AN AUTOMATED PYTHON BASED TOOL TO DETERMINE EQUILIBRIUM CONSTANTS (K) OF GASEOUS PHASE REACTIONS

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Abstract: Python coding has been applied to determine the K value of gaseous phase reactions from the reactants, products, reaction stoichiometry and reaction temperature by a complex model. The program determined K values has been found sufficiently close to the reported values for seven different reactions at three different temperatures. In the second part of the study, variation of reaction equilibrium constants with temperature has been studied for various industrial gaseous phase reactions such as, methanation reaction, hydrocarbon combustion, production of formaldehyde from methanol, methanol production from syngas and production of ethanol from ethylene around the optimum temperature range of the processes'. The K values have been shown increasing or decreasing trend with the increase of the temperature according to the endothermic or exothermic character of the reactions.

Keywords: Equilibrium constant; Python; Gaseous phase reaction; Industrial chemical reactions.

I. INTRODUCTION

Reaction equilibrium constant is one of the most important parameter in the field of chemistry and chemical engineering. As, none of the reaction ever goes to completion, from the said parameter, one get an idea about the progress of a reaction in terms of its reactants and products' concentration or partial pressure. If, a gaseous phase reaction can be represented by:

$$| \gamma_1 | A_1 + | \gamma_2 | A_2 \leftrightarrow | \gamma_3 | A_3 + | \gamma_4 | A_4 \quad \text{------ (1)}$$
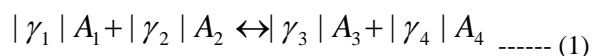
The chemical reaction equilibrium constant (K) can be represented by

$$K = \frac{C_{A_3}^{|\gamma_3|} \times C_{A_4}^{|\gamma_4|}}{C_{A_2}^{|\gamma_2|} \times C_{A_2}^{|\gamma_2|}} \quad \text{------ (2)}$$

Where, C_{A_i} represents the concentration of i-th chemical species in equilibrium and $|\gamma_i|$ is the stoichiometric coefficient of *i-th* chemical species. γ_i is considered as +ve for products and –ve for reactants. [Fogler, 2006; Levenspiel, 1999].

Determination of the values of chemical equilibrium constants (K) for different reactions at different temperature is an old practice in chemical industries. The famous Benesi–Hildebrand method was proposed in 1949, in which the method for determination of equilibrium constant (K) has been shown using the reaction of iodine and aromatic hydrocarbons by spectrophotometry [Benesi and Hildebrand, 1949]. The process was further modified by different researchers [Rose and Drago, 1959; Exner, 1997; Scott, 1956]. Tang et. al. has determined equilibrium constant for atom transfer radical polymerization using modified Fischer's equations [Venayak et.al., 2019]. Christensen et. al. and Eatough et. al. have publicized detailed description for the determination of equilibrium constant by titration calorimetry using data reduction technique for various kind of reactions [Christensen et. al., 1972; Eatough et. al., 1972]. Further, several researchers, have worked for the determination of reaction equilibrium constants such as, for cyano complexes [Beck, 1987], metal-ion complex [Högfeldt, 1982, Sillén et. al., 1964], fluoride complexes in aquous solutions [Bond and Hefter, 1980] etc. Hummel et. al. have reviewed regarding the availability of the equilibrium constants from different sources [Hummel et. al., 2019].

Determination of chemical equilibrium constant for gaseous phase reactions is also a trend in research. Different researchers have reported the equilibrium data for various reactions. Lau et. al. has found the temperature dependency of equilibrium constant for gaseous phase reaction $H_3O+(H_2O)_{n-1}$ + water = $H_3O+(H_2O)_n$ [21]. Wenzel and Sundmatcher have established a theoretical method for determination of equilibrium constant for gas-solid reactions [Wenzel and Sundmatcher, 2019]. Glasovac et.al. has reported gas-phase basicities of 7 biguanides using equilibrium and kinetics [Glasovac et.al., 2016].

Many previous attempts were done to determine chemical reaction equilibrium constant using software. Alderighiet.al. has reported a computer programme written on Windows to calculate the equilibrium constants of soluble and partially soluble species [Alderighi, 1999]. Formation constants of complex species in solution has been calculated by a computer programme named Miniquad [Sabatini, 1974]. A combination of 10 programmes entitled HYPERQUAD is applied to determine the equilibrium in solution [Gans, 1996]. Meshkov and Gamov have presented an algorithm for determination of equilibrium constants from UV-vis and potentiometric data [Meshkov and Gamov, 2019]. Paz-García et. al. has described a mathematical model for the determination of multiple species chemical equilibrium based on the extent of reaction using Newton–Raphson method [Paz-García et. al., 2013].

On the other hand, Python is a high level, free-to-use, general purpose programming language used for various scientific fields such as computational physics [Borcherds, 2007], chemistry [Pocasangre and Fujimitsu, 2018], psychology [Peirce, 2007], biotechnology [Venayak, 2019], chemical engineering [Khan et. al., 2019] and many more.

As per the author's knowledge, no specific methodology has been developed for determination of equilibrium constant (K) from standard enthalpies, Gibbs energy and heat capacity data. In this present work, effort has been made to produce a Python based tool for determination of reaction equilibrium constant (K) of gaseous phase reactions from the said properties. Further, the tool has been tested by comparing the model determined values with the reported values of K. Additionally, the values of K has been determined at different temperatures for the production of methane from synthesis gas, combustion of hydrocarbons, formaldehyde production from methanol, formation of methanol from synthesis gas and production of ethanol from the hydration of ethylene using this tool.

II. HARDWARE AND SOFTWARE:

The work was conducted on desktop computer (Intel (R); 2.93 GHz and 4 GB RAM). The working platform was Windows 10 (Microsoft Corporation) and Python 3.1 was used as the programming language.

III. METHODS

A. THEORY:

The variation of heat capacity (C_P) with temperature of a gaseous species can be found from the formula [Smith et. al., 2008]:

$$\frac{C_P}{R} = A + BT + CT^2 + DT^{-2}$$ ------ (3)

Where, R is the universal gas constant. The values of A, B, C and D of the gaseous chemical species could be obtained from Table 1. The data of Table 1 has been adapted from elsewhere [Smith et. al., 2008].

Table 1: Standard enthalpies, Gibbs energy and heat capacity data of components [Smith et. al., 2008]

Component	Standard enthalpy (Joule/mole)	Gibbs energy (Joule/mole)	Heat Capacity Data			
			A	**B**	**C**	**D**
Hydrogen (H_2)	0	0	3.249	4.22×10^{-4}	0	8.30×10^4
Oxygen (O_2)	0	0	3.369	5.06×10^{-4}	0	-2.27×10^4
Water (H_2O)	-241818	-228572	3.47	1.45×10^{-3}	0	1.21×10^4
Nitrogen (N_2)	0	0	3.28	5.93×10^{-4}	0	4.00×10^3
Ammonia (NH_3)	-46110	-16450	3.578	3.02×10^{-3}	0	-1.86×10^4
Nitric oxide (NO)	90250	86550	3.387	6.29×10^{-4}	0	1.40×10^3
Nitrogen di-oxide (NO_2)	33180	51310	4.982	1.20×10^{-3}	0	-7.92×10^4
Carbon monoxide(CO)	-110525	-137169	3.376	5.57×10^{-4}	0	-3.10×10^3
Carbon di-oxide (CO_2)	-393509	-394359	5.457	1.05×10^{-3}	0	-1.16×10^5

Sulfur di-oxide (SO$_2$)	-296830	-300194	5.699	8.01×10^{-4}	0	-1.02$\times10^5$
Hydrogen di-sulfide (H$_2$S)	-20630	-33560	3.931	1.49×10^{-3}	0	-2.32$\times10^4$
Nitrous oxide (N$_2$O)	82050	104200	5.328	1.12×10^{-3}	0	-9.28$\times10^4$
Methane (CH$_4$)	-74520	-50460	1.702	9.08×10^{-3}	-2.16×10^{-6}	0
Formaldehyde (HCHO)	-108570	-102530	2.264	7.02×10^{-3}	-1.88×10^{-6}	0
Methanol (CH$_3$OH)	-200660	-161960	2.211	1.22×10^{-2}	-3.45×10^{-6}	0
Ethane (C$_2$H$_6$)	-83820	-31855	1.131	1.92×10^{-2}	-5.56×10^{-6}	0
Propane (C$_3$H$_8$)	-104680	-24290	1.213	2.88×10^{-2}	-8.82×10^{-6}	0
Butane (C$_4$H$_{10}$)	-125790	-16570	1.935	3.69×10^{-2}	-1.14×10^{-5}	0
Ethanol (C$_2$H$_5$OH)	-235110	-168490	3.518	2.00×10^{-2}	-6.00×10^{-6}	0
Ethylene (C$_2$H$_4$)	52510	68460	1.424	14.39×10^{-3}	-4.39×10^{-6}	0
NA	0	0	0	0	0	0

Using Equation (3), the sensible heat integral between temperature T$_0$ and T could be calculated by:

$$\int_{T_0}^{T}\frac{C_P}{R}\,dT = AT_0(\tau-1)+\frac{B}{2}T_0^2(\tau^2-1)+\frac{C}{3}T_0^3(\tau^3-1)+\frac{D}{T_0}\left(\frac{\tau-1}{\tau}\right) \text{ ------ (4)}$$

Where,
$$\tau = \frac{T}{T_0}$$

Now, Equation (4) could be slightly modified to obtain the mean heat capacity between the same temperature limit by:

$$\frac{1}{T-T_0}\int_{T_0}^{T}\frac{C_P}{R}\,dT = A+\frac{B}{2}T_0(\tau+1)+\frac{C}{3}T_0^2(\tau^2+\tau+1)+\frac{D}{\tau T_0^2} \text{ ------ (5)}$$

As, the standard state specific heat capacity is represented by, C_P^0, the standard heat capacity change during the reaction can be represented by:

$$\Delta C_P^0 = \sum_i \gamma_i C_{pi}^0 \text{ ------ (6)}$$

Where, C_{Pi}^0 is the standard state specific heat of *i-th* component.

Now, the change of standard state of enthalpy ($d\Delta H^0$) can be calculated by:

$$d\Delta H^0 = \Delta C_P^0 dT \text{ ------ (7)}$$

After integration of Equation (7) between T$_0$ to T:

$$\Delta H^0 = \Delta H_0^0 + R \int_{T_0}^{T} \frac{\Delta C_P^0}{R} \quad \text{------ (8)}$$

Where ΔH^0 and ΔH_0^0 are change in heat of reaction at temperature T and at reference temperature T_0 respectively.

During the integration of second part of the Equation(8) between T_0 and T, using Equation (3), the result will be analog of Equation (4), such as:

$$\int_{T_0}^{T} \frac{\Delta C_P^0}{R} dT = (\Delta A) T_0 (\tau - 1) + \frac{\Delta B}{2} T_0^2 (\tau^2 - 1) + \frac{\Delta C}{3} T_0^3 (\tau^3 - 1) + \frac{\Delta D}{T_0} \left(\frac{\tau - 1}{\tau} \right) \quad \text{------ (9)}$$

Where, by definition, $\quad \Delta A = \sum_i \gamma_i A_i \quad , \quad \Delta B = \sum_i \gamma_i B_i \quad , \quad \Delta C = \sum_i \gamma_i C_i \quad \text{and} \quad \Delta D = \sum_i \gamma_i D_i \quad .$

However, the mean change of heat capacity between the same temperature ranges can be calculated using:

$$\frac{1}{T - T_0} \int_{T_0}^{T} \frac{\Delta C_P^0}{R} dT = \Delta A + \frac{\Delta B}{2} T_0 (\tau + 1) + \frac{\Delta C}{3} T_0^2 (\tau^2 + \tau + 1) + \frac{\Delta D}{\tau T_0^2} \quad \text{------ (10)}$$

It can be noted that Equation (10) is analogues to Equation (5)

Further, the entropy change of an ideal gas during the temperature change from T_0 to T and pressure change from P_0 to P can be represented by:

$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} - \ln \frac{P}{P_0} \quad \text{------ (11)}$$

Where, S represents entropy. Using Equation (3), at constant pressure, this equation can be modified to [Smith et. al., 2008]:

$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} = A \times \ln \tau + \left[BT_0 + \left(CT_0^2 + \frac{D}{\tau^2 T_0^2} \right) \left(\frac{\tau + 1}{2} \right) \right] (\tau - 1) \quad \text{------ (12)}$$

Now, applying constant pressure condition on the equation:

$$dH = TdS + VdP \quad \text{------ (13)}$$

And using $dH = C_P dT$, it can be said:

$$dS = C_P \frac{dT}{T} \quad \text{------ (14)}$$

Where, H, T, S, V and P represent enthalpy, temperature, entropy, volume and pressure respectively. Now, multiplying the entropy value of each species with stoichiometric number (γ_i), summing over all species and entreating the definition of standard entropy change of reaction provide:

$$d \Delta S^0 = \Delta C_P^0 \frac{dT}{T} \quad \text{------ (15)}$$

This, on integration gives:

$$\Delta S^0 = \Delta S_0^0 + R \int_{T_0}^{T} \frac{\Delta C_P^0}{R} \frac{dT}{T} \quad \text{------ (16)}$$

Where ΔS^0 and ΔS_0^0 are change of entropy at temperature T and at reference temperature T_0 respectively. Now, starting from:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{------ (17)}$$

Where ΔG^0 is change of Gibbs energy at standard state. ΔH^0 and ΔS^0 could be calculated using Equation (8) and Equation (16).Using those, Equation (17)could be modified to:

$$\Delta G^0 = \Delta H_0^0 + R \int_{T_0}^{T} \frac{\Delta C_P^0}{R} dT - T\Delta S_0^0 - RT \int_{T_0}^{T} \frac{\Delta C_P^0}{R} \frac{dT}{T} \quad \text{------ (18)}$$

Again; using $\Delta S_0^0 = \dfrac{\Delta H_0^0 - \Delta G_0^0}{T_0}$ and dividing the whole equation using RT modifies Equation (18) to:

$$\frac{\Delta G^0}{RT} = \frac{\Delta G_0^0 - \Delta H_0^0}{RT_0} + \frac{\Delta H_0^0}{RT} + \frac{1}{T} \int_{T_0}^{T} \frac{\Delta C_P^0}{R} dT - \int_{T_0}^{T} \frac{\Delta C_P^0}{R} \frac{dT}{T} \quad \text{------ (19)}$$

Now, as $\ln K = -\dfrac{\Delta G^0}{RT}$, where K is the reaction equilibrium constant, it can be said:

$$-\ln K = \frac{\Delta G_0^0 - \Delta H_0^0}{RT_0} + \frac{\Delta H_0^0}{RT} + \frac{1}{T} \int_{T_0}^{T} \frac{\Delta C_P^0}{R} dT - \int_{T_0}^{T} \frac{\Delta C_P^0}{R} \frac{dT}{T} \quad \text{------ (20)}$$

The first integral can be calculated using Equation (10) and second integral can be calculated using Equation (12)

B. COMPUTER PROGRAM:

As, the theory explained in the Section III (a) is complex in nature, a computer program is needed to executed it with ease. The program is coded in Python 3.1 in such a way that the user will be asked to input the reactants and products of a gaseous phase chemical reaction by the chemical formulae. Provision has been provided to input maximum of 2 reactants and products, whereas, reactions with more numbers of reactants or products also could be executed with small changes in the coding. In case of less than two reactants or products, the user may input "NA", instead of the chemical formula of the second reactant/product. Further, the user will be asked to input the stoichiometric numbers of each reactants and products. Additional, the user need to input the temperature of the reaction in Kelvin. With these input data,

the program will evaluate the value of the reaction equilibrium constant of the specific chemical reaction and the value of $\log_{10}K$ will be displayed.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{------ (21)}$$

$$NO + \frac{1}{2}O_2 \leftrightarrow NO_2 \quad \text{------ (22)}$$
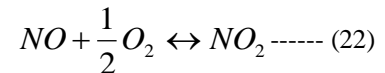
The screenshot for the execution of Equation (21) (i.e. a reaction of two reactants and two products) is shown in Figure 1 (a), whereas, Figure 1 (b) representing the implementation of the reaction of two reactants and one product i.e. Equation

(22).

```
Input 1st REACTANT (Formula in Capital Letters) ... CO
Input 2nd REACTANT (Formula in Capital Letters) ... H2O
Enter the stoichiometric coeffecient of 1st REACTANT ... 1
Enter the stoichiometric coeffecient of 2nd REACTANT ... 1
Input 1st PRODUCT (Formula in Capital Letters) ... CO2
Input 2nd PRODUCT (Formula in Capital Letters) ... H2
Enter the stoichiometric coeffecient of 1st PRODUCT ... 1
Enter the stoichiometric coeffecient of 2nd PRODUCT ... 1
Input the initial temperature (In Kelvin)... 600
The value of log Kp is = 1.5004517259568275
```

Figure 1 (a). Screenshot during the execution of Equation (21), reaction of two reactants and two products.

```
Input 1st REACTANT (Formula in Capital Letters) ... NO
Input 2nd REACTANT (Formula in Capital Letters) ... O2
Enter the stoichiometric coeffecient of 1st REACTANT ... 1
Enter the stoichiometric coeffecient of 2nd REACTANT ... .5
Input 1st PRODUCT (Formula in Capital Letters) ... NO2
Input 2nd PRODUCT (Formula in Capital Letters) ... NA
Enter the stoichiometric coeffecient of 1st PRODUCT ... 1
Enter the stoichiometric coeffecient of 2nd PRODUCT ... 0
Input the initial temperature (In Kelvin)... 1000
The value of log Kp is = -0.9131306622409465
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Figure 1 (b). Screenshot during the execution of Equation (22), reaction of two reactants and one product.

The whole programming concept is described in Algorithm – 1. The program is initiated at Step 1. At Step 2, the reactants and products enters in to the program through "input" function as string data types, whereas, the stoichiometric numbers of the chemical species and the reaction temperature as float data types with the help of "float" function. Further, in Step 3, the first reactant is searched throughout the first column of the Table 1. Table 1 tabulate the value of standard enthalpy, Gibbs energy and four heat capacity data for some sample chemical species in the subsequent columns. When the row for the same chemical species is found, the values of standard enthalpy, Gibbs energy and four heat capacity data are set into h1, g1, a1, b1, c1 and d1 respectively. The step is executed with the help of for loop. The same process is implemented in Step 4 to Step 6 for other reactants and products. The values of consequent standard enthalpy, Gibbs energy and four heat capacity data are set to the variables h2 to h4, g2 to g4 etc.

Algorithm – 1

Step 1   Start
Step 2   Input: Reactants as react1 & react2
Input: Products as prod1 & prod2
Input: Stoichiometric coefficients as gamma_react1,   gamma_react2, gamma_prod1 & gamma_prod2
Input: Temperature of reaction in Kelvin as temp
Step 3   Repeat this step for RowNumber from 1 to 21:
      If   react1 == Value of Table 1 (row= RowNumber, Column=1)
          h1= Value of Table 1 (row= RowNumber, Column=2)
          g1= Value of Table 1 (row= RowNumber, Column=3)
          a1= Value of Table 1 (row= RowNumber, Column=4)
          b1= Value of Table 1 (row= RowNumber, Column=5)
          c1= Value of Table 1 (row= RowNumber, Column=6)
          d1= Value of Table 1 (row= RowNumber, Column=7)
Step 4   Repeat this step for RowNumber from 1 to 21:
      If   react2 == Value of Table 1 (row= RowNumber, Column=1)
          h2= Value of Table 1 (row= RowNumber, Column=2)
          g2= Value of Table 1 (row= RowNumber, Column=3)
          a2= Value of Table 1 (row= RowNumber, Column=4)
          b2= Value of Table 1 (row= RowNumber, Column=5)
          c2= Value of Table 1 (row= RowNumber, Column=6)
          d2= Value of Table 1 (row= RowNumber, Column=7)
Step 5   Repeat this step for RowNumber from 1 to 21:
      If   prod1 == Value of Table 1 (row= RowNumber, Column=1)
          h3= Value of Table 1 (row= RowNumber, Column=2)
          g3= Value of Table 1 (row= RowNumber, Column=3)
          a3= Value of Table 1 (row= RowNumber, Column=4)
          b3= Value of Table 1 (row= RowNumber, Column=5)

	c3= Value of Table 1 (row= RowNumber, Column=6)
	d3= Value of Table 1 (row= RowNumber, Column=7)
Step 6	Repeat this step for RowNumber from 1 to 21:
	If prod2 == Value of Table 1 (row= RowNumber, Column=1)
	h4= Value of Table 1 (row= RowNumber, Column=2)
	g4= Value of Table 1 (row= RowNumber, Column=3)
	a4= Value of Table 1 (row= RowNumber, Column=4)
	b4= Value of Table 1 (row= RowNumber, Column=5)
	c4= Value of Table 1 (row= RowNumber, Column=6)
	d4= Value of Table 1 (row= RowNumber, Column=7)
Step 7	delH=gamma_prod2×h4+gamma_prod1×h3-gamma_react2×h2-gamma_react1×h1
	delG=gamma_prod2×g4+gamma_prod1×g3-gamma_react2×g2-gamma_react1×g1
	del_a=gamma_prod2×a4+gamma_prod1×a3-gamma_react2×a2-gamma_react1×a1
	del_b=gamma_prod2×b4+gamma_prod1×b3-gamma_react2×b2-gamma_react1×b1
	del_c=gamma_prod2×c4+gamma_prod1×c3-gamma_react2×c2-gamma_react1×c1
	del_d=gamma_prod2×d4+gamma_prod1×d3-gamma_react2×d2-gamma_react1×d1
Step 8	temp0=298.15
	tau=temp/temp0
Step 9	idcph=(del_a + del_b×temp0×(tau+1)/2 + del_c×temp0×temp0×(tau×tau + tau + 1)/3 + del_d/tau/temp0/temp0)×(temp - temp0)
	idcps=del_a×ln(tau) + (del_b×temp0 + (del_c×temp0×temp0 + del_d/tau/tau/temp0/temp0)×((tau + 1)/2))×(tau - 1)
	eq_const=exp(-((delG - delH)/8.314/temp0 + delH/8.314/temp + idcph/temp - idcps))
Step 10	logK = log (eq_const)
Step 11	Print logK
Step 12	Stop

$$delG = \sum_i \gamma_i \Delta G_i^0,$$

In Step 7, delH, delG, del_a, del_b, del_c and del_d variables are delineated according to the definition:

$$delH = \sum_i \gamma_i \Delta H_i^0, \quad \Delta A = \sum_i \gamma_i A_i, \quad \Delta B = \sum_i \gamma_i B_i, \quad \Delta C = \sum_i \gamma_i C_i \quad \text{and} \quad \Delta D = \sum_i \gamma_i D_i.$$

Step 8 is used to calculate tau according to: $\tau = \dfrac{T}{T_0}$. Further, in Step 9, equilibrium constant is calculated rendering to the Equation (20). The first integral is calculated in the variable "idcph" using Equation (10) and the second integral "idcps" using Equation (12). In Step 10 and Step 11, the value of $\log_{10}K$ has been calculated and displayed. Finally, in Step 12, the program is terminated.

IV. RESULT AND DISCUSSION:

A. VALIDATION OF THE PROCESS/COMPUTER PROGRAM:

In this part of the study, equilibrium constants of seven different reactions were determined at three different temperatures viz. 2000 K, 1500 K and 800 K using the coded computer program. Further, the found values are compared with the experimental values of reaction equilibrium constant for the same reactions at same temperatures. The experimental values are collected from some other source [Fogler, 2006]. The result is reported in Table 2. It was found that the deviations between the determined and reported values are between 0.11 and 0.1. The results prove the validity of the model.

Table 2: Comparison of calculated and reported values of K at different temperatures.

Sl. No.	Reaction	Temperature (K)	Reported Values of log(K) [Fogler]	Calculated Values of log(K)
01	$CO + 0.5O_2 \leftrightarrow CO_2$	2000	2.9	2.95
		1500	5.7	5.37
		800	13.3	13.94
02	$SO_2 + 3H_2 \leftrightarrow H_2S + 2H_2O$	2000	0.97	0.83
		1500	3.5	2.89
		800	9.4	9.88
03	$CO + H_2O \leftrightarrow CO_2 + H_2$	2000	-0.6	-0.52
		1500	-0.3	-0.29
		800	0.6	0.70
04	$NO + 0.5O_2 \leftrightarrow NO_2$	2000	-2.4	-2.39
		1500	-1.8	-1.91
		800	-0.2	-0.16
05	$0.5N_2 + 1.5H_2 \leftrightarrow NH_3$	2000	-4.8	-4.93
		1500	-4.2	-4.42
		800	-2.7	-2.64
06	$NO + 0.5N_2 \leftrightarrow N_2O$	2000	-4.3	-4.28
		1500	-4.2	-4.24
		800	-4.0	-4.03
07	$0.5N_2 + 0.5O_2 \leftrightarrow NO$	2000	-1.7	-1.64
		1500	-2.5	-2.44
		800	-5.1	-5.21

B. EQUILIBRIUM CONSTANT FOPR METHANATION REACTION:

Methane is a colorless, odorless gas mostly used as a fuel. It could be produced from CO or CO_2 through hydrogenation under nickel based catalysts. The reactions are as follows:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \text{ ------ (23)}$$
$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \text{ ------ (24)}$$

The reactions are favorable in the range of 550 K to 750 K [Cheng et. al., 2017]. Thus, in this study, the reaction equilibrium constants for the production of methane from CO and CO_2 are studied between 550 K and 800 K. The results are shown in Figure 2. It was found that, the value of equilibrium constants (K) decreases with the increase of the temperature for both of the reactions. The value of $\log_{10}K$ has been decreased from the value of 7.1 to 1.7 during the increment of the temperature from 570 K to 780 K for the Equation (23). Another observation is that, the K value for the reaction represented by Equation (23) is higher than the K value for the reaction represented by Equation (24) for same temperature. For 700 K, the value of $\log_{10}K$ has been found as 3.4 and 2.4 for Equation (23) and Equation (24) respectively. Both of these phenomena could be explained by LeChatelier's principle. As the both of the reactions are exothermic in nature, thus, the progress of the reactions towards product side will be retarded at higher temperatures, which in consequence will lead to the decrease in the value of equilibrium constant [Levenspiel, 1999]. Sehested et.al. has also reported same type of observations during the methanation of carbon monoxide under nickel catalyst [Sehested et. al., 2005].
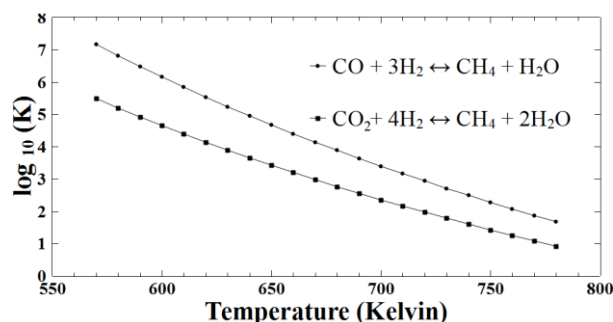

Figure 2. Variation of $\log_{10}K$ for the methanation reactions w.r.t. temperature.

B. EQULILIRIUM CONSTANT FOR HYDROCARBON COMBUSTION:

Combustion of lower chain hydrocarbon for obtaining energy is an old practice for human civilization. But, reaction kinetics and equilibrium constant of such reactions are needed for various scientific calculations, such as the design and application of IC engines [Olikara and Borman, 1975]. Here,

an effort has been made to find the reaction equilibrium constants for the combustion of four lower chain hydrocarbons, viz. methane, ethane, propane and butane for the wide temperature range of 0 °C (373 K) to 1000 °C (1373 K). It was found that, for propane and butane, the values of equilibrium constant approaches infinity below 353 K and 473 K respectively. Thus for such cases, the K values were found for the rest of the range.

The data were intrigued in Figure 3. It was seen that, the value of equilibrium constants decrease w.r.t. the increase of the temperature for all of the alkanes. For methane, the value of $\log_{10} K$ has been decreased from a value of 153.3 to 32.9 during the increment of the temperature from 373 K to 1373

K. This incident could be explained in the light of Le Chatelier's principle as all of the reactions are exothermic in nature. Same kind of trend were reported by other researchers [Wagman et. al., 1945]. Another observation is that, for the same temperature, the value of equilibrium constant increases with the carbon number in the hydrocarbon chain. At a particular temperature of 673 K, the value of $\log_{10} K$ has been determined as 62.2, 113.6, 164.2 and 214.8 for methane (C_1), ethane (C_2), propane (C_3) and butane (C_4) respectively. This happens because of the gradual increase in the enthalpy of combustion reactions with the increase of the carbon number in the hydrocarbon. Westbrook and Dryer have reported same kind of tendency during the oxidation of hydrocarbon fuels [Westbrook and Dryer, 1981].
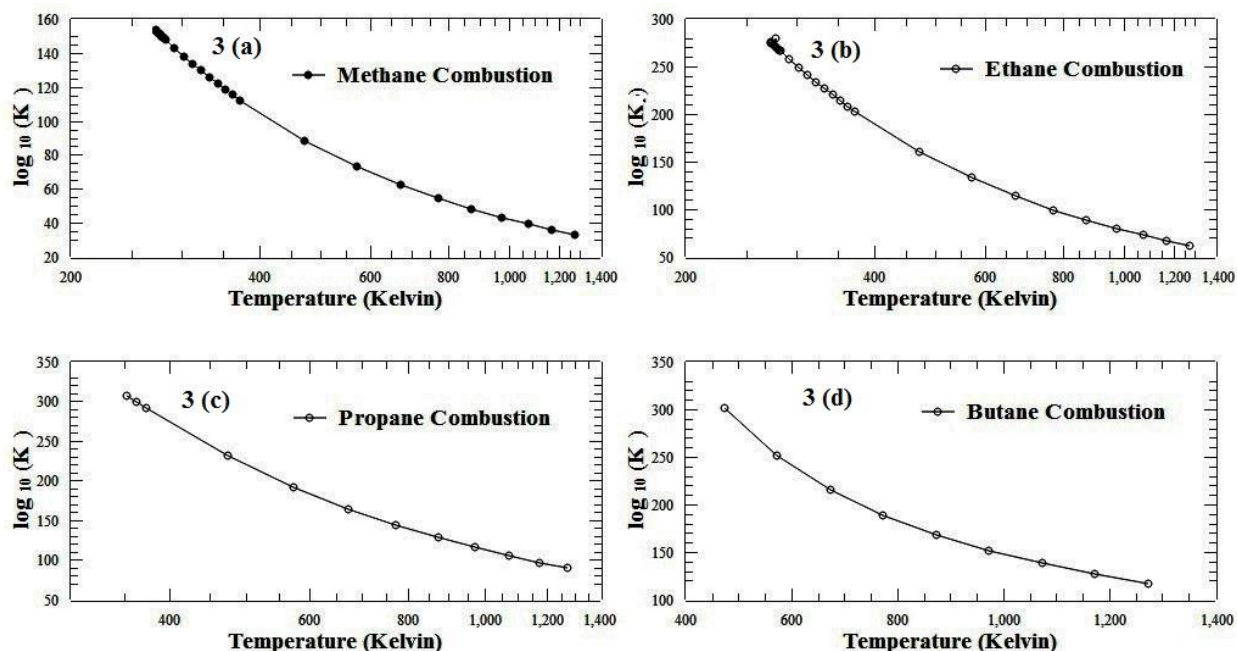

Figure 3. Variation of equilibrium constants w.r.t temperature for the combustion of (a): Methane (b) Ethane (c) Propane (d): Butane.

C. EQUILIBRIUM CONSTANT FOR PRODUCTION OF FORMALDEHYDE FROM METHANOL:

Formaldehyde is applicable in the production of vaccine, anti-infective drugs, resin, paint, polymer etc. One of the routes for production of formaldehyde is the pyrolytic decomposition of methanol. This process is mostly conducted by two different reactions viz:

$$CH_3OH + \frac{1}{2}O_2 \leftrightarrow HCHO + H_2O \text{ ------}$$
$$(25)$$
$$CH_3OH \leftrightarrow HCHO + H_2 \text{ ------ (26)}$$
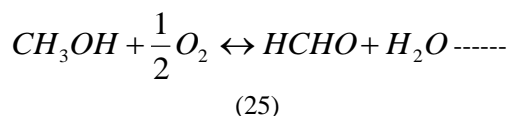
Equation (25) represents the formox process which is conducted under iron and molybdenum or vanadium oxides catalyst at a temperature range of 523 K to 673 K. On the other hand, Equation (26) is conducted between 788 K and 823 K under silver based catalyst [Bahmanpour et. al., 2014]. Thus the variation of reaction equilibrium constant (K) for this first reaction is studied between 500 K and 700 K and the second process is studied between 750 K and 850 K.

It is observed that, for the reaction represented by Equation (25), the value of equilibrium constant (K) decreases w.r.t. the increase of the temperature. On the contrary; the value of equilibrium constant increases w.r.t. the increase of the temperature for the case of Equation (26). The cause lies in the nature of the reactions. The first reaction is exothermic (ΔH_r=-

159 kJ/mol) and the second reaction is endothermic (ΔH_r= 84 kJ/mol) in nature [Bahmanpour et. al., 2014]. For the exothermic reactions, high temperature hinders the progress of the reaction in the product side which ultimately decreases the value of K. However, the K value for endothermic reaction

increases over the increment of the reaction temperature. Same kind of trend was found by other researchers during the methanol oxidation with air under molybdenum catalyst [Adkins and Peterson, 1931]. The result is displayed in Figure 4 (a) and 4 (b).
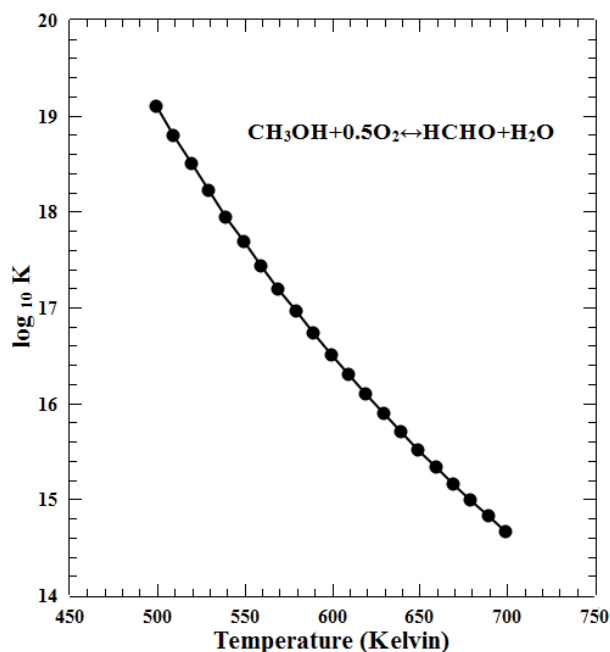
Figure 4 (a). Variation of $\log_{10}$K w.r.t. temperature for Equation (25).
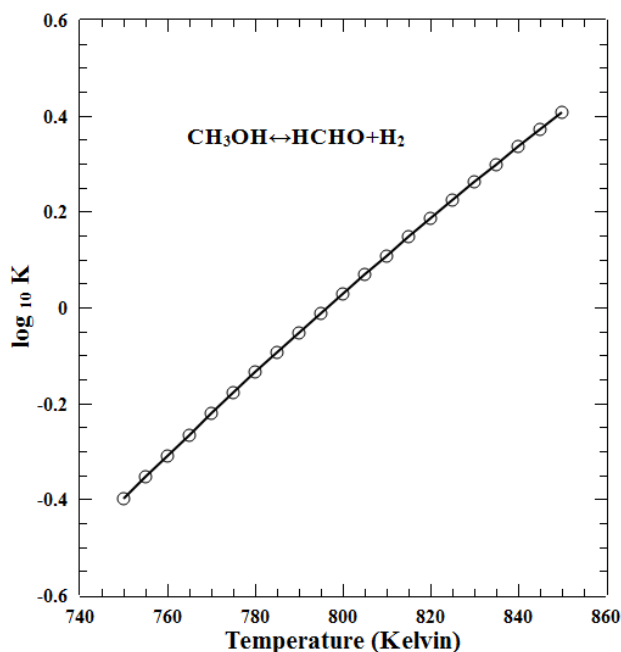
Figure 4 (b). Variation of $\log_{10}$K w.r.t. temperature for Equation (26).

$\log_{10}$K has been decreased from a value of -1.17 at 450 K to a value of -4.04 at 600 K. The fact could be explained by the fact that the reaction is exothermic in nature. Same kind of trend has been observed by Agny and Takoudls during the synthesis of methanol from syngas using a mixture of zinc and copper oxide catalyst [Agny and Takoudls, 1985].

D. K VALUE FOR PRODUCTION OF METHANOL BY HYDROGENATION OF CO:

Methanol or methyl alcohol ($C_{H3}OH$) is used for the production of many important chemicals viz., acetic acid, formaldehyde, hydrocarbons, etc or it could be directly used as a fuel. A main pathway for production of methanol is the hydrogenation of carbon monoxide. The process is conducted around 250 °C (523 K) under alumina supported copper and zinc oxide. The chemical reaction of this process is as follows: [Lee, 1989].

$$CO + H_2 \leftrightarrow CH_3OH \ (\Delta H_R = -90135 \ J/mole)$$ ------
(27)
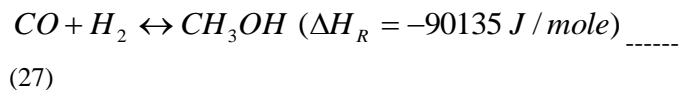
The trend of K value has been determined between 450 K and 600 K perceiving the optimum temperature. The observation is exhibited in Figure 5 (a).It is observed that the value of K decreased w.r.t. the increase of the temperature. The value of

E. K VALUE FOR PRODUCTION OF ETHANOL BY ETHYLENE HYDRATION:

Ethanol is an alcohol is well known for its anti-microbial properties and its use as a fuel. One of the paths for production of it is the hydration of ethylene. According to Robert A. Britton, the process can be conducted under acidic medium. The optimum temperature range is 530 °F (550 K) to 600 °F (589 K). The chemical equation of the process is as follows [Borcherds, 2007]:

$$C_2H_4 + H_2O \leftrightarrow C_2H_5OH \ (\Delta H_r = -45792 \ J/mole)$$
------ (28)
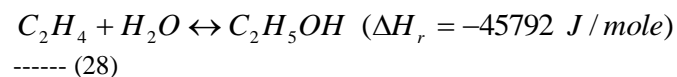
This process is studied between 550 K and 600 K. The value of $\log_{10}K$ has been decreased gradually. The value has been decreased from -2.2 to -2.6 during the increment of the temperature from 550 K to 600 K. Reviewers have been found the same trend for the industrial processes in different publications [Hidzir et. al., 2014]. The trend is depicted in Figure 5 (b).
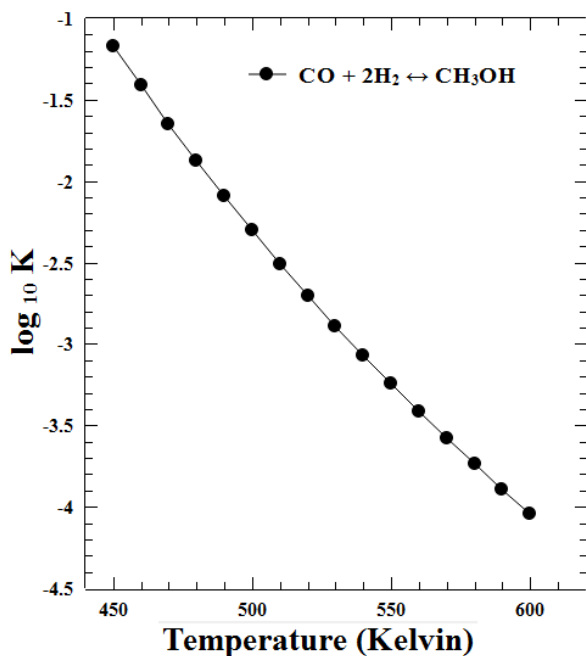

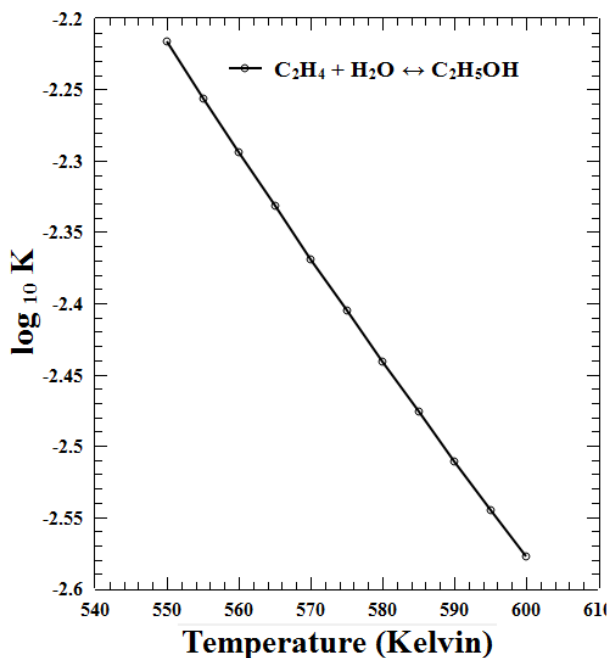Figure 5 (a). Variation of $\log_{10}K$ w.r.t. temperature for methanol production by hydrogenation of CO.

Figure 5 (b). Variation of $\log_{10}K$ w.r.t. temperature for ethanol production by hydration of ethanol.

In the same way, K values for other industrial/chemical processes also could be determined.

V. CONCLUSION:

A Python based tool has been prepared to determine the reaction equilibrium constant (K) for gaseous phase reactions. The tool consists of user-friendly interface and very easy-to-use. After inputting the reactants, products, stoichiomentric coefficients and the reaction temperature, the program automatically searches the database for the standard enthalpy, Gibbs energy and heat capacity data. Further, the value of K is determined and displayed. The program determined K values has been compared with the reported values of K for different reactions at different temperatures. The obtained results are enough close to the reported data which proves the significance of the programmed tool. Further, the tool has been applied to determine the K values for different gaseous phase industrial reactions. The variations of K value for these reactions w.r.t. temperature are also studied. K values of methanation reaction and hydrocarbon combustion has been found to be decreased with the increase of the temperature. Two different reactions for the production of formaldehyde from methanol has shown decreasing and increasing trend according to their exothermic and endothermic nature. Equilibrium constants for the production of methanol from syngas and production of ethanol by the hydration of ethylene also shown decreasing trend w.r.t. the increase of temperature.

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