Numerical Solution of Equations Describing a Simultaneous Thermochemical Reaction Equilibrium

Andrew Adewunmi[1]*
[1]*The Federal University Oye Ekiti*

Abstract*— This study investigates the equilibrium mole fractions of simultaneous thermochemical reactions involved in the hydrogenation of propyne (C_3H_4) to propene (C_3H_6) and subsequently to propane (C_3H_8) across a range of temperatures. Utilizing a Gibbs free energy minimization approach, the equilibrium constants (K_1 and K_2) for these exothermic reactions were calculated using thermodynamic data from Perry's Chemical Engineers' Handbook. The analysis, performed in Microsoft Excel with the Solver tool, accounts for temperature-dependent enthalpy and entropy changes to predict equilibrium compositions. Results indicate that at lower temperatures (below 600 K), the equilibrium strongly favors propane formation due to high equilibrium constant values, with significant propene presence. Above 600 K, the equilibrium shifts toward reactants, with propyne and hydrogen mole fractions increasing, particularly beyond 1200 K, as depicted in a stacked area graph. These trends align with Le Châtelier's principle for exothermic reactions. The findings underscore the critical role of temperature optimization in achieving desired product selectivity, particularly for propene in industrial hydrogenation processes. This thermodynamic analysis provides insights into reaction behavior, supporting the design of efficient catalytic systems.

***Keywords*— Chemical Equilibrium; Thermochemical Reactions; Propyne Hydrogenation; Microsoft Excel Solver**

I. INTRODUCTION

Chemical equilibrium is the state in a reversible reaction where the rate of the forward reaction equals the rate of the reverse reaction. At this point, the concentrations of reactants and products remain constant over time, and there is no net change in the system's composition, although the reactions themselves continue to occur at equal rates. This condition corresponds to a minimum in Gibbs free energy (ΔG), indicating a thermodynamically stable system.

The position of equilibrium is influenced by several factors, including concentration, pressure, and notably, temperature. According to Le Châtelier's Principle, if a system at equilibrium is subjected to a change in temperature, the system will adjust to counteract that change. For exothermic reactions, in which heat is released, an increase in temperature causes the equilibrium to shift toward the reactants. Conversely, in endothermic reactions, heat acts as a reactant, and increasing temperature shifts the equilibrium toward the products.

The hydrogenation of propyne (C_3H_4) is an important reaction in petrochemical processing. It involves the addition of hydrogen (H_2) to propyne in the presence of a metal catalyst, typically palladium (Pd), platinum (Pt), or nickel (Ni). This process proceeds through two consecutive and exothermic reactions: the first step converts propyne to propene (C_3H_6), and the second converts propene to propane (C_3H_8). Both steps release heat and are thus thermodynamically favored at lower temperatures.

Temperature plays a critical role in determining the direction and extent of this equilibrium. At higher temperatures, due to the exothermic nature of both hydrogenation steps, the equilibrium shifts toward the reactants, decreasing the overall conversion of propyne to the more saturated products. Additionally, while high temperatures increase the rate of reaction, they can reduce the selectivity toward intermediate products like propene, favoring full hydrogenation to propane. On the other hand, lower temperatures promote the forward reaction thermodynamically, increasing the yield of desired products. However, excessively low temperatures can reduce the reaction rate significantly, which is why catalysts are essential—they allow the reaction to proceed efficiently even under milder thermal conditions.

In industrial practice, an optimal temperature is carefully selected to balance these thermodynamic and kinetic considerations. Typically, moderate

temperatures are used to achieve high selectivity for propene while maintaining a reasonable reaction rate. The design and operation of hydrogenation systems must, therefore, take into account both equilibrium behavior and catalytic performance to achieve efficient and selective conversion of propyne.

II. MATERIALS AND METHODS

The hydrogenation of propyne (methylacetylene) occurs through two consecutive reactions, both of which are exothermic and typically catalyzed by transition metals such as palladium (Pd), nickel (Ni), or platinum (Pt).

Step 1: Partial Hydrogenation of Propyne to Propene
This step involves the addition of one mole of hydrogen to propyne, forming propene (propylene). When the reaction conditions and catalyst are carefully controlled, this step can proceed with high selectivity.

$$C_3H4 + H_2 \rightleftharpoons C_3H_6$$

Step 2: Complete Hydrogenation of Propene to Propane
In the second step, an additional mole of hydrogen converts propene into propane. This step typically proceeds when hydrogen is in excess or when temperature is high.

$$C_3H_6 + H_2 \rightleftharpoons C_3H_8$$

According to literature, selectivity toward propene is maximized at moderate temperatures, generally in the range of 500 K to 600 K. Within this range, both reactions can occur, but the partial hydrogenation (propyne to propene) tends to dominate if the catalyst is optimized and hydrogen concentration is carefully controlled. However, at temperatures above 600 K, the second hydrogenation step becomes more thermodynamically and kinetically favored, leading to a higher proportion of propane formation and reduced selectivity for propene.

Since both steps are exothermic, temperature control is critical. Excessive heat release can shift the equilibrium toward the reactants and, more dangerously, cause thermal runaway. Moreover, due to the flammability of hydrogen, proper handling and safety measures are essential.

One of the key challenges in this reaction sequence is over-hydrogenation, where desired propene is further converted to propane. This loss of selectivity is a major concern in industrial applications. Hence, the choice and design of catalysts are crucial. However, catalysts such as Pd and Ni are susceptible to carbon deposition (coking), which can lead to deactivation and performance degradation over time.

In the following chapters, the results of a thermodynamic analysis conducted at various temperatures are presented. The analysis was performed using Microsoft Excel, employing the Solver tool to optimize equilibrium conditions and conversions.

III. RESULTS

This section shows the behavoir exhibited by the reaction under equilibrium. The behavoirs are step wise shown below

3.1. Temperature Dependence/ Van't Hoff Plot

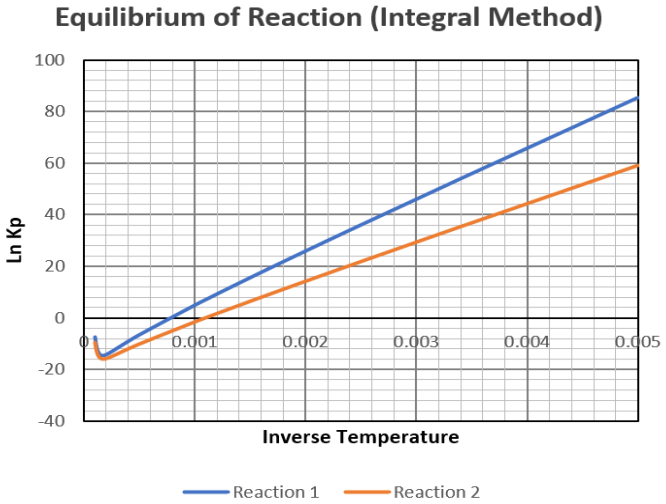

Figure 1. Ln Kp vs 1/T graph (from Van Hoff Relationship).

3.1.1. Reaction Progress

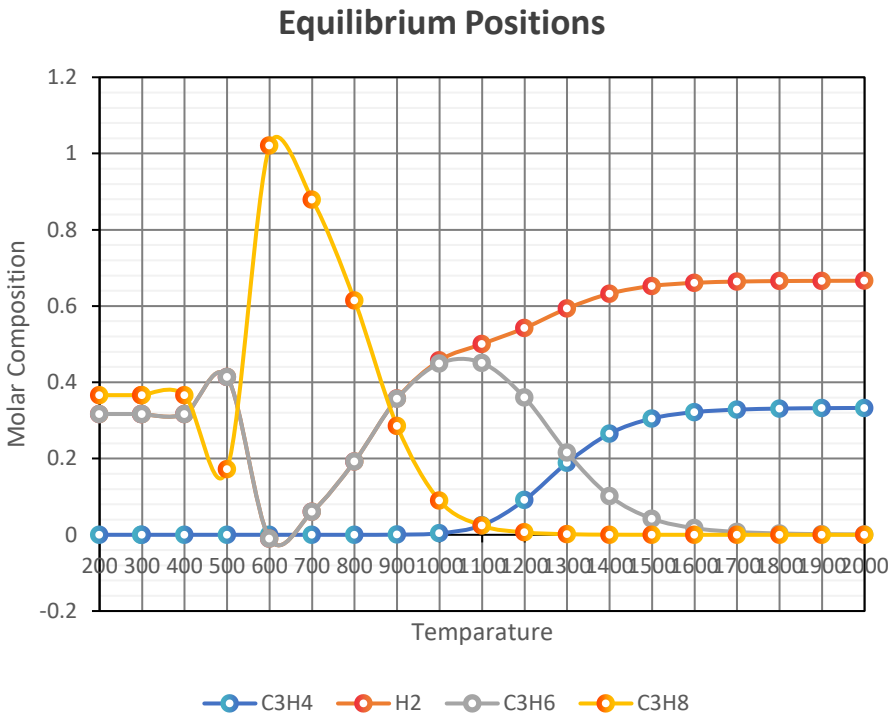

Figure 2. Reaction Progress graph.

3.2. Figures, Tables and Schemes

	A	B	C	D		
COMPONENT	(J/mol·K)	(J/mol·K²)	(J/mol·K³)	(J/mol·K⁴)	hf (KJ/mol)	sf (KJ/mol)
C_3H_4 (Propyne)	37.093	0.09968	-5.30E-05	1.091E-08	0	130.67
H2 (Hydrogen)	29.066	-0.001916	0.000004002	-1.36E-09	185.4	248
C_3H_6 (Propene)	37.726	0.10894	-5.79E-05	1.196E-08	20.43	267.12
C_3H_8 (Propane)	47.517	0.11504	-6.11E-05	1.262E-08	-103.92	270.05

Table 1. Thermodynamic Data Table.

Component	Initial	Change	Out/Equilibrium
C_3H_4	1	-ξ1	1-ξ1
H_2	2	-ξ1-ξ2	2-ξ1-ξ2
C_3H_6	0	ξ1-ξ2	ξ1-ξ2
C_3H_8	0	ξ2	ξ2
Total	3	-ξ1-ξ2	3-ξ1-ξ2

Table 2. Equilibrium Constant Table

3.3. Formatting of Mathematical Components

$$\Delta H_R(T) = \Delta H_R^0(T_o) + \int_{T_{REF}}^{T} \sum \upsilon i C_p(T) dT \quad (1)$$

$$\Delta S_R(T) = \Delta S_R^0(T_o) + \int_{T_{REF}}^{T} \sum \frac{\upsilon i C_p(T) dT}{T} \quad (2)$$

$$K_P = \frac{P_{Pr}^{\upsilon i}}{P_{Re}^{-\upsilon i}} \times P_0^{-\upsilon i} \quad (3)$$

$$K_1 = \frac{P_{C_3H_6}}{P_{C_3H_4} \times P_{H_2}} \times P_0{}^1 \quad (4)$$

$$K_2 = \frac{P_{C_3H_8}}{P_{C_3H_6} \times P_{H_2}} \times P_0{}^1 \quad (5)$$

IV. DISCUSSION

The negative slope observed in the van't Hoff plot (ln Kp versus 1/T) for both reactions is a direct consequence of their exothermic nature, as it reflects a decrease in the equilibrium constant (Kp) with increasing temperature. This behavior aligns with thermodynamic principles, specifically Le Chatelier's principle, which predicts that for exothermic reactions (where $\Delta H_R < 0$), the equilibrium shifts toward reactants as temperature rises to counteract the heat input. The negative slope is quantitatively supported by the Gibbs-Helmholtz equation, **Error! Reference source not found.** where **Error! Reference source not found.**, indicating that an increase in T reduces ln Kp when ΔH_R is negative, consistent with the data for the hydrogenation of propyne to propene and propene to propane.

As temperature increases beyond 600 K, the areas representing C_3H_8 and C_3H_6 decrease, while the area for propyne (C_3H_4) begins to grow, signaling a shift in the equilibrium position toward reactants. At higher temperatures (above 1200 K), the graph illustrates a pronounced increase in the areas for C_3H_4 and hydrogen (H_2), with H_2 becoming a dominant species and its mole fraction rising steadily. This trend is consistent with the decrease in equilibrium constants (K1 and K2) at elevated temperatures favoring the reverse reactions (dehydrogenation) and reflecting the exothermic character of the forward reactions. The stacked nature of the graph effectively highlights the competitive equilibrium shifts, with the increasing H_2 area suggesting an initial excess of hydrogen that becomes more prominent as temperature rises.

V. CONCLUSIONS

The thermodynamic analysis of the consecutive hydrogenation reactions of propyne (C_3H_4) to propene (C_3H_6) and propane (C_3H_8), conducted using Gibbs free energy minimization, shows the significant influence of temperature on the equilibrium composition. At lower temperatures (below 600 K), the equilibrium favors the formation of propane (C_3H_8) as the dominant product, while at higher temperatures (above 1200 K), the system shifts toward the reactants propyne (C_3H_4) and hydrogen (H_2), with H_2 mole fraction increasing markedly. These trends, validated by the decrease in equilibrium constants (K1 and K2) with rising temperature, identifying the critical role of temperature optimization in controlling product selectivity. The findings reinforce the importance of tailoring temperature conditions in industrial hydrogenation processes to maximize the yield of desired products, such as propene at intermediate temperatures, while mitigating reactant dominance at elevated temperatures.

REFERENCES

[1] Smith, J. M.; Van Nes.; Introduction to chemical engineering thermodynamics 7th ed. 2005.

[2] Perry, R. H.; Green, D. W.; Perry's Chemical Engineering Handbook. 9th ed.;