbar^2 \nabla^2 , \quad (9.5)$$

where  $\nabla^2$  is the Laplacian. Therefore the kinetic energy operator in three dimension is given by the following expression:

{3d3}

$$\hat{K} = -\frac{\hbar^2}{2m} \nabla^2 . \quad (9.6)$$

Finally the time independent hamiltonian operator in three dimensions can be written as:

{3d4}

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(x, y, z). \quad (9.7)$$

{3d5} In many cases the potential has spherical symmetry in other words  $\hat{V}$  is a function of the radius, e.g.,

$$\hat{V}(x, y, z) = \hat{V}(r), \quad (9.8)$$

{3d6} where

$$r = \sqrt{x^2 + y^2 + z^2}. \quad (9.9)$$

{3d7} For these systems we have to use spherical coordinates,  $(r, \theta, \phi)$ , instead of cartesian coordinates,  $(x, y, z)$ . The relation between these coordinates are given by:

$$x = r \sin(\theta) \cos(\phi) \quad (9.10)$$

$$y = r \sin(\theta) \sin(\phi) \quad (9.11)$$

$$z = r \cos(\theta). \quad (9.12)$$

{3d8a} In spherical coordinates the Laplacian is given by:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \quad (9.13)$$

In the following sections we will consider two important three dimensional problems. First we will consider a rigid rotator and the hydrogen atom.

## 9.1 Rigid rotator

A quantum mechanical rotator is simple model to study molecular rotations. In this case we consider two atoms separated a distance  $R$  apart. For this system we also use the reduced mass which reduces the two body problem to a one body problem. In contrast with the harmonic oscillator we consider a fixed distance between the atoms. In this way we are eliminating the molecular vibrations. In other words we consider a rigid rotator.

Recalling from classical mechanics the kinetic energy of a rigid rotator is given terms of the angular momentum. Using the angular momentum the kinetic energy is given by:

$$K = \frac{1}{2I} L^2, \quad (9.14)$$

where  $I$  is the moment of inertia,

$$I = \mu R^2, \quad (9.15)$$

and  $L$  is the angular momentum.

Classically the angular momentum is a 3-dimensional vector. In cartesian coordinates the three components of the angular momentum are equal to:

$$L_x = y p_z - z p_y \quad (9.16)$$

$$L_y = z p_x - x p_z \quad (9.17)$$

$$L_z = x p_y - y p_x. \quad (9.18)$$

Now we translate these expression into quantum operators we get

$$\hat{L}_x = -i \hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad (9.19)$$

$$\hat{L}_y = -i \hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad (9.20)$$

$$\hat{L}_z = -i \hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (9.21)$$

$$(9.22)$$

Since the rigid rotator shows spherical symmetry we need to transform the angular momentum operator from cartesian to spherical coordinates. This transformation follows from Eqs. (9.10), and, after tedious but otherwise straightf orward algebra, we get the following expressions of the angular momentum operator in spherical coordinates:

$$\hat{L}_x = -i \hbar \left[ -\sin(\phi) \frac{\partial}{\partial \theta} - \cot(\theta) \cos(\phi) \frac{\partial}{\partial \phi} \right] \quad (9.23)$$

$$\hat{L}_y = -i \hbar \left[ -\cos(\phi) \frac{\partial}{\partial \theta} - \cot(\theta) \sin(\phi) \frac{\partial}{\partial \phi} \right] \quad (9.24)$$

$$\hat{L}_z = -i \hbar \frac{\partial}{\partial \phi} \quad (9.25)$$

{3d14}

$$\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right]. \quad (9.26)$$

{3d15}

In the case of the rigid rotator no potential energy is present, which means that the Hamiltonian is given by

$$\hat{H} = \frac{1}{2\mu R^2} \hat{L}^2. \quad (9.27)$$

{3d16}

Thus the time-dependent Schrödinger reduces to

$$\hat{H}\psi_n = \frac{1}{2\mu R^2} \hat{L}^2\psi_n = E_n\psi_n. \quad (9.28)$$

{3d17}

Since the rigid rotator has spherical symmetry we will use spherical coordinates and find

$$-\frac{\hbar^2}{2\mu R^2} \left[ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right] \psi_n = E_n\psi_n. \quad (9.29)$$

{3d18}

The solution to a very similar equation has been found, namely

$$\left[ \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right] Y_\ell^m(\theta, \phi) = -\ell(\ell+1)Y_\ell^m(\theta, \phi), \quad (9.30)$$

{3d19}

where  $Y_\ell^m$ s are called the Spherical Harmonics. Therefore we can use this result to express  $\psi$ , i.e.,

$$\psi_n \longrightarrow Y_\ell^m(\theta, \phi), \quad (9.31)$$

{3d22}

where  $\ell = 0, 1, 2, 3, \dots$ , and  $m = 0, \pm 1, \pm 2, \pm 3, \dots, \pm \ell$ . Also the spherical harmonics have the following structure:

$$Y_\ell^m(\theta, \phi) = N_{\ell, m} P_\ell^{|m|}(\cos(\theta)) \exp\{i m \phi\}, \quad (9.32)$$

{3d22a}

where  $P_\ell^{|m|}$  are the Legendre polynomials. The first couple of Spherical Harmonics are:

$$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}, \quad (9.33)$$

$$Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos(\theta), \quad (9.34)$$

$$Y_1^{-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin(\theta) \exp\{-i\phi\}, \quad (9.35)$$

$$Y_1^1(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin(\theta) \exp\{+i\phi\}. \quad (9.36)$$

Using these results the energy levels for the rigid rotator are given by:

$$E_\ell = \frac{\hbar^2}{2I} \ell(\ell + 1). \quad (9.37)$$

For each  $\ell$  we have  $2\ell + 1$  different spherical harmonics, i.e.,

$$Y_\ell^m \rightarrow Y_\ell^0, Y_\ell^{\pm 1}, Y_\ell^{\pm 2}, \dots, Y_\ell^{\pm \ell}. \quad (9.38)$$

Notice that of these function correspond to the same energy level, e.g, Eq. (9.37). We say that the level is degenerate when linear independent functions have the same energy. Thus for the rigid rotator hamiltonian operator the degree of degeneracy of each energy level,  $E_\ell$ , is  $2\ell + 1$ .

Finally if we compare Eqs. (9.26) and (9.30) we find that the Spherical Harmonics are eigenfunction of the square of the angular momentum operator,  $\hat{L}^2$ ,

$$\hat{L}^2 Y_\ell^m(\theta, \phi) = \hbar^2 \ell(\ell + 1) Y_\ell^m(\theta, \phi). \quad (9.39)$$

Moreover if we use Eq. (9.25) we find that the spherical harmonics are also eigenfunctions of the z component of the angular momentum operator, e.g.,

$$\hat{L}_z Y_\ell^m(\theta, \phi) = -i\hbar \frac{\partial}{\partial \phi} Y_\ell^m(\theta, \phi) = m\hbar Y_\ell^m(\theta, \phi). \quad (9.40)$$

Consequently, the Spherical harmonics are eigenfunction of the square of the angular momentum operator, the z-component of the angular momentum operator and the rigid rotator hamiltonian operator.

### 9.1.1 Particle on a ring

In this section we consider a circular motion on the x-y plane of a single particle. For this system the total energy is given by the kinetic energy,

$$\{rt22\} \quad K = \frac{1}{2I} L_z^2. \quad (9.41)$$

\{rt23\} Therefore, in the absence of potential energy, the hamiltonian is given by:

$$\hat{H} = -\frac{\hbar^2}{2I} \frac{\partial}{\partial \phi^2}. \quad (9.42)$$

\{rt24\} The time-dependent Schrödinger equation is given by:

$$-\frac{\hbar^2}{2I} \frac{\partial}{\partial \phi^2} \psi_m(\phi) = E_m \psi_m(\phi), \quad (9.43)$$

\{rt25\} with boundary condition  $\psi_m(\phi) = \psi_m(\phi + 2\pi)$ . The solutions to Eq. (9.43) are :

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp \{i m \phi\}. \quad (9.44)$$

\{rt26\} The energy is quantized energy,

$$E_m = \frac{\hbar^2}{2I} m^2, \quad (9.45)$$

with values  $m = 0, \pm 1, \pm 2, \dots$ . This model can be applied to aromatic molecules like benzene.

## 9.2 Rotational transitions

\{rt1\} Since we have an expression for the quantized energy, we can calculate the energy difference between levels. First we consider the  $\ell^{th}$  level with energy given by Eq. (9.37). Now we consider the transition  $\ell \rightarrow \ell + 1$ . The energy difference is given by:

$$\Delta_{\ell+1,\ell} \equiv E_{\ell+1} - E_\ell$$

$$\begin{aligned}
 &= [(\ell + 1)(\ell + 2) - \ell(\ell + 1)] \frac{\hbar^2}{2I} \\
 &= 2(\ell + 1) \frac{\hbar^2}{2I}, \tag{9.46}
 \end{aligned}$$

with  $\ell = 0, 1, 2, 3, \dots$ . In the case of transition from the  $\ell^{\text{th}}$  energy level to the  $\ell - 1$  we get {rt2}

$$\begin{aligned}
 |\Delta_{\ell-1,\ell}| &\equiv |E_{\ell-1} - E_\ell| \\
 &= 2\ell \frac{\hbar^2}{2I}, \tag{9.47}
 \end{aligned}$$

with  $\ell = 1, 2, 3, \dots$ . Notice that for these transition the unit of energy is  $\hbar^2/2\mu R^2$ . For example in the case of hydrogen chloride  $H^{35}Cl(g)$  we have find that the distance between the atoms is equal to 127.5 pm and the reduce mass equal to  $1.6267 \times 10^{-27} kg$ . Table 2 shows the characteristic frequencies and times for rotational transitions  $\ell = 0 \rightarrow \ell = 1$ .

<b>TABLE 2</b>			
Molecule	$\frac{\hbar^2}{2\mu R^2}$	$\bar{\nu}_{0 \rightarrow 1}$	$t_{0 \rightarrow 1}$
$H^{35}Cl$	$21.2 \text{ cm}^{-1}$	$42.4 \text{ cm}^{-1}$	$787 \text{ fs}$
$H^{79}Br$	$18.8 \text{ cm}^{-1}$	$37.6 \text{ cm}^{-1}$	$5900 \text{ fs}$
$CO$	$2.7 \text{ cm}^{-1}$	$5.4 \text{ cm}^{-1}$	$15000 \text{ fs}$

Finally from Tables 1 and 2 we notice that {rt3}

$$t_{ch}^{rot} \sim 1000 \text{ fs} = 1 \text{ ps} \tag{9.48}$$

$$t_{ch}^{vib} \sim 10 \text{ fs} \tag{9.49}$$

### 9.2.1 Rotational selection rules

In the case of rotations we have that the transition coefficient has the form {rt4}

$$T_{f,i} \propto \langle f | \vec{\mu} \cdot \vec{E}_o | i \rangle = \mu E_o \langle f | \cos(\theta) | i \rangle . \quad (9.50)$$

where we considered the electric field in the z-direction. Since rotations do not change the value of  $\mu$  we need molecules with permanent dipole moment,

$$\mu \approx \mu_o \approx \text{constant} . \quad (9.51)$$

Therefore Eq. (9.50) reduces to

$$T_{f,i} \propto \mu_o E_o \langle \ell', m' | \cos(\theta) | \ell, m \rangle , \quad (9.52)$$

where we have the notation

$$Y_\ell^m(\theta, \phi) \longrightarrow | \ell, m \rangle , \quad (9.53)$$

$$Y_{\ell'}^{m'*}(\theta, \phi) \longrightarrow \langle \ell', m' | . \quad (9.54)$$

In terms of integrals Eq. (9.52)

$$T_{f,i} \propto \mu_o E_o \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin(\theta) Y_{\ell'}^{m'*}(\theta, \phi) \cos(\theta) Y_\ell^m(\theta, \phi) . \quad (9.55)$$

Equation can be split into a product of two integrals using Eq. (9.32),

$$T_{f,i} \propto \mu_o E_o N_{\ell', m'}^* N_{\ell, m} \int_0^\pi P_{\ell'}^{|m'|} \cos(\theta) P_\ell^{|m|} \sin(\theta) d\theta \int_0^{2\pi} \exp \{ i(m' - m)\phi \} d\phi , \quad (9.56)$$

But the integral over  $\phi$  is equal to  $2\pi$  times a Kroneker delta,

$$\int_0^{2\pi} \exp \{ i(m' - m)\phi \} d\phi = 2\pi \delta_{m', m} . \quad (9.57)$$

This result simplifies Eq. (9.56) to

$$T_{f,i} \propto \delta_{m', m} \mu_o E_o N_{\ell', m}^* N_{\ell, m} \int_0^\pi P_{\ell'}^{|m|} \cos(\theta) P_\ell^{|m|} \sin(\theta) d\theta . \quad (9.58)$$

From the Legendre polynomial properties, we find the following relation:

$$\cos(\theta)P_\ell^{m|\ell|}(\cos(\theta)) = \frac{\ell - |m| + 1}{2\ell + 1}P_{\ell+1}^{m|\ell|}(\cos(\theta)) + \frac{\ell + |m|}{2\ell + 1}P_{\ell-1}^{m|\ell|}(\cos(\theta)) , \quad (9.59)$$

which reduces Eq. (9.58) to

$$T_{\ell',m';\ell,m} \propto \delta_{m',m} \mu_o E_o \{C' \langle \ell', m|\ell + 1, m \rangle + C \langle \ell', m|\ell - 1, m \rangle\} , \quad (9.60)$$

where we have used the bracket notation, and the C's are constants. Notice that

$$\langle \ell', m|\ell + 1, m \rangle \sim \text{Const.} \delta_{\ell',\ell+1} \quad (9.61)$$

$$\langle \ell', m|\ell - 1, m \rangle \sim \text{Const.} \delta_{\ell',\ell-1} \quad (9.62)$$

where we have used the orthonormal properties of the Legendre polynomials. Thus

$$T_{\ell',m';\ell,m} \neq 0 \quad (9.63)$$

only if  $m' = m$  and  $\ell' = \ell \pm 1$ . In other words we get a rotational transition if

$$\Delta m = 0 , \quad (9.64)$$

$$\Delta \ell = \pm 1 . \quad (9.65)$$

The latter relations are the rotational selection rules

### 9.3 Vibrational-Rotational transitions

When combined, the vibrational and rotational transitions follow three condition:  $\Delta n = \pm 1$ ,  $\Delta m = 0$  and  $\Delta \ell = \pm 1$ . For example if we consider the vibrational transition  $n = 0 \rightarrow n = 1$ , we have two options for the rotational transition. The system is allowed to change from  $n = 0$ ,  $\ell$  to  $n = 1$ ,  $\ell \pm 1$ . First we consider the  $\Delta \ell = 1$ . In this case the change in energy is given by the following relation:

$$\Delta E_R = \frac{h\nu}{2} + \frac{\hbar^2}{2I}2(\ell + 1), \quad (9.66)$$

which is called the R branch of a vibro-rotational spectra, and it consists of the following transitions:

$$\begin{aligned}
n = 0 \rightarrow n = 1 \quad \ell = 0 \quad \rightarrow \ell = 1 \\
n = 0 \rightarrow n = 1 \quad \ell = 1 \quad \rightarrow \ell = 2 \\
n = 0 \rightarrow n = 1 \quad \ell = 2 \quad \rightarrow \ell = 3 \\
n = 0 \rightarrow n = 1 \quad \ell = 3 \quad \rightarrow \ell = 4 \\
n = 0 \rightarrow n = 1 \quad \ell = 4 \quad \rightarrow \ell = 5 \\
n = 0 \rightarrow n = 1 \quad \ell = 5 \quad \rightarrow \ell = 6 \\
\vdots
\end{aligned} \tag{9.67}$$

Therefore the energy between these transitions is equal to  $2\hbar^2/2I$ .

The second case considers the transition from  $n = 0 \rightarrow n = 1$  and  $\ell \rightarrow \ell + 1$ , or the so-called P branch. For the P branch the energy involved in the transition is equal to:

{rt20}

$$\Delta E_P = \frac{h\nu}{2} - \frac{\hbar^2}{2I}2\ell . \tag{9.68}$$

{rt21}

The following transitions constitute the P branch:

$$\begin{aligned}
n = 0 \rightarrow n = 1 \quad \ell = 1 \quad \rightarrow \ell = 0 \\
n = 0 \rightarrow n = 1 \quad \ell = 2 \quad \rightarrow \ell = 1 \\
n = 0 \rightarrow n = 1 \quad \ell = 3 \quad \rightarrow \ell = 2 \\
n = 0 \rightarrow n = 1 \quad \ell = 4 \quad \rightarrow \ell = 3 \\
n = 0 \rightarrow n = 1 \quad \ell = 5 \quad \rightarrow \ell = 4 \\
n = 0 \rightarrow n = 1 \quad \ell = 6 \quad \rightarrow \ell = 5 \\
\vdots
\end{aligned} \tag{9.69}$$

The R and the P branch explains some of the features of the IR spectra of diatomic molecules like  $H^{35}Cl$ .

## 9.4 Hydrogen atom

In the case of a hydrogen-like atom, we consider an electron moving around a positive charged nucleus. This means that the potential

energy is given by the electrostatic potential between these two charged particles,

$$V(r) = - \frac{Z |e|^2}{4\pi\epsilon_0 r} , \quad (9.70)$$

where  $Z|e|$  represents the nuclear charge, and  $r$  is the distance between the charges. As in previous sections the two body problem is reduced to a one body problem is we described the system using the reduced mass. In this case the hamiltonian operator is given by:

$$\hat{H} = - \frac{\hbar^2}{2\mu} \nabla^2 + \hat{V}(r) , \quad (9.71)$$

where the reduced mass is given by:

$$\mu = \frac{m_e m_{Nuclear}}{m_e + m_{Nuclear}} . \quad (9.72)$$

Since the potential is spherical symmetric we use spherical coordiantes to study this system. Combining Eqs. (9.13) and (9.26) we express Eq. (9.71) as

$$\hat{H} = - \frac{\hbar^2}{2\mu} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{1}{\hbar^2 r^2} \hat{L}^2 \right\} + V(r) . \quad (9.73)$$

Therefore the time independent Schrödinger equation reduces to:

$$- \hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \psi \right) + \hat{L}^2 \psi + 2\mu r^2 V(r) \psi = 2\mu r^2 E \psi . \quad (9.74)$$

Notice that if we assume a solution as

$$\psi_{n,\ell,m}(r, \theta, \phi) = R_{n,\ell}(r) Y_\ell^m(\theta, \phi) , \quad (9.75)$$

we can reduce the partial differential Eq. (9.74) to an ordinary differential equation for  $R_n(r)$ , i.e.,

$$- \hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} R_{n,\ell}(r) \right) + \hbar^2 \ell(\ell+1) R_{n,\ell}(r) + 2\mu r^2 V(r) R_{n,\ell}(r) = 2\mu r^2 E R_{n,\ell}(r) . \quad (9.76)$$

Since we want well behaved wave functions and also normalizable, a polynomial solution to Eq. (9.76),

$$R_{n,\ell}(r) = (-1)N_{n,\ell} \left( \frac{2r}{nr_o} \right)^\ell \exp \left\{ -\frac{r}{n r_o} \right\} L_{n+\ell}^{2\ell+1} \left( \frac{2r}{nr_o} \right), \quad (9.77)$$

where the  $L_{n+\ell}^{2\ell+1}$  are the Associated Laguerre polynomials, and

$$r_o = \frac{\epsilon_o h^2}{\pi \mu Z |e|^2} \equiv \frac{a}{Z}. \quad (9.78)$$

The constant in Eq. (9.77) is equal to

$$N_{n,\ell} = \left[ \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right]^{\frac{1}{2}} \left( \frac{2Z}{na} \right)^{\frac{3}{2}}. \quad (9.79)$$

The constant  $a$  is related to the Bohr radius,  $a_o$ , as

$$a = \frac{m_e}{\mu} a_o, \quad (9.80)$$

where

$$a_o = \frac{\epsilon_o h^2}{\pi m_e |e|^2} = 52.9 \text{ pm}. \quad (9.81)$$

The Bohr radius,  $a_o$ , was first introduced phenomenologically in Bohr's atomic theory. The same quantity appears as we solve the time-independent Schrödinger equation. Also we find that for each  $n$  the energy is given by:

$$E_n = -\frac{\mu Z^2 |e|^4}{8\epsilon_o^2 h^2} \frac{1}{n^2}, \quad (9.82)$$

for  $n = 1, 2, 3, \dots$ . Also the  $\ell$ 's satisfy an inequality relation,

$$0 < \ell \leq n - 1. \quad (9.83)$$

Notice that energy levels depend only on  $n$ . Thus for each  $n$  we get  $n$  wave functions with different  $\ell$ , and for each  $\ell$  we get  $2\ell + 1$  wave functions with different  $m$ . This means that the  $n^{\text{th}}$  hydrogen level is degenerate with degeneracy equal to:

$$\begin{aligned}
\text{Degeneracy} &= \sum_{\ell=0}^{n-1} (2\ell + 1) \\
&= 2 \sum_{\ell=0}^{n-1} \ell + \sum_{\ell=0}^{n-1} 1 \\
&= 2 \frac{(n-1)n}{2} + n \\
&= n^2 .
\end{aligned} \tag{9.84}$$

In general the  $n^{\text{th}}$  hydrogen-like energy level is  $n^2$  degenerate.

### 9.4.1 Hydrogen-like atom's ground state

The ground state or lowest system's energy is given by  $n = 1$ , which means that  $\ell = 0$  and  $m = 0$ . The ground state wave function is given by the following expression:

{ha12b}

$$\begin{aligned}
\psi_{1,0,0}(r, \theta, \phi) &\equiv R_{1,s}(r) Y_0^0(\theta, \phi) \\
&= 2 \left(\frac{1}{r_0}\right)^{3/2} \exp\left\{-\frac{r}{r_0}\right\} \frac{1}{\sqrt{4\pi}} \\
&= \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a}\right)^{3/2} \exp\left\{-\frac{Zr}{a}\right\} ,
\end{aligned} \tag{9.85}$$

where we have used Eq. (9.78) and introduced the following notation:

{ha13}

$$\begin{aligned}
\ell &= 0, 1, 2, 3, 4, 5 \\
&\equiv s, p, d, f, g, h .
\end{aligned} \tag{9.86}$$

The ground state energy is equal to:

{ha13b}

$$\begin{aligned}
E_1 \equiv E_g &= -\frac{\mu Z^2 |e|^4}{8 \epsilon_0^2 h^2} \\
&= -\frac{1}{2} \frac{Z|e|^2}{4\pi\epsilon_0 r_0} \\
&= -\frac{\mu Z^2}{m_e} 13.6 \text{ eV} .
\end{aligned} \tag{9.87}$$

Once we have the ground state wave function, we can consider the probability of finding the electron within a differential volume  $d\vec{r}$  centered around  $\vec{r}$ . This probability is given by the product of the absolute value of the wave function times the differential element of volume in three dimensions. The differential volume element is given by:

{ha14}

$$\begin{aligned} d\vec{r} &= dx dy dz \\ &= dV \\ &= r^2 dr \sin(\theta) d\theta d\phi . \end{aligned} \quad (9.88)$$

Using Eq. (9.88) the probability of finding an electron at a particular point in space is

{ha15}

$$\begin{aligned} P \{ \vec{r}, \vec{r} + d\vec{r} \} &= \psi_{1,0,0}^*(r, \theta, \phi) \psi_{1,0,0}(r, \theta, \phi) r^2 dr \sin(\theta) d\theta d\phi \\ &= \frac{1}{\pi} \left( \frac{Z}{a} \right)^3 \exp \left\{ -\frac{2Zr}{a} \right\} r^2 dr \sin(\theta) d\theta d\phi . \end{aligned} \quad (9.89)$$

If we want just the probability of finding the particle between a sphere of radius  $r$  and a sphere of radius  $r + dr$ , we have to integrate over all possible angles, e.g.,

{ha16}

$$\begin{aligned} P \{ r, r + dr \} &= \frac{1}{\pi} \left( \frac{Z}{a} \right)^3 \exp \left\{ -\frac{2Zr}{a} \right\} r^2 dr \int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\phi \\ &= 4 \left( \frac{Z}{a} \right)^3 \exp \left\{ -\frac{2Zr}{a} \right\} r^2 dr . \end{aligned} \quad (9.90)$$

Therefore the probability density is given by:

{ha17}

$$P_{1s}(r) = 4 \left( \frac{Z}{a} \right)^3 \exp \left\{ -\frac{2Zr}{a} \right\} r^2 . \quad (9.91)$$

With the help of Eq. (9.91) we can calculate the expected radial distance,

{ha18}

$$\langle 1s | r | 1s \rangle = \int_0^\infty r P_{1s}(r) dr = \frac{3}{2} \frac{a}{Z} , \quad (9.92)$$

where  $a$  is given by Eq. (9.78). Now we can calculate the following probability:

{ha19}

$$P \left\{ 0 \leq r \leq \frac{a}{Z} \right\} = \int_0^{r_o} P(r) dr = \frac{1}{2} \int_0^2 u^2 \exp \{-u\} du = 0.323. \quad (9.93)$$

This is the probability of finding the electron at a distance equal or less than  $r_o$ . In the case of the Hydrogen atom  $Z = 1$ , and the nuclear mass,  $m_{Nuclear}$ , is equal to the mass of a proton,  $m_p$ . Also in this case  $a$  and  $a_o$  are almost the same, {ha20}

$$r_o = a = \frac{m_e + m_p}{m_p} a_o = 1.00055 a_o. \quad (9.94)$$

Another interesting feature is the shape of the density probability. For example we can calculate the radial distance,  $r_{max}$ , at which the density probability acquires its maximum value. In this case we have to solve the following equation: {ha21}

$$\left. \frac{d}{dr} P(r) \right|_{r=r_{max}} = 0. \quad (9.95)$$

The solution to Eq. (9.95) is {ha22}

$$r_{max} = r_o = \frac{a}{Z}. \quad (9.96)$$

Thus for a hydrogen atom the most probable distance at which we could find the electron is equal to  $1.00055 a_o$ . This result coincides with Bohr's assumption.

### 9.4.2 Hydrogen-like atom's first excited state.

The first excited state is given by  $n = 2$ . This state is 4 fold degenerate. This means that we have four linear independent wave function. From those 4 choices, we consider the  $n = 2$ ,  $\ell = 0$ ,  $m = 0$  wave function e.g., {ha23}

$$\begin{aligned} \psi_{2,0,0}(r, \theta, \phi) &\equiv \psi_{2s}(r) \\ &= \frac{1}{\sqrt{32 \pi r_o^3}} \left[ 2 - \frac{r}{r_o} \right] \exp \left\{ -\frac{r}{2r_o} \right\}. \quad (9.97) \end{aligned}$$

Using this wave function the density probability for the 2s state is given by: {ha24}

$$P_{2s}(r) = \frac{r^2}{8r_o^3} \left[2 - \frac{r}{r_o}\right]^2 \exp\left\{-\frac{r}{r_o}\right\} . \quad (9.98)$$

{ha25} Notice that this probability is zero for  $r = r_o$ . This is called a node of the wave function. Also this density probability has two maxima, and the expected radial distance is equal to:

$$\langle 2s | r | 2s \rangle = 6 \frac{a}{Z} . \quad (9.99)$$

{ha26a} Since Eq. (9.97) has no angular dependance the wave is spherical symmetric. But not all of the  $n = 2$  wave fubctions share the spherical symmetry. For example, if we consider the wave functions with  $n = 2$  and  $\ell = 1$ , we have three wave functions,

$$\psi_{2,1,0} = R_{2,1}(r) Y_1^0(\theta, \phi) , \quad (9.100)$$

{ha26b}

$$\psi_{2,1,1} = R_{2,1}(r) Y_1^1(\theta, \phi) , \quad (9.101)$$

{ha26c}

$$\psi_{2,1,-1} = R_{2,1}(r) Y_1^{-1}(\theta, \phi) . \quad (9.102)$$

The explicit angular part of Eqs. (9.100)- (9.102) is given by Eqs. (9.34)- (9.36).

{ha28} Notice that in general the Spherical Harmonics are complex functions. Often we are interested in the directionality of the wave function. Thus we represent the angular part separately from the radial part. To represent the directionality we use orbitals rather than the spherica Harmonics because Spherical Harmonics are complex functions. Therefore we construct linear combinations of Spherical Harmonics to represent orbitals. For example we use  $Y_1^1$  and  $Y_1^{-1}$  to define the  $P_x$  and  $P_y$  orbitals, i.e.,

$$2P_x = \frac{1}{\sqrt{2}} [Y_1^1 + Y_1^{-1}] = \sqrt{\frac{3}{4\pi}} \sin(\theta) \cos(\phi) , \quad (9.103)$$

{ha29}

$$2P_y = \frac{1}{\sqrt{2}} \left[ \frac{Y_1^1 - Y_1^{-1}}{i} \right] = \sqrt{\frac{3}{4\pi}} \sin(\theta) \sin(\phi) . \quad (9.104)$$

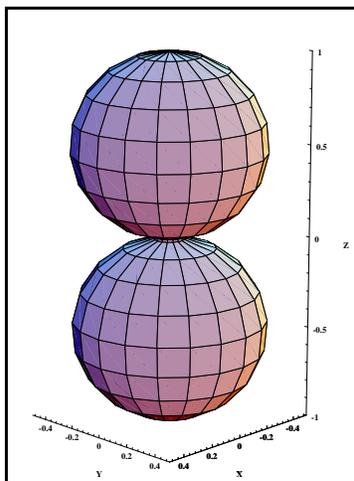


Figure 9.1: pz orbital

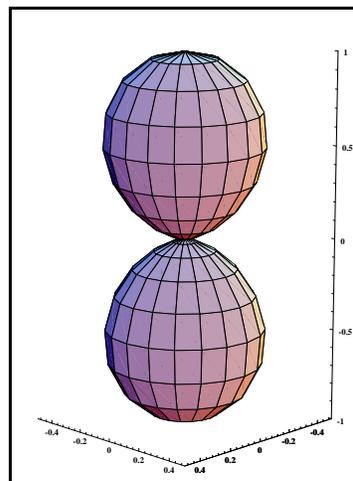


Figure 9.2: pz squared

Since  $Y_1^0$  and  $Y_0^0$  are pure real functions we define the  $2P_z$  and  $2S$  orbitals as:

$$2P_z = Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos(\theta), \quad (9.105)$$

$$2S = Y_0^0 = \frac{1}{\sqrt{4\pi}}. \quad (9.106)$$

These four orbitals are used to define hybrid orbitals like the  $sp$ ,  $sp^2$  and  $sp^3$  in molecular orbital theory.

## 9.5 Single atom representation

To characterize single atoms we use hydrogen-like quantum numbers and energy levels. For example we use the following quantum numbers:

$$n \rightarrow \textit{Principal} \quad 1, 2, 3, 4, \dots \quad (9.107)$$

$$\ell \rightarrow \textit{Angular} \quad 0, 1, 2, 3, 4, \dots, n-1. \quad (9.108)$$

$$n \rightarrow \text{Magnetic } 0, \pm 1, \pm 2, \pm 3, \pm 4, \dots, \pm \ell . \quad (9.109)$$

Before we consider any atomic representation we will consider the dynamics of the electronic cloud. If we consider that the electronic charge moves around a closed loop it will generate a magnetic dipole,  $\mu_M$ . From classic electrodynamics we know that a magnetic dipole is given by:

$$\mu_M = I A , \quad (9.110)$$

where  $I$  is the current and  $A$  is the area enclosed by the loop. The area is equal to  $\pi r^2$  and the current is given by:

$$I = \frac{q v}{2\pi r} , \quad (9.111)$$

where  $q$  is the circulating charge. Thus the magnetic dipole reduces to:

$$\mu_M = \frac{1}{2} \frac{q}{m} r m v = \frac{q}{2m} L , \quad (9.112)$$

where  $L$  is the angular momentum. Therefore in the case of an electron the magnetic dipole in three dimensions is given by the following expression:

$$\vec{\mu}_M = - \frac{|e|}{2m_e} \vec{L} . \quad (9.113)$$

In the presence of a magnetic field the dipole moment will interact with it. In this case the potential energy is given by:

$$V = - \vec{\mu}_M \cdot \vec{B} . \quad (9.114)$$

If we consider the magnetic field in the  $z$ -direction Eq. (9.114) reduces to:

$$V = - \mu_z B_z = \frac{|e| B}{2 m_e} L_z . \quad (9.115)$$

Consequently the potential energy operator of the orbiting electron in the presence of a magnetic field in the  $z$ -direction is

$$\hat{V} = \frac{|e| B}{2 m_e} \hat{L}_z . \quad (9.116)$$

Equation (9.116) predicts no splitting of the hydrogen-like energy levels for  $\ell = 0$  wave functions. But some experiments showed some fine structures that could not be explained. To solve this problem Goudsmit and Uhlenbeck postulated a new quantum number in 1925. This new quantum property is called the intrinsic angular momentum,  $S$ , or electronic spin. Since this quantum property is an angular momentum when applied on the electronic spin wave function,  $\chi$ , we get

$$\hat{S}\chi = \sqrt{s(s+1)} \hbar \chi, \quad (9.117) \quad \{\text{at11}\}$$

$$\hat{S}_z\chi = m_s \hbar \chi, \quad (9.118) \quad \{\text{at12}\}$$

with

$$s = \frac{1}{2} \quad (9.119) \quad \{\text{at13}\}$$

$$m_s = \pm \frac{1}{2}. \quad (9.120)$$

The innovation in Goudsmit and Uhlenbeck's postulate was the fractional value for the intrinsic angular momentum. This value was needed to explain experimental data.

Since the electron has an intrinsic angular momentum it generates a dipole moment,

$$\hat{\mu}_S = -g_e \frac{|e|\hbar}{2m_e} \hat{S}, \quad (9.121) \quad \{\text{at14}\}$$

where  $g_e$  is correction factor from Eq. (9.113). This means that in the presence of a magnetic field in the z-direction the hamiltonian of hydrogen-like atoms contains two extra terms, i.e.,

$$\hat{H} = \hat{H}_o + \frac{|e|\hbar B}{2m_e} \hat{L}_z + g_e \frac{|e|\hbar B}{2m_e} \hat{S}_z, \quad (9.122) \quad \{\text{at15}\}$$

where  $\hat{H}_o$  is the unperturbed hydrogen-like hamiltonian.

When dealing with atoms, we have to consider spin and electron-electron interaction. By introducing the electron-electron interaction the hydrogen-like energy levels split reducing the degeneracy, e.g.,

\{\text{at16}\}

$$\begin{array}{rcccc}
 & \ell = 0 & \ell = 1 & \ell = 2 & \\
 & & 4p \text{ ———} & 4d \text{ ———} & \\
 4s \text{ ———} & & & & 3d \text{ ———} \\
 3s \text{ ———} & & 3p \text{ ———} & & \\
 2s \text{ ———} & & 2p \text{ ———} & & \\
 1s \text{ ———} & & & & 
 \end{array} \tag{9.123}$$

Still each level is  $2\ell + 1$  degenerate and each level can accommodate two electrons. But these electrons have to satisfy Pauli exclusion principle which stipulates that no two electrons can have the same quantum numbers  $n$ ,  $\ell$ ,  $m$ , and  $m_s$ . For example we consider 22 electrons. These electrons are accommodated as:

{at17}

$$(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^4 . \tag{9.124}$$

But the four d-electrons have several possibilities since the level is 5 fold degenerate. For multiple electrons we usually consider the total atoms spin, angular momentum and total angular momentum,

{at18}

$$\vec{L} = \sum_{i=1}^n \vec{L}_i \tag{9.125}$$

{at19}

$$\vec{S} = \sum_{i=1}^n \vec{S}_i \tag{9.126}$$

{at20}

$$\vec{J} = \vec{L} + \vec{S} , \tag{9.127}$$

{at21}

with

$$|J| = \{ |\vec{L} + \vec{S}|, |\vec{L} + \vec{S}| - 1, \dots, ||\vec{L}| - |\vec{S}|| \} . \tag{9.128}$$

{at22}

With this definitions the atomic notation

$${}^{2S+1}L_J \tag{9.129}$$

is used. In order to accommodate these electrons we follow Hund's rules.

**Hund's rules**

- 1) - The state with the largest value of total  $S$  is the most stable.
- 2) - If total  $S$  is the same, the largest total  $L$  is the most stable.
- 3) - If  $S$  and  $L$  are the same, subshell less half full with the smallest  $J$  is the most stable. On the other hand subshell half or more than half full with largest  $J$  is the most stable.



# Chapter 10

## Time dependent Schrödinger equation

Time dependent Schrodinger equation, {td1}

$$\hat{H}\Phi(x,t) = i\hbar \frac{\partial}{\partial t}\Phi(x,t), \quad (10.1)$$

provides us with the necessary tools to study the dynamical properties of quantum mechanical systems. One of the most important systems for chemist is the interaction of matter with electromagnetic radiation. To be more specific as chemist we are interested in molecule's response to the interaction with electromagnetic radiation. For such interaction we find out that the electric field can be written as: {td2}

$$\vec{E} = \vec{E}_o \cos(2\pi \nu_r t), \quad (10.2)$$

where  $\nu_r$  is the radiation frequency and  $\vec{E}_o$  is the amplitud of the electric field. In the presence of an electric field the molecule's dipole moment will respond. The interacion energy is given by the following equation: {td3}

$$V_I(t) = -\vec{\mu} \cdot \vec{E} = -\vec{\mu} \cdot \vec{E}_o \cos(2\pi \nu_r t), \quad (10.3)$$

where  $\vec{\mu}$  is the molecule's dipole moment.

For simplicity we consider the electric field in the x-direction, e.g., {td4}

$$V_I(t) = -\mu_x E_o \cos(2\pi \nu_r t) \equiv \hat{H}_I, \quad (10.4)$$

where we have define  $\hat{H}_I$  as the interaction hamiltonian. If now we consider a diatomic molecule in the presence of an electric field pointing in the x-direction, the hamiltonian operator has two contributions. One from the harmonic oscillator and a second from the interaction between the electric field and molecule's dipole moment,

$$\hat{H} = \hat{H}_{HO} - \mu_x E_{ox} \cos(2\pi \nu_r t) . \quad (10.5)$$

In order to solve Eq. (10.1) we assume that the electromagnetic field is not going to alter significantly the Harmonic Oscillator, but it is only a small perturbation.

Thus in general we will consider hamiltonians which we can write as:

$$\hat{H} = \hat{H}_o + \hat{H}_I(t) , \quad (10.6)$$

where we can solved  $\hat{H}_o$  for its wave functions and energy levels. The interaction term  $\hat{H}_I(t)$  is small time-dependent pertubation, and it will not modify significantly the original wave functions and energy levels.

## 10.1 A simple two-level system

For the sake of simplicity, let us assume a hypothetical two-states unperturbed time independent hamiltonian,  $\hat{H}_o$ , such that we know the solutions to:

$$\hat{H}_o \psi(x) = E_n \psi(x), \quad (10.7)$$

with  $n = 1, 2$ , and

$$\int_{-\infty}^{\infty} \psi_n^*(x) \psi_m(x) dx = \delta_{m,n} , \quad (10.8)$$

wher  $\delta_{m,n}$  is the Kroneker delta, and it is equal to unity if  $m = n$  and zero if  $m \neq n$ .

If this is the case, the two solutions to the time-dependent Schrodinger equation of the unperturbed hamiltonian are:

$$\Psi_1(x, t) = \psi_1(x) \exp \left\{ - \frac{i}{\hbar} E_1 t \right\} , \quad (10.9)$$

$$\Psi_2(x, t) = \psi_2(x) \exp\left\{-\frac{i}{\hbar} E_2 t\right\}. \quad (10.10)$$

Furthermore we will consider the case when the system is initially at state 1. Thus we can write a general wave function solution of  $\hat{H}$  as a linear combination of the unperturbed wave functions as {td10}

$$\Psi(x, t) = a_1(t) \Psi_1(x, t) + a_2(t) \Psi_2(x, t), \quad (10.11)$$

where {td11a}

$$a_1(0) = 1 \quad (10.12)$$

and {td11b}

$$a_2(0) = 0. \quad (10.13)$$

Now we use Eq. (10.11) in the time-dependent Schrödinger equation remembering that the hamiltonia has two parts, e.g., {td12}

$$\begin{aligned} (\hat{H}_0 + \hat{H}_I)(a_1(t) \Psi_1(x, t) + a_2(t) \Psi_2(x, t)) = \\ i \hbar \partial_t (a_1(t) \Psi_1(x, t) + a_2(t) \Psi_2(x, t)). \end{aligned} \quad (10.14)$$

Equation (10.14) can be reduce to {td13}

$$\begin{aligned} a_1(t) \hat{H}_I \Psi_1(x, t) + a_2(t) \hat{H}_I \Psi_2(x, t) = \\ i \hbar \Psi_1(x, t) \frac{da_1(t)}{dt} + i \hbar \Psi_2(x, t) \frac{da_2(t)}{dt}, \end{aligned} \quad (10.15)$$

where we have used Schrödinger time-dependent equation for  $\Psi_i(x, t)$  {td14}

$$\hat{H}_0 \Psi_i(x, t) = i \hbar \frac{\partial}{\partial t} \Psi_i(x, t). \quad (10.16)$$

From Eq. (10.15) we can get two equations for the rate of change of the  $a_i(t)$ . First we multiply Eq. (10.15) by  $\Psi_2^*(x, t)$ , and second we integrate over the system's space. These two steps yield {td15}

$$\begin{aligned} a_1(t) \int_{-\infty}^{\infty} \Psi_2^*(x, t) \hat{H}_I \Psi_1(x, t) dx + a_2(t) \int_{-\infty}^{\infty} \Psi_2^*(x, t) \hat{H}_I \Psi_2(x, t) dx = \\ i \hbar \frac{da_1(t)}{dt} \int_{-\infty}^{\infty} \Psi_2^*(x, t) \Psi_1(x, t) dx + i \hbar \frac{da_2(t)}{dt} \int_{-\infty}^{\infty} \Psi_2^*(x, t) \Psi_2(x, t) dx \end{aligned} \quad (10.17)$$

Now if we use the orthonormality of the wave functions, {td16}

$$\int_{-\infty}^{\infty} \Psi_i^*(x, t) \Psi_j(x, t) dx = \delta_{i,j} , \quad (10.18)$$

we get

{td17a}

$$\begin{aligned} i\hbar \frac{da_2(t)}{dt} &= a_1(t) \int_{-\infty}^{\infty} \Psi_2^*(x, t) \hat{H}_I \Psi_1(x, t) dx \\ &+ a_2(t) \int_{-\infty}^{\infty} \Psi_2^*(x, t) \hat{H}_I \Psi_2(x, t) dx \end{aligned} \quad (10.19)$$

{td18}

Moreover we can use Eqs.(10.9) - (10.10) and get

$$\begin{aligned} i\hbar \frac{da_2(t)}{dt} &= a_1(t) \exp \left\{ \frac{i}{\hbar} (E_2 - E_1) t \right\} \int_{-\infty}^{\infty} \psi_2^*(x, t) \hat{H}_I(t) \psi_1(x, t) dx \\ &+ a_2(t) \int_{-\infty}^{\infty} \psi_2^*(x, t) \hat{H}_I(t) \psi_2(x, t) dx . \end{aligned} \quad (10.20)$$

Since we are considering a small perturbation to the system we expect that  $a_2 \approx 0$  but not zero, and  $a_1 \approx 1$  but not unity. Thus we can neglect the  $a_2$  term in Eq. (10.20) and obtain the following relation:

{td19}

$$i\hbar \frac{da_2(t)}{dt} = a_1(t) \exp \left\{ \frac{i}{\hbar} (E_2 - E_1) t \right\} \langle 2 | \hat{H}_I(t) | 1 \rangle , \quad (10.21)$$

{td20}

where we have introduced the bracket notation

$$\langle n | \hat{H}_I(t) | m \rangle \equiv \int_{-\infty}^{\infty} \psi_n^*(x, t) \hat{H}_I(t) \psi_m(x, t) dx . \quad (10.22)$$

{td21}

Now we can use the specific  $H_I(t)$  defined by Eq. (10.5) and get

$$i\hbar \frac{da_2(t)}{dt} = a_1(t) E_{ox} \cos(2\pi \nu_r t) \exp \left\{ \frac{i}{\hbar} (E_2 - E_1) t \right\} \langle 2 | \hat{\mu}_x | 1 \rangle . \quad (10.23)$$

{td22}

Equation (10.23) can be written as

$$i\hbar \frac{da_2(t)}{dt} \approx E_{ox} F(t) \langle 2 | \hat{\mu}_x | 1 \rangle , \quad (10.24)$$

{td23}

where we have defined

$$\begin{aligned} F(t) &= \frac{1}{2} \left\{ \exp \left\{ \frac{i}{\hbar} [h\nu_r + (E_2 - E_1)] t \right\} \right. \\ &+ \left. \exp \left\{ -\frac{i}{\hbar} [h\nu_r - (E_2 - E_1)] t \right\} \right\} \end{aligned} \quad (10.25)$$

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and we considered  $a_1(t) \approx 1$ . Now we can integrate Eq. (10.24) over time from zero to  $t$  and get

$$a_2(t) = E_{ox} \langle 2 | \hat{\mu}_x | 1 \rangle \left\{ \frac{1 - \exp \left\{ \frac{i}{\hbar} [h\nu_r + (E_2 - E_1)] t \right\}}{h\nu_r + (E_2 - E_1)} + \frac{1 - \exp \left\{ -\frac{i}{\hbar} [h\nu_r - (E_2 - E_1)] t \right\}}{h\nu_r - (E_2 - E_1)} \right\}. \quad (10.26)$$

The square of the absolute value of  $a_2(t)$  is the transition probability from state 1 to state 2 and is given by

$$|a_2(t)|^2 = |E_{ox}|^2 |\langle 2 | \hat{\mu}_x | 1 \rangle|^2 \left\{ \frac{A}{(h\nu_r + (E_2 - E_1))^2} + \frac{B}{(h\nu_r - (E_2 - E_1))^2} \right\} \quad (10.27)$$

We notice that the largest value occurs when

$$h\nu_r = |E_2 - E_1|, \quad (10.28)$$

which means that a photon either absorbed or emitted has an energy equal to the difference between the level involved in the transition. Also we notice that the transition probability will be equal to zero if

$$\langle 2 | \hat{\mu}_x | 1 \rangle = 0. \quad (10.29)$$

This condition tells us that the only transition allowed are those with

$$\langle 2 | \hat{\mu}_x | 1 \rangle \neq 0. \quad (10.30)$$

Therefore the analysis of Eq. (10.30) yields the so-called selection rules.

## 10.2 Selection rules for the Harmonic Oscillator

Results from the two-level system can be generalized to a multiple level system like the Harmonic Oscillator. Namely we can say that if the

system at  $t = 0$  is at level  $n$ , e.g.,  $a_n(0) = 1$ , the transition coefficient,  $a_m(t)$ , to level  $m$  is given by: {td27}

$$T_{m,n} \equiv a_m(t) \approx \langle m | \hat{\mu}_x | n \rangle \int_0^t F_{m,n}(t') dt' , \quad (10.31)$$

where the integral yields a function of time with maximum values when

{td28}

$$h \nu_r = |E_m - E_n| \quad (10.32)$$

For the Harmonic Oscillator we will derive the selection rules from the expectation value of the dipole moment operator,  $\hat{\mu}_x$ ,

{td29}

$$\langle m | \hat{\mu}_x | n \rangle \equiv \int_{-\infty}^{\infty} \psi_m^*(x) \hat{\mu}(\ell) \psi_n(x) dx , \quad (10.33)$$

where  $\ell$  is the distance between the atoms, and  $x$  is the displacement from equilibrium. In order to analyze Eq. (10.33) we consider a Taylor expansion around the equilibrium distance between atoms,  $\ell_o$ ,

{td30}

$$\mu(\ell) = \mu(\ell_o) + \left( \frac{d\mu}{d\ell} \right)_{\ell=\ell_o} (\ell - \ell_o) + \dots , \quad (10.34)$$

where  $\mu(\ell_o) \equiv \mu_o$  is the permanent dipole moment, and  $x \equiv \ell - \ell_o$  the displacement from equilibrium. For example in the case of a diatomic molecule the dipole moment is given by

{td31}

$$\mu = q \ell = q \ell_o + q x . \quad (10.35)$$

Using these definition we can approximate the dipole moment operator as

{td32}

$$\hat{\mu}(\ell) = \mu_o + \left( \frac{d\mu}{d\ell} \right)_{\ell=\ell_o} \hat{x} + \dots . \quad (10.36)$$

Therefore its expectation value is given by:

{td33}

$$\begin{aligned} \langle m | \hat{\mu}(\ell) | n \rangle &= \langle m | \mu_o | n \rangle + \left( \frac{d\mu}{d\ell} \right)_{\ell=\ell_o} \langle m | \hat{x} | n \rangle + \dots \\ &= \mu_o \delta_{m,n} + \left( \frac{d\mu}{d\ell} \right)_{\ell=\ell_o} \langle m | \hat{x} | n \rangle + \dots , \end{aligned} \quad (10.37)$$

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where we have used the orthonormality property of the harmonic oscillator's wave functions, e.g.,

$$\langle m | \mu_o | n \rangle = \mu_o \langle m | n \rangle = \mu_o \delta_{m,n} . \quad (10.38)$$

Consequently if  $m \neq n$  the transition coefficient reduces to:

$$T_{m,n} \propto \left( \frac{d\mu}{d\ell} \right)_{\ell=\ell_o} \langle m | \hat{x} | n \rangle . \quad (10.39)$$

We notice that  $T_{m,n}$  is equal to zero if the vibration does not change the dipole moment of the molecule. In this case we say that the molecule is IR inactive. For example hydrogen,  $H - H$ , or nitrogen,  $N \equiv N$ , have no permanent dipole, and the vibration does not change the dipole moment. On the other hand hydrogen chloride,  $H - Cl$ , has a permanent dipole, and vibration changes the value of the dipole moment. Thus  $H_2$  and  $N_2$  are IR inactive, and  $HCl$  is IR active. In the case of a triatomic molecule the permanent dipole moment may be zero, but certain vibrations may change its value, while other vibrations may not. For example carbon dioxide,  $O = C = O$ , has a zero permanent dipole moment, but

$$\begin{aligned} \leftarrow O = C = O \rightarrow & \longrightarrow \frac{d\mu}{d\ell} = 0 \\ O \rightarrow = \leftarrow C = O \rightarrow & \longrightarrow \frac{d\mu}{d\ell} \neq 0 \\ O \downarrow = C \uparrow = O \downarrow & \longrightarrow \frac{d\mu}{d\ell} \neq 0 . \end{aligned} \quad (10.40)$$

The second condition for nonvanishing transition coefficient,  $T_{m,n}$ , is given by the expectation value

$$\langle m | \hat{x} | n \rangle = \int_{-\infty}^{\infty} \psi_m^*(x) x \psi_n(x) dx . \quad (10.41)$$

In the case of the Harmonic Oscillator its wave functions satisfy the following relation:

$$x \psi_n(x) = c_- \psi_{n-1}(x) + c_+ \psi_{n+1}(x) , \quad (10.42)$$

where the  $c_{\pm}$ s are constants. Using this mathematical relation between the wave functions of the H.O. we get from Eq. (10.41)

{1d38}

$$\langle m|\hat{x}|n\rangle = c_-\langle m|n-1\rangle + c_+\langle m|n+1\rangle \quad (10.43)$$

Therefore the transition coefficient is zero if the final state,  $m$ , is not equal to  $n-1$  or  $n+1$ . In other words, the allowed final states of a H.O. are either  $n \pm 1$ . This result is known as a selection rule for a dipole moment transition for a Harmonic Oscillator, e.g.,

{1d39}

$$\Delta n = \pm 1 . \quad (10.44)$$

Other selection rules are obtained following similar analysis of the interaction hamiltonian,  $\hat{H}_I$ , and the mathematical properties of the known wave functions of the unperturbed hamiltonian  $\hat{H}_0$ .

Table 1 contains typical values of wave numbers and characteristic times for diatomic molecules.

TABLE 1		
Molecule	$\bar{\nu}_{Obs}$	$t_{ch} = (\bar{\nu}c)^{-1}$
$H^{35}Cl$	2950 $cm^{-1}$	11.3 $fs$
$H^{79}Br$	2559 $cm^{-1}$	13.0 $fs$
$CO$	2169 $cm^{-1}$	15.0 $fs$

A femtosecond, fs, is equal to  $10^{-15}$  s. The characteristic time represents the time of a full oscillation. As a reference time we mention that the time for bond-breaking or bond-forming is of the order of 10 to 100 fs.

# Chapter 11

## Statistical mechanics

### 11.1 Introduction

The thermodynamic laws are of macroscopic nature. Therefore any microscopic theory must be consistent with the laws of thermodynamics. In other words if we believe that the laws of mechanics, either classical or quantum, are a true description of microscopic particles, we must be able to derive the laws of thermodynamics from the microscopic description. Namely our goal is to describe a system which on the average consists of approximately  $10^{23}$  particles. These particles can be either atom or molecules. On one hand thermodynamics is concerned with the macroscopic properties of matter at equilibrium. For example in thermodynamics we are interested in knowing the volume,  $V$ , pressure,  $P$ , temperature,  $T$ , internal energy,  $U$ , enthalpy,  $H$ , chemical potential,  $\mu$ . On the other hand we have accepted the idea that a system is composed of atoms and molecules, and we know that the motion of these particles has to be responsible of the system's macroscopic properties. From the theoretical point of view the link between the microscopic and macroscopic worlds is important since this link will give us the means to test microscopic theories. . The aim of Statistical Mechanics is to establish a connection between the detailed laws of quantum or classical mechanics and thermodynamics. It deals with relations between macroscopic equilibrium properties and microscopic force laws like the Newton's laws or Schrödinger equation. Statistical Mechanics

originates from Maxwell and Boltzmann's works on the kinetic theory of gases (1860-1900). Major advances were made by Gibbs and Einstein in the early 20<sup>th</sup> century (1900-1905). Originally scientists believed that molecules obeyed classical mechanics. In some cases this assumption led to incorrect results. For example the heat capacity of polyatomic gases. When quantum mechanics was developed, necessary modifications in classical statistical mechanics were made. These changes were able to give a better description of the previously incorrect results. Before we continue, we will consider the deterministic nature of classical and quantum mechanics. Classical mechanics is a deterministic theory. This means that Newton's laws predict the values of the system's variables at later times if the initial values at  $t = 0$  are given. For example let us consider that at  $t = 0$  we have the initial positions,  $\vec{q}_0^\Gamma$ , and momenta,  $\vec{p}_0^\Gamma$ , of a set of  $10^{23}$  molecules, , , where we have defined the following notation:

{st1}

$$\vec{q}_0^\Gamma \equiv \{r_1^\vec{r}(0), r_2^\vec{r}(0), r_3^\vec{r}(0), \dots, r_N^\vec{r}(0)\} , \quad (11.1)$$

{st2}

$$\vec{p}_0^\Gamma \equiv \{p_1^\vec{r}(0), p_2^\vec{r}(0), p_3^\vec{r}(0), \dots, p_N^\vec{r}(0)\} . \quad (11.2)$$

In principle we are able to calculate the particles' future positions,  $\vec{q}^\Gamma(t)$ , and momenta,  $\vec{p}^\Gamma(t)$  by solving Newton's second law.

Determinism in quantum mechanics is more sophisticated in nature. But a similar predictability follows from its laws. Namely, given the initial wave function at time  $t = 0$ , the time behavior of the wave function is described by Schrödinger equation, i.e.,

{st3}

$$\partial_t \Psi(\vec{q}^\Gamma, t) = \frac{i}{\hbar} \hat{H} \Psi(\vec{q}^\Gamma, t) . \quad (11.3)$$

Future values of the wave function is obtained by solving Schrödinger equation,

{st4}

$$\Psi(\vec{q}^\Gamma, t) = \exp\left\{\frac{i}{\hbar} H t\right\} \Psi(\vec{q}^\Gamma, 0) . \quad (11.4)$$

With  $\Psi(\vec{q}^\Gamma, t)$  we can calculate the expected or average value of any physical property at time  $t$ .

The problem resides in solving  $10^{23}$  equations and keeping track of  $2 \times 10^{23}$  values or solve Schrödinger equation for  $10^{23}$  interacting

particles. We could say that some years ago we could not solve them. But maybe now with the help of supercomputers the task is possible. The answer is no. Now a days the fastes computers are able to handle up to  $10^9$  particles for periods of the order of  $10^{-7}s$ . Not even dilute systems can be dealt by supercomputers since dilute systems consist of  $10^{18}$  particles.

Since macroscopic measurements involve much longer times that the characteristic microscopic times, we can trade determinism by statistics. After all pressure,  $P$ , can not critically depend on each of the microscopic particle's path. Notice the difference in times scales. For example, time,  $\tau$  between collisions is of the order of  $10^{-10}$  seconds, and characteristic thermodynamic times are of the order of  $10^{-1}$  seconds. Thus we can consider the macroscopic values as time averages of the microscopic events.

In Statistical Mechanics the state of a system has two meanings. One the thermodynamic state is given by the values of enough macroscopic parameters ( $N, P, T, \dots$ ). Second the quantum state is specified by an  $N$  particles wave function,  $\Psi_j(\vec{q}_N^{(\Gamma)}, t)$ , which a solution of the  $N$ -body Schrödinger equation. From this wave function the probability of finding the particles at a particular set of positions is given by  $|\Psi_j(\vec{q}_N^{(\Gamma)}, t)|^2$ . For  $10^{23}$  interacting particles is impossible in practice to calculate  $\Psi_j(\vec{q}_N^{(\Gamma)}, t)$ . In summary a macroscopic state is a thermodynamic state which is an observable. On the other hand a microscopic state is a quantum state which is not an observable.

Since we are dealing a large number of particles, a large number of different microstates are compatible with a given macrostate. For example the translational energy levels lie very close from each other. Also we can find a large number of different ways in which we can populate the energy levels, and still end up with the same total energy. Classically a state is specified by the position,  $r(\vec{t})$ , and  $p(\vec{t})$ , of every particle of the system at any time  $t$ . The energy is given by: {st5}

$$E_T = \sum_{i=1}^N \frac{p_i^2}{2m_i} + \sum_{i<j} Y_{ij}(\vec{r}_i, \vec{r}_j) . \quad (11.5)$$

Also, other macroscopic properties are time averages. For example, pressure is given by: {st6}

$$P = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \frac{F(t')}{A} dt' . \quad (11.6)$$

But time averages can not be carried out in practice.

Notice that the macrostate is consistent with a large number of different microstates. Using this property we define an ensemble, which is a hypothetical collection of large number of copies of the system. Each of these copies is consistent with the macroscopic state i.e.,  $N, V, T$ .

# Chapter 12

## Complex dynamics

### 12.1 Introduction

For the last twenty-five years sustained oscillations of the concentration of a chemical substance have been the subject of intensive study. In spite of theoretical predictions of damped oscillations and sustained oscillations by Lotka and Hirniakand [1, 2] in 1910 and Lotka [3] in 1920, and the experimental observation of cyclic changes in the iodate catalyzed decomposition of hydrogen peroxide by Bray in 1921[4], both experimentalists and theorists virtually ignored the field of chemical oscillations. The First Symposium on Biological and Biochemical Oscillators was organized in 1968, forty seven years after Bray's paper appeared in the Journal of the American Chemical Society.

In the early 1950's Belusov [5] observed cyclic color changes in the bromination of citric acid catalyzed by cerium. However, the world scientific community did not gain access to the experimental details of these cyclic color changes, since Belusov's first findings were rejected for publication in 1951, and another six years of detailed experimentation were again rejected in 1957 [6]. Out of his work Belusov published an abstract in an obscure symposium in 1959 [5] and kept the original manuscript; he never tried again to publish his results. For years the Belusov protocol for chemical oscillations was known only to researchers and students at the Moscow State University, until one of those stu-

dents, Zhabotinsky, initiated a careful and detailed investigation of the Belusov reaction during the first half of the 1960's. In the final analysis, Zhabotinsky substituted citric acid for malonic acid and published his findings in 1964 [7]. By 1967 the first paper written in English reached the West, causing immense interest among many researchers.

An interesting aspect of the Belusov-Zhabotinsky (B-Z) reaction centers around the original motivation that led Belusov to the celebrated reaction. Originally, his interest in biochemistry, and in particular in the Krebs cycle [8], motivated Belusov to seek a simple experimental model in which a carbohydrate was oxidized in the presence of a catalyst. In other words, the B-Z reaction was intended as a model of an enzyme catalyzed reaction. This connection between enzyme kinetics and the B-Z reaction is often forgotten and rarely mentioned. Most likely, this omission can be traced to the differences between an enzyme and its model counterpart  $C_e$ , the complicated mechanism underlining the chemical oscillations in the B-Z reaction and the mathematical analyses needed to understand some of the reduced models of the B-Z reaction. From the biochemical point of view, these differences are difficult to reconcile with a biological model. Therefore, the search for a model of chemical oscillation in enzyme kinetics that is both biochemically relevant and mathematically simple enough to present to an undergraduate audience is worthwhile from the pedagogical point of view.

In the present discussion we consider glycolysis, centering around the allosteric properties of phosphofructokinase (PFK). For nearly thirty years oscillations in the concentration of nucleotides in the glycolytic pathway have been documented in the case of yeast cells and cell-free extract [9]. For example, reduced nicotinadenine dinucleotide (NADH) oscillations in yeast extract have been observed and determined to be flux dependent; a minimum external flux is required to sustain oscillations in the concentration of NADH. Moreover, Hess and Boiteux [10] observed that phosphofructokinase plays an essential role in these oscillations. If PFK's substrate, fructose-6-phosphate (F-6-P), is added to cell-free extracts, the nucleotide concentrations oscillate. On the other hand, after the injection of PFK's product, fructose-1,6-bisphosphate (F-1,6-bP), no oscillations are observed. Based on these observations

and on the allosteric properties of PFK, two models were suggested in the late 1960's. One, by Higgins [11], is based on the activation of PFK by its product. The second model [12] is based on the activation and inhibition properties of PFK by adenosine triphosphate (ATP), adenosine diphosphate (ADP) and adenosine monophosphate (AMP). The latter links PFK with pyruvate kinase, while the former does not.

In the next section we discuss the steps along the glycolytic pathway which are relevant to the Higgins model. Next we reduce the model to two variables and discuss its similarities with Lotka's models and the origin of the autocatalytic step. Finally, we scale the model, do a linear stability analysis and discuss the bifurcation diagram of the reduced, two-variable Higgins model.

## 12.2 Higgins Model

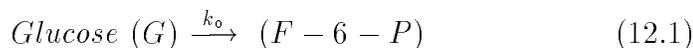
The interest in the origin of periodic biological processes like the circadian clock has motivated researchers to look for the chemical basis of oscillations in biochemical systems [13]-[15]. One of these systems is glycolysis, in which six-membered sugars are converted anaerobically into tricarboxylic acids. This process allows the phosphorylation of ADP. In the case of glycolysis the addition of glucose to an extract containing the main metabolites triggers cyclic, or periodic, behavior in the concentrations of metabolites. This periodic change in the concentrations of the glycolytic metabolites is termed glycolytic relaxation oscillations. In particular, relaxation oscillations in the concentration of NADH are readily observed using spectrophotometric methods on yeast extracts. For the past twenty-five years, researchers have studied mostly relaxation oscillations which are due to a single injection of glucose. In this case, the system relaxes to equilibrium. Conversely, if constant or periodic injection is applied, a system is pushed away from equilibrium and can achieve nonequilibrium steady states.

Researchers have found that phosphofructokinase (PFK), which catalyzes the conversion of F-6-P to F-1,6-bP, is the regulatory enzyme for glycolytic oscillations [16]-[17]. This regulation is the result of the activation and inhibition properties of PFK. For example, in liver, PFK is activated by F-2,6-bP [18] which is an isomer of F-1,6-bP. And in

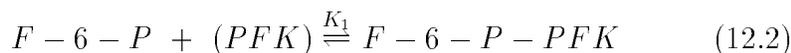
muscle, PFK is inhibited by ATP. Based on these facts, most kinetic models of glycolytic oscillations have centered around either PFK's inhibition [12] or its activation [11]. One of the models based on the activation of PFK by fructose biphosphate is the Higgins model. This model considers only two enzymatic reactions with a constant external source of glucose. Condensing two steps of the glycolytic path into one, the Higgins model assumes a first order conversion of glucose to F-6-P. Following this first step, the Higgins model considers the enzymatic conversion of F-6-P to F-1,6-bP by PFK and F-1,6-bP to glyceraldehyde-3-phosphate (G-3P) by aldolase (ALD). In this model, the regulation consists only of the activation of an inactive Phosphofructokinase ( $\overline{PFK}$ ) by F-1,6-bP. Under this assumption, the Higgins model sustains oscillations in the concentration of F-6-P, F-1,6-bP and the enzymes. Using further simplifications, such as the steady-state approximation for PFK, the model reduces to three time-dependent species with autocatalytic conversion of F-6-P to F-1,6-bP. Finally, if one considers a steady-state approximation for ALD, one obtains a two-species model which is able to sustain oscillations.

The following equations depict the steps along the glycolytic pathway that are relevant to the Higgins model:

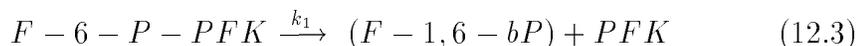
{glu}



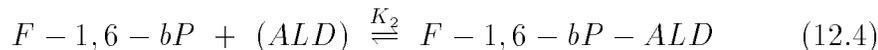
{f6p}



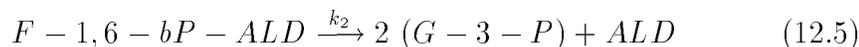
{pfk}



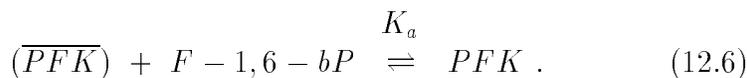
{f16bisP}



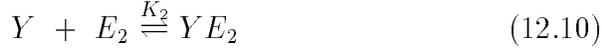
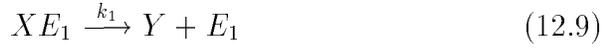
{ald}



{act}



For the sake of a simple notation, the following mechanism, which is equivalent to Eq. (12.1)-(12.6), will be used:



where G stands for glucose, X for F-6-P,  $E_1$  for PFK, Y for F-1,6-bP and  $E_2$  for ALD. Using these equations, the mass action laws for the six species model are as follows:

$$\frac{d[X]}{dt} = k_o G_o - k_{E_1}^+ [E_1][X] + k_{E_1}^- [E_1 X] \quad (12.13)$$

$$\frac{d[Y]}{dt} = k_1 [E_1 X] - k_{E_2}^+ [E_2][Y] + k_{E_2}^- [E_2 Y] - k_a^+ [\bar{E}_1][Y] + k_a^- [E_1] \quad (12.14)$$

$$\frac{d[E_1]}{dt} = k_{E_1}^- [E_1 X] - k_{E_1}^+ [E_1][X] + k_1 [E_1 X] - k_a^- [E_1] + k_a^+ [\bar{E}_1][Y] \quad (12.15)$$

$$\frac{d[E_1 X]}{dt} = -k_{E_1}^- [E_1 X] + k_{E_1}^+ [E_1][X] - k_1 [E_1 X] \quad (12.16)$$

$$\frac{d[\bar{E}_1]}{dt} = k_a^- [E_1] - k_a^+ [\bar{E}_1][Y] \quad (12.17)$$

$$\frac{d[E_2]}{dt} = k_{E_2}^- [E_2 Y] - k_{E_2}^+ [E_2][Y] + k_2 [E_2 Y] = -\frac{d[E_2 Y]}{dt} \quad (12.18)$$

Using the steady-state approximation for all of the enzymes, we obtain a minimal two variable model [19]

$$\frac{d[X]}{dt} = k_o G_o - k_{ac}[X][Y] \quad (12.19)$$

$$\frac{d[Y]}{dt} = k_{ac}[X][Y] - \frac{V_{2m} \frac{[Y]}{K_{2M}}}{1 + \frac{[Y]}{K_{2M}}}, \quad (12.20)$$

where  $k_{ac}$  is given by the following equation:

$$k_{ac} = \frac{K_a \frac{V_{1m}}{K_{1M}}}{1 + K_a[Y] + \frac{K_a}{K_{1M}}[X][Y]} \quad (12.21)$$

and

$$K_{iM} = \frac{k_i + k_{E_i}^-}{k_{E_i}^+} \quad (12.22)$$

$$V_{im} = k_i E_i^o \quad (12.23)$$

$$K_a = \frac{k_a^+}{k_a^-} . \quad (12.24)$$

In Eq.(12.23)  $E_i^o$  represents the stoichiometric concentration of the  $i^{th}$  enzyme. Also in the Higgins model,  $k_{ac}$  is simplified even further to

$$k_{ac} = \frac{V_{1m} K_a}{K_{1M}} = \frac{k_1 k_{E_1}^+ E_i^o K_a}{k_1 + k_{E_1}^-} . \quad (12.25)$$

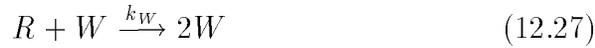
Equations (12.19)-(12.25) constitute the Minimal Higgins (MH) model .

### 12.2.1 Comparison with the Lotka Model

The Minimal Higgins Model as expressed by Eqs. (12.19) and (12.20) shows some similarities with the Lotka's models. For example, in the original Lotka model of 1910, species reproduction is proportional to the amount of food, which is kept constant; namely



This elementary step, in conjunction with the following steps:



define what is known as the Lotka Model and the differential equations describing the time behavior of the population are given in Table I.

Table I	
Model	Differential equations
<b>Lotka 1910</b>	$\frac{d[R]}{dt} = k_R G_o - k_W [R][W]$ $\frac{d[W]}{dt} = k_w [R][W] - k_D [W]$
<b>Lotka 1920</b>	$\frac{d[R]}{dt} = k_R G_o [R] - k_W [R][W]$ $\frac{d[W]}{dt} = k_w [R][W] - k_D [W]$
<b>Minimal Higgins</b>	$\frac{d[X]}{dt} = k_o G_o - k_{ac} [X][Y]$ $\frac{d[Y]}{dt} = k_{ac} [X][Y] - \frac{V_{2m} [Y]}{K_{2M} + [Y]}$
<b>Schankenberg</b>	$\frac{d[X]}{dt} = k_o G_o - k_S [X][Y]^2$ $\frac{d[Y]}{dt} = k_s [X][Y]^2 - k_D [Y]$

Notice that the first differential equations in the MH model and the Lotka's 10 model are the same. In the 1920 paper, Lotka introduced a species dependent external flux, namely

{10t4}



which is an autocatalytic step and substitutes Eq.(12.26). In this case, the differential equations describing the time behavior of the populations are given in Table I. In both Lotka's models cases, the concentration of grass,  $G_0$ , is kept constant. Notice that the 1920 model is a variation of the 1910 model which yields oscillation in the population. Consequently, we can think of the MH model as a variation of the 1910 model where we have included an enzymatic step instead of a first order step.

These two Lotka models are the simplest schemata in which oscillations in the populations can be observed. A meaningful interpretation of this model is in population dynamics. For example if we define G as grass, R as rabbit and W as wolf, the explanation of the oscillatory behavior seems quite logical. As the rabbits consume the grass and reproduce, their numbers grow, while the amount of grass decreases. As the rabbit population grows, the wolves have plenty of rabbits available for consumption, and they, too, reproduce. However, as the wolf population increases, the rabbit population decreases. As the rabbit population decreases, the wolves start to die, since there are not enough rabbits. As a consequence, grass becomes more plentiful, and the rabbits start the cycle again. Unfortunately, the first Lotka model yields only damped oscillation and the second model gives sustained oscillations for any initial condition, which is a severe restriction if we want to model realistic chemical and biochemical systems. In contrast, the Minimal Higgins model shows stable steady states, damped and sustained oscillations. The richness of this model stems from the second differential equation which includes an enzymatic Michaelis-Menten step. Moreover, the autocatalytic step in the MH model can be traced to the activation of PFK by its product. The fourth model in Table I is due to Schnakemberg [22]. In this model, the bimolecular autocatalytic step in the Lotka 1910 model is replaced by a trimolecular step. This change appears as a cubic term in the differential equations. With this

change, the model shows sustained oscillations. But the connection between the cubic autocatalytic term and a biochemical justification has not been achieved.

## 12.3 Stability Analysis

In this section we present a linear stability analysis [20] of the Minimal Higgins model. For this purpose, we scale the differential equation such that the dimensionless differential equations depend only on two parameters rather than on five. Namely, we get from Eqs. (12.19)-(12.20)

$$\frac{dX}{d\tau} = A - XY \quad (12.30)$$

$$\frac{dY}{d\tau} = XY - \frac{qY}{1+Y} \quad (12.31)$$

where we have defined the following dimensionless quantities:

$$\tau = k_{ac}K_{2M}t \quad (12.32)$$

$$X = \frac{[X]}{K_{2M}} \quad (12.33)$$

$$Y = \frac{[Y]}{K_{2M}} \quad (12.34)$$

$$A = \frac{k_o G_o}{K_{2M}^2 k_{ac}} \quad (12.35)$$

$$q = \frac{V_{2m}}{K_{2M}^2 k_{ac}} \quad (12.36)$$

The first step in the stability analysis is to find the steady state solution. In general this is done by setting the left hand side of the differential equations equal to zero and solving for the concentrations. From Eqs.(12.30)-(12.31), we obtain for the scaled MH model the following steady state solutions:

$$x^{ss} = q - A \quad (12.37)$$

$$y^{ss} = \frac{A}{q - A} \quad . \quad (12.38) \quad \{y^{ss}\}$$

Clearly from Eqs.(12.37)-(12.38), we can see that the physically meaningful solutions have to satisfy the following condition:  $q > A$ . Only values of A less than q give meaningful physical results, i.e.,  $x^{ss}$  and  $y^{ss}$  have to be positive.

Once these stationary states are obtained, stability analysis studies what happens to all components of the system when the system is perturbed slightly from its steady state. For this purpose we first calculate the relaxation matrix, R, which is the Jacobian associated to a set of ordinary differential equations (ODEs) [20]. For the scaled MH model, we obtained the following matrix:

$$R = \begin{pmatrix} -y^{ss} & -x^{ss} \\ y^{ss} & x^{ss} - \frac{q}{(1+y^{ss})^2} \end{pmatrix} \quad . \quad (12.39)$$

Next, we have to find the eigenvalues,  $\lambda_{\pm}$  of R, which are the solutions of the following characteristic polynomial:

$$\lambda^2 + \left[ \frac{(1 + y^{ss})(y^{ss} - x^{ss}) + x^{ss}}{1 + y^{ss}} \right] \lambda + \left[ \frac{x^{ss} y^{ss}}{1 + y^{ss}} \right] = 0 \quad . \quad (12.40)$$

In this case the solutions of the quadratic Eq.( 12.40) are

$$\lambda_{\pm} = -\frac{1}{2} \left[ \frac{(1 + y^{ss})(y^{ss} - x^{ss}) + x^{ss}}{1 + y^{ss}} \right] \pm \frac{1}{2} \sqrt{\left[ \frac{(1 + y^{ss})(y^{ss} - x^{ss}) + x^{ss}}{1 + y^{ss}} \right]^2 - 4 \left[ \frac{x^{ss} y^{ss}}{1 + y^{ss}} \right]} \quad (12.41)$$

Equation (12.41) can be reduced to the following expression:

$$\lambda_{\pm} = \frac{P_R(A, q) \pm \sqrt{P_I(A, q)}}{2q(q - A)} \quad , \quad (12.42)$$

where we have defined the following functions:

$$P_R(A, q) = A [A^2 - 2Aq + q^2] \quad (12.43)$$

{pi}

$$P_I(A, q) = A \left[ A^5 - 4qA^4 + 2q(3q + 1)A^3 - 4q^2(q + 2)A^2 + q^2(q^2 + 10q + 1)A - 4q^2 \right] \quad (12.44)$$

Equations (12.43,12.44) have been obtained both by analytical methods and with the help of the software package MATHEMATICA [21].

From Eqs.(12.41)-(12.44) , we can analyze four possible eigenvalues:  
 a)  $P_R < 0$  and  $P_I > 0$ . In this case, the eigenvalue is pure real and negative. Thus the steady state solution is a stable fixed point [20].  
 b)  $P_R < 0$  and  $P_I < 0$ . In this case, the eigenvalue has a negative real part and a nonzero imaginary part. For this eigenvalue, we find damped oscillations.  
 c)  $P_R > 0$  and  $P_I > 0$ . In this case, the eigenvalue is pure real and positive. The steady state is unstable.  
 d)  $P_R > 0$  and  $P_I < 0$ . In this case, the eigenvalue has a positive real part and a nonzero imaginary part. The steady state is unstable and moves away to unstable oscillations.

Also, we can construct a plot of A vs. q. Figure 1, depicts such a diagram, and the different lines represent curves where A - q,  $P_R$  and  $P_I$  are equal to zero. These curves delimit different regions in parameter space. In region A, we observe stable fixed points, in region B, we observe damped oscillations, and region C, we observe sustained oscillations.

For a fixed value of q, the value of A at which  $P_R(A, q)$  is equal to zero,  $A_c$ , defines the bifurcation point. Values of A greater than  $A_c$  are in regions A or B, and for values less than  $A_c$  are in region C. Thus for  $A_c < A < q$  the system reaches a fixed point e.g. Figure 2 and 3. For  $A < A_c$ , the systems reaches a limit cycle e. g. Figure 4. The diagram of A versus oscillation amplitude is called a bifurcation diagram [20] depicted by Figure 5.

## 12.4 Summary

The minimal Higgins model is a simple two species model that shows sustained oscillations in enzyme kinetics. The steps in the mechanism have a biochemical justification and the step responsible of the oscillation is a Michaelis-Menten step. Also, the stability analysis is simple and accessible both analytically or with the help of MATHEMATICA. For example the bifurcation points are obtained by fixing either A or q

and solving a simple quadratic equation, e.g. Equation(12.43).

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## Figure captions

### Figure 1

Parameter space diafram for the Minimal Higgins model. The line  $q = A$  is represented by a continous line (—);  $P_R(A, q) = 0$  is represented by a dash line (-----);  $P_I(A, q) = 0$  is represented by dash-space line (- - -).

### Figure 2

Example from region A. In this case  $q = 10$  and  $A = 8.50$ . a)  $x$  vs  $t$ ; b)  $x$  vs.  $y$ .

### Figure 3

Example from region B. In this case  $q = 10$  and  $A = 6.87$  a)  $x$  vs  $t$ ; b)  $x$  vs.  $y$ .

### Figure 4

Example from region C. In this case  $q = 10$  and  $A = 6.50$ . a)  $x$  vs  $t$ ; b)  $x$  vs.  $y$ .

### Figure 5

Bifurcation diagram with  $q = 10$ .