



APPLICATION OF MATHEMATIC IN PHYSICAL CHEMISTRY

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ABSTRACT

Mathematics is considered as centre of physical science. It acts as to develop the knowledge in the fields of physical chemistry and other branches. This is widely applied to study the stoichiometric laws, broadly spectroscopic, Electrochemistry, Nuclear Chemistry, Chemical Kinetics, Chemical reaction energetics, Photochemistry; Calculations of vanderwaals constants, graphical representation can be easily evaluated. Any theory can be easily reduced to simple lucid form. In the author views mathematics is very much useful for the development of physical sciences (Physical Chemistry) and other branches.

KEYWORDS: Integration, Derivation, Hess Law, Enthalpy.

INTRODUCTION

Chemistry is a rich and complex science, exhibiting a diversity of reproducible and precisely describable predictions. Many predictions are quantitative numerical predictions and also many are of a qualitative (non-numerical) nature, though both are susceptible to sophisticated mathematical formalization. [1]. Mathematical inscriptions related to derivatives and integrals are a fundamental part of the language of physical chemistry. Consider, for instance, a type of mathematical relationship commonly encountered in a junior-level chemical thermodynamics course, the Maxwell Relations. Also referred to as the equality of mixed second partial derivatives of exact differentials, the Maxwell Relations provide a way to relate macroscopic observable quantities such as temperature and pressure to more abstract chemical properties such as entropy or Gibb's Energy [2].

With greatly enhanced modern computing facilities, the time for using this potential may be approaching. The foundation mathematics for crystal structure analysis is contained within the infinite set of determinants that comprise the necessary and sufficient conditions for a Fourier series to be nonnegative [3].

Research on the students' ability to translate mathematical equations and symbols into descriptions of the macroscopic system under study have not been extensively investigated in chemistry education research. The vast majority of studies related to thermodynamics have been done to document student difficulties and misconceptions in thermodynamics contexts and have taken place either in K-12 classrooms or introductory courses with few exceptions. Greenbowe and Meltzer's (2003)[4] work focused on thermochemical concepts related to solution calorimetry. Jasien and Oberem (2002) [5] focused on thermal equilibrium and energy transfer. Thomas and Schwenz's (1998) [6] work focused on physical chemistry students' concepts of the first and second law of thermodynamics. These studies largely focused on conceptual understandings related to thermodynamics contents rather than difficulties tied to how students make physical sense from mathematics inscriptions in physical chemistry contexts.

1.1 Use of Mathematics in Chemical Reaction.

App physical or chemical change in inverse are accompanied by change in energies as like chemical energy, mechanical energy. Chemical reactions and energetic is known as thermodynamic. It is a branch of sciences which deals with transformation of heat from one system to another system [i.e. Thermo = to heat and dynamics = to transfer]. It is chemical change but it tells only with initial and final state of system. This paper deals only use of mathematics in derivation.

a. First Law of thermodynamic:

- Energy is neither created nor destroyed but it can be converted from one form to another.
- Energy of the universe remains constant.
- Energy of isolated system must remain constant but it is transferred from one form to another.
- It is never possible to construct a perpetual motion machine which produces work without consuming any energy.

Hence mathematically this law is expressed as

$$q = \Delta E + w \text{ or } \Delta E = q - w$$

$q = \pm$ quantity of heat absorbed, $w =$ work done by the system, $w = p\Delta v$,

$\Delta E =$ Change in internal energy.

b. Mathematics used in the calculation of

a. Concept of maximum work

Let us consider an ideal gas enclosed with weightless frictionless piston. Over this infinitesimal pressure exerted on it then change in work done

$$dw = (p - dp)dv$$

Then $dw = pdv - dpdv \therefore dpdv = \text{constant}$

$$dw = pdv$$

$$dw = \frac{nRT}{v} dv \quad \therefore PV = nRT \quad P = \frac{nRT}{v}$$

On integrate between the limits V_1 to V_2 .

$$\int dw = nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$w_{max} = nRT [\ln V]_{V_1}^{V_2}$$

$$w_{max} = nRT \ln \frac{V_2}{V_1}$$

$$w_{max} = 2.3.3nRT \log_{10} \frac{V_2}{V_1} \text{ for 'n' moles of an ideal gas } n = \frac{W}{M}$$

$$w_{max} = 2.3.3nRT \log_{10} \frac{P_1}{P_2} \therefore P_1 V_1 = P_2 V_2 \quad ; \quad \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

(Boyle's law at constant temperature)

$$w_{max} = -2.3.3nRT \log_{10} \frac{P_1}{P_2} \text{ for one mole of ideal gas.}$$

– sign indicates the heat energy increases the system decreases.

b. P – V type of work

Change in work done $dw = f \times d \times l$

$$= P \times (V_2 - V_1)$$

$$= P \Delta V$$

Then total work done by the system on the surroundings will be obtained by the integration of the factor PdV i.e

$$w = \int_{V_1}^{V_2} P dV$$

The mechanical work at constant pressure throughout the process then

$$\begin{aligned} w &= P[V]_{V_1}^{V_2} \\ &= P(V_2 - V_1) \\ &= P\Delta V \end{aligned}$$

c. C_p and C_v Gaseous system

Let us consider the definition of enthalpy $H = E + PV$

Where $PV = nRT$ for 'n' moles of gas

$PV = RT$ for one mole of gas

Hence $H = E + RT$

Differentiate w.r.t. Temperature at constant Pressure

Then

$$\left[\frac{dH}{dT}\right]_p = \left[\frac{dE}{dT}\right]_V + R$$

$$C_p = C_v + R \quad \because \left[\frac{dH}{dT}\right]_p = C_p \text{ and } \left[\frac{dE}{dT}\right]_V = C_v$$

$$C_p - C_v = R \text{ or } C_p > C_v$$

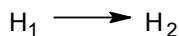
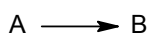
d. Thermochemistry:

It is a branch of chemistry which deals with energy changes in chemical reactions.

Thermochemistry is useful for the calculation the variation of Heat of reaction with temperature observed Kirchoff's [6], Hess Law of Heat constant summation [7]. Lavoisier [8] and Laplaces [9]. They illustrated by using their practical examples as follows

d.1. Kirchoff's Law: The effect of temperature on heat of reaction at constant pressure. The exact influence of temperature can be worked by applying the first law of thermodynamics.

Consider a simple hypothetical reaction,



A = one or more reactants; B = one or more products taking place at constant pressure,

A = H_1 initial state of enthalpy of Reactants,

B = H_2 Final state of enthalpy of Product

Then, $\Delta H = H_2 - H_1$

Differentiate this equation w.r.to temperature at constant pressure, we get

$$\left[\frac{d\Delta H}{dT}\right]_p = \left[\frac{dH_2}{dT}\right]_p - \left[\frac{dH_1}{dT}\right]_p$$

$$= C_{p_2} - C_{p_1}$$

$$d\Delta H = \Delta C_p dT$$

On integration between the limitation at ΔH_1 to ΔH_2 and T_1 to T_2

$$\begin{aligned} \int_{\Delta H_1}^{\Delta H_2} d\Delta H &= \Delta C_p \int_{T_1}^{T_2} dT \\ \therefore [\Delta H]_{\Delta H_1}^{\Delta H_2} &= \Delta C_p [T]_{T_1}^{T_2} \\ \Delta H_2 - \Delta H_1 &= \Delta C_p (T_2 - T_1) \\ \Delta C_p &= \frac{\Delta H_2 - \Delta H_1}{(T_2 - T_1)} \end{aligned}$$

This relationship was first worked out by Kirchoff's and is known as Kirchoff's equation. If the reaction takes place at constant volume then

$$\Delta C_v = \frac{\Delta E_2 - \Delta E_1}{(T_2 - T_1)}$$

According to the first law of thermodynamics, the two energies should be identical, i.e. Mathematically

$$\Delta H_1 + \Delta C_p'(T_2 - T_1) = \Delta H_2 + \Delta C_p(T_2 - T_1)$$

$$\Delta C_p' - \Delta C_p = \Delta C_p = \frac{\Delta H_2 - \Delta H_1}{\Delta T} \text{ where } (T_2 - T_1) = \Delta T$$

It is helpful for the calculations of ΔH , ΔT or ΔC_p if two difference should be known.

d.2. Hess's Law of constant Heat Summation:

[Hess or Ussain Chemist in 1840]

"The change in enthalpy accompanying with a chemical reactions which is depend upon the path followed by initial and final states"

Let us consider the formation of the A to B reaction

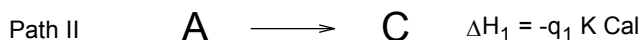
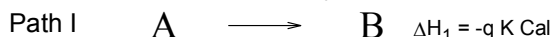


Initial State

Final State

$\Delta H = -q$ K Cal as path I

The formation B in three steps as Path II



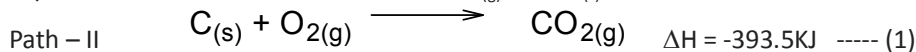
It is observed that the resulting amount of the heat evolved in the step I is equal to the algebraic sum of the amount of the heat evolved in various steps followed by the path II is same. Hence the Hess law,

$$\sum \Delta H = -q \text{ ----- (1) step I path I}$$

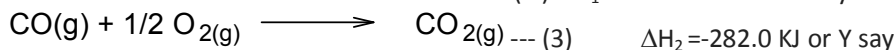
$$\Delta H_1 + \Delta H_2 + \Delta H_3 = -q_1 - q_2 - q_3 \text{ Path - II (Step II)}$$

$$\therefore \sum \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Experimental Proof : The formation of $CO_{2(g)}$ from $C_{(s)}$ with O_2 .



Path - II : The formation of $CO_{2(g)}$ followed by two step as partially combustion of $C_{(s)}$ with O_2 .



It is observed that resulting amount of heat evolved in step-I followed by path I is equal to the algebraic sum of amount of heat evolved followed by various step (I and II) i.e. path II is same.

Evidently, $x + y = -393$ KJ

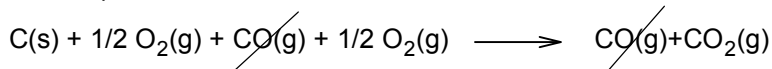
$$x = -393.5 - y$$

$$y = -393.5 - (-282.0)$$

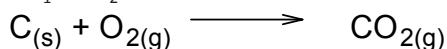
$$x = -111.5 \text{ KJ/mole}$$

Where x = the heat of the combustion of carbon to give carbon monoxide

-111.5KJ/mole



$$\Delta H_1 + \Delta H_2 = -282.0 - 111.5 = -393.5 \text{ KJ}$$



$$\Delta H = \Delta H_1 + \Delta H_2$$

Graphical representation of Hess Law

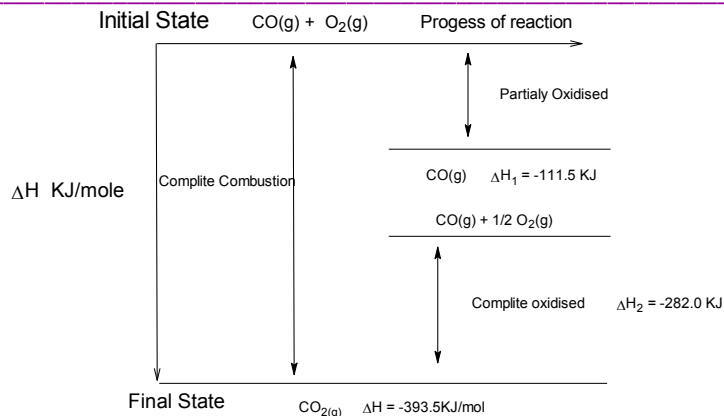
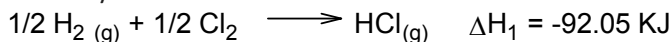


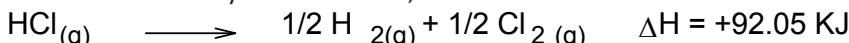
Fig.1. Application of Hess's law in calculating heat of combustion of carbon monoxide
d.3. The Lavoisier and Laplace Law (1780)

The heat evolved or absorbed in the course of chemical change is equal to the heat absorbed (or evolved) when the reaction is reversed. The importance of the law is that thermochemical equation can be reversed.

Evidently the chemical reaction is



Or This reaction may also written as,



Hence mathematics used to study of carnot cycle in case of

Stroke I Isothermal expansion $q_2 = w_1 = RT_2 \log \frac{V_2}{V_1}$

Stroke II Adiabatic compression $w_2 = C_v(T_2 - T_1)$

Stroke III Isothermal compression $-q_1 = -w_3 = RT_1 \log \frac{V_4}{V_3}$

Stroke IV Adiabatic Compression $-w_4 = -C_v(T_2 - T_1)$

Then heat absorbed

$$\begin{aligned} q &= q_2 + (-)q_1 \\ &= RT_2 \log \frac{V_2}{V_1} + RT_1 \log \frac{V_4}{V_3} \\ \therefore w &= RT_2 \log \frac{V_2}{V_1} - RT_1 \log \frac{V_3}{V_4} \end{aligned}$$

$$\therefore w = R(T_2 - RT_1) \log \frac{V_2}{V_1}, \quad q = w$$

$$w = R(T_2 - T_1) \log \frac{V_3}{V_1}$$

$$q_2 = RT_2 \log \frac{V_2}{V_1}$$

Hence $w = q_2 \frac{(T_2 - T_1)}{T_2}$, Since $\frac{(T_2 - T_1)}{T_2} < 1$ It follow that $w < q_2$.

In this way applications of mathematics is used in every steps and every topics of physical sciences.

CONCLUSION:

- Without mathematical concept, physical chemistry difficulty to present and prove their mathematical derivation.

- Use of derivatives, integration formulas easy to find solution of their problems, modifications of formulas.
- Easy to (reduce) induct the theoretical concept.
- Learner are having good opportunities to score their marks.
- Reductions of the theory, concept, easier to understanding, elaborate and illustrate the thermodynamically-chemical reactions by graphs and maps.
- It is quite significance to study the thermodynamical formulas and solutions.
- The chemical thermodynamics is generally based on universal laws by carnot, Clapyron-clasius, Kirchoffs, Hess's maxwells, Boltzmann's etal scientist.
- Presently trends mathematics is known as mile stone in physical chemistry as well as research field conducted by scientist.
- Teachers is an tool to formulate the mathematical ideas in chemical thermodynamics, other topics like electrochemistry, surface chemistry, chemical kinetics, spectroscopy and photochemistry.
- Students must be adopting the ideas, thoughts in regular teaching, research fields given by the teachers.
- Tracing the mathematical graphs in research laboratory teaching.
- Mathematics is to create the awareness of the learners in physical chemistry.

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