

A Semi Empirical Method to Determine Infinity Concentration or Pressure for Reacting Systems

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Abstract—Chemical equilibria are dynamic in nature and at this condition the forward and backward reaction rates are equal. In chemical reacting systems including industrial reactors where the reversible reactions are taking place, prediction of infinity concentration or infinity pressure is practically important due to being involved in their kinetic models.

Developed method can predict the infinity concentration or pressure in three steps with good accuracy. Having the limited time-concentration data, at the first step the numerical values of the coefficients for logarithmic, power and exponential models are determined using non-linear regression technique. And the best model among them is then specified using statistical parameters.

At the second step, the rate of change of concentration or pressure is computed using backward difference technique and the time required to reach equilibrium is estimated. Finally the value of infinity concentration or pressure is then computed with the aid of results obtained in the two previous steps.

Comparison of the thirteen predicted infinity concentration or pressure to those reported in literature, revealed that the average relative absolute deviation is less than 3.5 percent.

Keywords; Infinity concentration, Infinity Pressure, Equilibrium concentration/ pressure, Equilibrium constant, Minimization of Gibbs free energy, Linear Regression, Non-linear Regression

I. INTRODUCTION

A Researcher sometimes faces with a chemically reacting system and he or she needs to know the variation of concentration of components as a function of time.

This helps him to correctly interpret the behavior of the system under study. Most of the reactions are considered reversible and the value of concentration

at infinite time or equilibrium concentration enters to the reaction or process kinetic models.

Due to time and cost limitations, the time – concentration experiments only proceeds to a finite time scale, and it is needed to have acceptable prediction for infinite time or equilibrium concentration.

There are four reported methods in the literature to predict this equilibrium concentration:

1. Tradition method of using equilibrium constants
2. Minimization of the total Gibbs free energy of the reacting system
3. Guggenheim and Kezdy- Swinbourne graphical methods
4. Duhne empirical method

The traditional method has been discussed in every standard classical physical chemistry , chemical thermodynamics, or chemical engineering textbooks [1-7].

The limitation of this method for predicting the infinite concentration is the lack of availability of accurate equation for equilibrium constant as a function of temperature.

Dantzig, Johnson, and White described the Gibbs free energy minimization method for the first time[8]. Mathematics of this method has been discussed extensively by Zeleznik and Gordon [9]. Comparison of this method with others was described in classic work of Van Zeggeren and Storey [10].

In Gibbs free energy minimization separate equilibrium reactions were not considered and only

the probable constituents and their distributions were emphasized in such a manner that the total Gibbs free energy of the system be minimized.

For solved examples one may refer to [7, 11-14]. Gueret and Daroux [15] use this method for methane pyrolysis reaction. Amin and Istadi [16] used it for hydrocarbon synthesis with methane and carbon dioxide. Irandoukht and his colleagues used it for propane amoxidation to acrylonitrile [17] and oxidative coupling of methane [18]. If chemical reactions are first or second order, the graphical method of

II. INVESTIGATION OF THE LIMITATIONS OF PREVIOUS METHODS

In traditional method of using equilibrium constant, one should note that the numerical value of K_p is a function of Gibbs free energy change of reaction under study and this Gibbs free energy change of reaction, in turn is a function of Gibbs free energy of reactants and products.

In literature very different forms of equations for calculating Gibbs free energy of the components have been published. Using different functions for Gibbs free energy of the components yield different values for equilibrium constant, K_p , of the reaction under study. The subject described above is equally valid for Gibbs free energy minimization method. In addition we know that the Gibbs free energy of the components involved in a chemical reaction are functions of specific heat of those components, i. e. $\Delta G_i = f(C_{p,i}(T))$.

Different forms of specific heat as a function of temperature are also reported in literature for components. Table1 shows such variation of specific heat function forms.

These differences are enough large that Tolukian and his colleagues collected a several volume book related to specific heat functions [23, 24].

In graphical methods, Guggenheim and Kezdy-Swinbourne assume that the reactions are only first or second order. In the graphical methods concentrations or pressures should also be available

Guggenheim, and Kezdy-Swinbourne [19, 32] were recommended.

Conceptually for reaching the equilibrium condition infinite time is required. Due to uncertainty of experimental data, Duhne [20] considered only the last 34 percent of data and fitted them with the following equation

$$P_t = a + \frac{b}{t}$$

At infinite time the second term will be eliminated and the infinite concentration or equilibrium pressure will be obtained as $P_\infty = a$.

at t , and $t + \tau$. In Guggenheim method τ is a fixed value number between 2 to 3 times of half- life of the reaction, meanwhile τ is a fixed value number between 1 to 1.5 times of half- life of the reaction in Kezdy-Swinbourne method.

Numerical examples for graphical methods were discussed by Espenson [19]. These important limitations make graphical methods have very limited applications.

TABLE 1. Different forms of specific heat functions

number	function	application	reference
1	$C_p = a + bT + cT^2 + dT^3$	compounds	34
2	$C_p/R = A + BT + DT^2$	solids	7
3	$C_p/R = A + BT + CT^2$	liquids	7
4	$C_p/R = A + BT + CT^2 + DT^2$	gases	7
5	$C_p = A + BT + CT^2 + DT^3$	Gases and liquids	26
6	$C_p = A + BT + CT^2 + DT^2$	elements	27
7	$C_p = A + BT + CT^2$	compounds	27
8	$C_p = A + BT + CT^2$	Organic compounds	4
9	$C_p = A + BT$	Simple and inorganic compounds	4
10	$C_p = A + BT + CT^2 + DT^2$	Inorganic compounds	28

Duhne, assume in his work that experimental infinity time be equal to mathematical infinity. On the other hand the form of function, he suggested, may not be suitable for other cases.

III. PROPOSED SEMI- EMPIRICAL METHOD

To overcome the above limitations, we propose a semi empirical method for determination of infinity concentration or pressure which is independent of the reaction order and also is free of the limitations of the above mentioned methods. We describe our method in three below steps:

Step 1- Determination of the most adequate model for fitting available time-concentration data.

We consider here three models, which are, logarithmic, power and exponential models as follows:

$$\text{Model-1} = a_1 \ln(t) + b_1 \quad (2)$$

$$\text{Model-2} = a_2 t^{b_2} \quad (3)$$

$$\text{Model-3} = a_3 e^{b_3 t} \quad (4)$$

a_i and b_i are the parameters for the models and can be estimated using non-linear regression technique.

The best model is the one that possesses the lowest value of the sum of the squared of residuals (SSE) as defined in (5) to (7), or the one that possesses the highest value of coefficient of determination (R^2) defined in (8).

$$\text{SSE}_{\text{model-1}} = \sum_{i=1}^n [P_{i,\text{exp}} - (a_1 \ln(ti) + b_1)]^2 \quad (5)$$

$$\text{SSE}_{\text{model-2}} = \sum_{i=1}^n [P_{i,\text{exp}} - a_2 t_i^{b_2}]^2 \quad (6)$$

$$\text{SSE}_{\text{model-3}} = \sum_{i=1}^n [P_{i,\text{exp}} - a_3 e^{b_3 t_i}]^2 \quad (7)$$

$$R^2 = \text{SSE} / \text{SST} \quad (8)$$

$$\text{SST} = \sum_{i=1}^n [P_{i,\text{exp}} - P_{\text{average}}]^2 \quad (9)$$

Step 2- Estimation of the time required to reach to equilibrium condition or the value of infinity time.

To obtain the value of this estimation using available data, we assume that the following two important

approximations are valid, $\frac{dP}{dt} = \frac{\Delta P}{\Delta t}$ for calculating the point rates and backward differencing of $\frac{\Delta p_i}{\Delta t_i} = \frac{p_{i+1} - p_i}{t_{i+1} - t_i}$

Plotting the point rates against time, one obviously observe that the relationship is declining for chemical equilibrium reactions, one may also conclude that, the equilibrium reactions are dynamic in nature and the value of point rate become zero at equilibrium condition. By extrapolating, we can find the time at which point rate becomes zero. This value is the

estimation of infinity time, or the time required to reach to equilibrium.

Practically extrapolating the point rate-time data can be easily done using linear regression technique as follows:

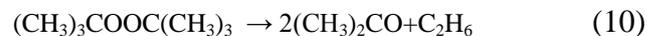
A-If the data were less than 10 pairs, fit a straight line using the last two data pairs and obtain the time at which this line crosses time axis. This is considered as t_{∞} .

B-If there are more than 10 data pairs, fit a straight line using the last three data pairs and obtain t_{∞} .

Step 3- Apply the obtained infinity time from step 2, in the most appropriate model from step-1 and calculate the infinity concentration or pressure which is an estimation of equilibrium concentration or pressure.

A. Application of the Proposed Semi- Empirical Method

Raley et al. studied the decomposition of di- t- butyl peroxide at 154.6°C and partial pressure of nitrogen at 4.2 mm Hg.



Froment, Bischoff, and De Wilde [23] reported total pressure against time in minutes which is tabulated in Table 2.

TABLE 2. Time- total pressure data provided by Raley, Rust, and Vaughn [23]

Number	Time, (minute)	Total pressure (Hg)
1	0	173.5
2	2	187.3
3	3	193.4
4	5	205.3
5	6	211.3
6	8	222.9
7	9	228.6
8	11	239.8
9	12	244.4
10	14	254.5
11	15	259.2
12	17	268.7
13	18	273.9
14	20	282.0
16	21	286.8

Step-1 Finding the most appropriate model among three

The calculated parameters of the models using non linear regression are shown in Table 3. The table also shows sum of squared of residuals and coefficient of determination of the models.

TABLE 3. Regression coefficients, residual sum of squares, and coefficient of determination for the models

Model type	a	b	SSE	R ²
Logarithmic	100.898	141.384	910.38	0.9346
Power	151.666	0.19973	506.470	0.9638
Exponential	185.5616	0.02159	177.648	0.9872

Fig. 1 to 3 compare the model predicted, and experimental pressures for three models described before. In these Figures the points refer to experimental total pressures, and the solid lines used for model predicted total pressures.

Exponential model has the lowest SSE (177.6485), and highest R² (0.98728), so it is the most suitable model for this case.

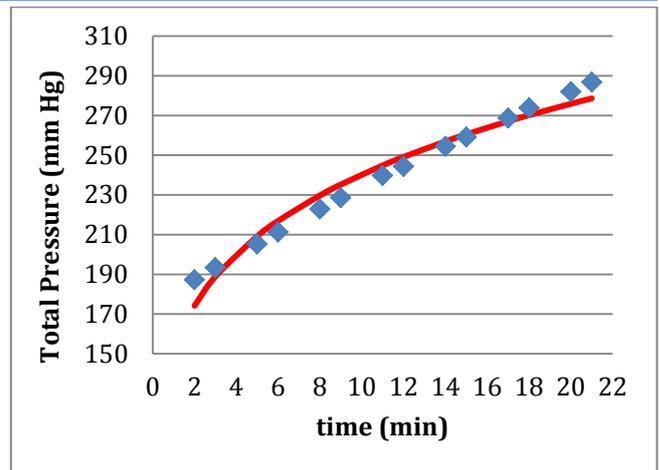


Fig. 2 Power model prediction and experimental total pressure against time

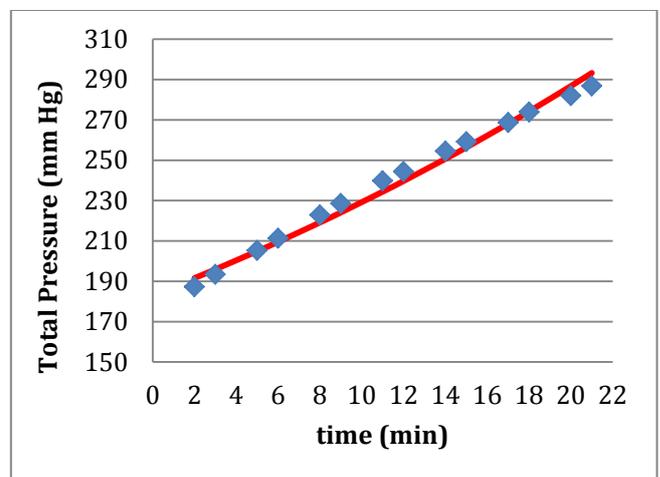


Fig. 3 Exponential model prediction and experimental total pressure against time

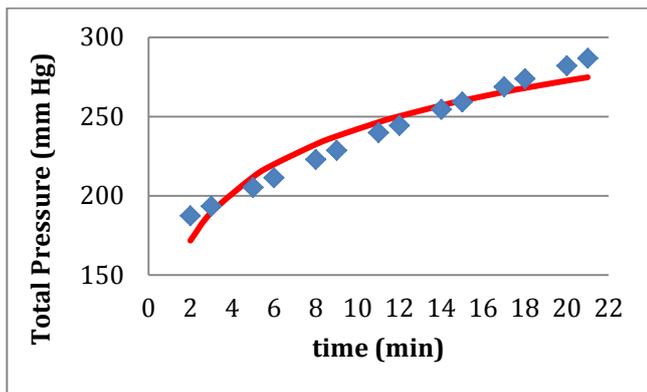


Fig. 1 Logarithmic model prediction and experimental total pressure against time

Step-2 The point rate calculated using $\frac{\Delta p_i}{\Delta t_i} = \frac{p_{i+1} - p_i}{t_{i+1} - t_i}$ are tabulated in Table 4.

Since there are 15 data points, we use the last three data pairs of (1,5.2) , (20,4.05), and (21,4.8) for fitting a straight line $\frac{\Delta p_i}{\Delta t_i} = c + d(t_i)$, using linear regression technique, the values of c and d can be estimated as 8.546 and -0.1964.

By equating this equation to zero, the value of t^∞ will be estimated as 43.509.

Step-3 Using the obtained t^∞ in step-2 and putting it in exponential mode of step-1 the infinite pressure will be calculated to 485.65.

Comparison of this figure to that reported by Forment [23], 491.8 we observe that the relative absolute deviation (RAD %) is only 1.249 percent. Summary of this case and obtained results are tabulated in the first row of Table 5.

TABLE 4 Calculation of Point rates

t_i	2	3	5	6	8	9	11
$\frac{\Delta P_i}{\Delta t_i}$	6.9	6.1	5.95	6	5.8	5.7	5.6
t_i	12	14	15	17	18	20	21
$\frac{\Delta P_i}{\Delta t_i}$	4.6	5.05	4.7	4.75	5.2	4.05	4.8

IV. MORE APPLICATIONS OF PROPOSED SEMI-EMPIRICAL METHOD

Table-5 shows the results of the application of our method with the data reported in literature in other twelve cases. The percent of relative absolute deviations are also reported in Table 5.

TABLE 5 Comparison of the computed infinity or equilibrium concentration/ pressure using our semi-empirical method with that of reported in literature

Case number	Reference with page number	Number of data pairs	Predicted infinity time using our method	Reported equilibrium concentration/ pressure	Calculated equilibrium concentration/ pressure using our method	Percent of relative absolute deviation
1	[21] & [23], pp 51-52	15	43.5	491.8	485.65	1.249
2	[22] & [23], pp 57	16	465.09	565.3	575.87	1.869
3	[29], pp 87	5	301.64	0.494	0.0526	6.547
4	[29], pp 88	17	499.5	5.8	5.992	3.308
5	[29], pp 90	8	19	150	149.705	0.197
6	[29], pp 91	8	14	9.4	9.137	2.8
7	[32] & [19], pp 26	14	68928	16.8	16.377	2.513
8	[19], pp 39	9	26.428	0.351	0.364	3.793
9	[20]	6	240	4.9	4.97	1.4205
10	[31], pp 322	6	70.368	17.1	17.05	0.288
11	[31], pp 325	7	12.557	1.51	1.414	6.348
12	[33], pp 239	5	434.04	0.922	0.899	2.397
13	[30], pp 94	7	148.5	11.02	12.392	12.446
Average of percent of relative absolute deviation for all 13 cases						3.475

V. CONCLUSION

The infinity concentration or pressure is actually the equilibrium concentration or pressure. The numerical values of the quantities enter to the kinetic model of the reaction and kinetic model of the reacting process as well.

Here we proposed a semi-empirical method in three steps, to predict the infinity concentration or pressure with reasonable accuracy. This method is also capable to estimate the infinity time which is the required time to reach to equilibrium.

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