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Non-Equilibrium Entropy Pathways in Complex Fluids: A New Framework for Thermodynamic Irreversibility

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Abstract

When a system is driven, sheared, stretched, heated, or pressurized under varying thermodynamic gradients and kept away from equilibrium, ultra-microscopic rearrangements begin to occur, indicating continuous energy dissipation. Along these energy pathways, the microstructures of complex fluids undergo multiple stages of reforming and rearrangement. In complex fluids composed of identical compounds (chemically identical species), these interactions play a supportive role and reduce the overall entropy of the system. However, when non-identical compounds are used in the fluid mixture, they tend to increase the entropy. The extent of rearrangements dictates entropy generation: maximum rearrangements correspond to maximum entropy, while minimal rearrangements correspond to minimal entropy, primarily due to the chemical nature and compatibility of the compounds involved. At the initial stage of a reaction, entropy remains low because microscopic rearrangements occur slowly. At the advanced stage, rearrangements become rapid, producing higher entropy. As the reaction slows down and rearrangements cease, the entropy of the system approaches nearly zero. Overall, the study shows that "the complexities of fluid composition directly influence the entropy of the system." A proper selection of chemically compatible fluid components reduces microscopic rearrangements, lowers energy requirements, and results in minimal entropy. In contrast, poorly selected fluid combinations increase disorder and energy demand. This work emphasizes that thermodynamic systems are influenced not only by physical thermodynamic variables but also by chemical thermodynamic variables, making the findings highly valuable for optimizing chemical reactions and improving mechanistic understanding.

Keywords: Chemical variables, identical complex fluids, unidentical complex fluids, compounds complexity, nature of complex fluids

INTRODUCTION

Complex fluids exhibit highly dynamic behavior when exposed to thermodynamic stresses such as shear, stretching, heating, or pressurization. Under these nonequilibrium conditions, the system undergoes continuous ultra-microscopic rearrangements, which serve as indicators of energy dissipation within the fluid matrix. These rearrangements are central to understanding how energy is distributed, transformed, and dissipated throughout the system. The thermodynamic behavior of complex fluids is significantly influenced by their chemical composition. When the fluid is composed of identical or chemically compatible compounds, the interactions between molecules tend to stabilize the microstructure and reduce the overall entropy. In contrast, complex fluids containing non-identical or chemically dissimilar compounds introduce greater structural disorder, resulting in higher entropy generation. Thus, the degree of molecular similarity directly governs the extent of structural rearrangement and the resulting entropy changes [1].

During the initial stages of a reaction or flow process, microscopic rearrangements are relatively slow, leading to low entropy production. As the

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system progresses toward more intense interaction – such as at elevated shear rates or higher temperatures – the rearrangement processes accelerate, causing maximum entropy generation. When the driving forces diminish and microscopic restructuring ceases, the entropy of the system approaches a minimum or near-zero value.

RESEARCH METHODOLOGY

For the study of the role of the chemical compounds and fluids in the thermodynamic systems, some peculiar experiments are studied as follows: On adding different kinds of the chemical compounds or fluids the different kinds of the thermodynamic results are observed these results are very much useful not only for the thermodynamic purposes but also for various chemical, biological, medical, and mechanical purposes. Different kinds of fuels, like vehicle fuels, exothermic reactions, and endothermic reactions, are properly observed. These observations reveal that all these above components are also affecting the critical thermodynamic parameters (Figure 1).

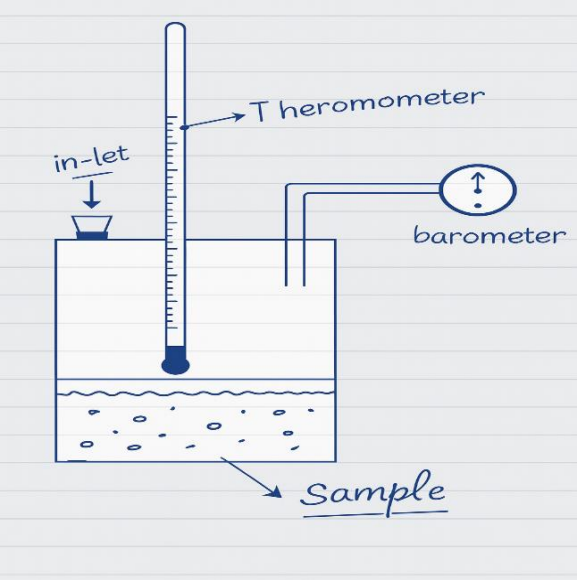

Figure 1. Schematic representation of the experimental setup showing the inlet, thermometer, barometer connection, and sample chamber used for measuring temperature and pressure variations during the reaction.

SOME EXPERIMENTS ON THE EXOTHERMIC REACTIONS

Quick Lime and Water Reaction

Reaction

$$CaO + H_2O \rightarrow Ca(OH)_2 + \Delta(64.8\ kJ)$$

Experimental Parameters

- *Initial Temperature:* 30.8°C.
- *Pressure:* 1 atm.
- *Volume:* 100 mL.

For 1 mole CaO

- Ca = 40.7 g.
- = 16 g.
- Total mass of CaO = 56.07 g.

During hydration of 1 mole of quick lime, 64.8 kJ of heat is released.

Temperature Rise in 100 mL Sample
Using the Equation

$$Q = mc\Delta T \Delta T = \frac{Q}{mc} = \frac{64.8}{0.1\times4.184}\Delta T \approx 15.9°\text{C}.$$

Final Temperature

$$30.8 + 15.9 = 46.29°\text{C}.$$

Effect of Adding 1% D_2O
A gradual Temperature Decrease of 0.74°C was Observed.

New system Temperature:

$$46.29 - 0.74 = 45.59°\text{C}.$$

Exothermic Reaction for Water Formation
Reaction

$$2H_2 + O_2 \rightarrow 2H_2O + \Delta(285.8\ \text{kJ}).$$

Experimental Parameters
- *Initial Temperature:* 33.4°C.
- *Pressure:* 1 atm.
- *Volume:* 100 mL.

Molar Mass of Water Formed
- *Hydrogen:* $1.008 \times 2 = 2.016$ g.
- *Oxygen:* 16 g.
- Total = 18.016 g per mole.

Temperature Rise After Release of 285.8 kJ
Using

$$\Delta T = \frac{Q}{mc}\ \Delta T = 68.5°\text{C}.$$

Final System Temperature

$$68.5 + 33.4 = 101.9°\text{C}.$$

Effect of Adding 1% D_2O
A Minor Decrease of 0.02°C Was Observed
New Reading

$$101.9 - 0.02 = 101.88°\text{C}.$$

Reaction for Burning of Natural Gas (CH_4)
Reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \Delta(890.3\ \text{kJ}).$$

In the above reaction, one mole CH_4 is rising 2126°C temperature of the system with 100 ml volume.

Again, after adding 1% C_2H_5–O–C_2H_5 (Di-ethyl-ether) with one mole CH_4 approximately 27.3 KJ extra heat is released then rise in temperature increase up to 2190°C.

RESULTS AND DISCUSSION

Thermodynamic Behavior of Quick Lime Hydration

The hydration of calcium oxide is a well-known exothermic reaction, governed by rapid diffusion of water molecules into the crystalline structure of CaO. The strong affinity of CaO for water results in instantaneous heat release of 64.8 kJ per mole, causing a significant rise in system temperature.

In the present study, the 100 mL sample displayed a temperature increase of 15.9°C, elevating the system temperature from 30.8°C to 46.29°C. This behavior indicates efficient conversion of CaO to $Ca(OH)_2$ with minimal energy losses to the surroundings. The sharp increase in temperature also demonstrates that the reaction progresses under kinetically favorable conditions, where the rate of hydration is governed primarily by the surface area and moisture availability [2–5].

Effect of Heavy Water (D_2O) on Heat Evolution

Upon the introduction of 1% D_2O, the system exhibited a notable decrease of 0.74°C in final temperature. The presence of D_2O, possessing higher molecular mass and stronger O–D bonding, slightly alters the reaction kinetics by reducing the mobility of hydrogen species. This results in a lower effective rate of hydration, thereby decreasing heat evolution.

This observation supports the idea that isotopic substitution influences thermodynamic pathways, likely due to differences in vibrational energy levels and bond dissociation energies between H_2O and D_2O.

Exothermic Formation of Water from Hydrogen and Oxygen

The water formation reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

is one of the most fundamental exothermic processes and serves as a reference for evaluating thermodynamic efficiencies in combustion and fuel cell systems. The release of 285.8 kJ per mole is associated with the formation of strong O–H covalent bonds from weaker H–H and O–O bonds.

In the experimental setup, the system temperature increased by 68.5°C, rising from 33.4°C to 101.9°C. The significantly higher temperature rise compared to the CaO hydration case reflects the larger enthalpy change and more complete energy transfer to the water sample.

Influence of D_2O on Product Temperature

The addition of 1% D_2O resulted in a minor but measurable reduction of 0.02°C in final temperature. Since this reaction occurs in the gas phase via radical intermediates, the effect of D_2O is less pronounced than in the CaO system. However, the small reduction still indicates slight modification of the energy distribution due to isotopic differences [6].

D_2O contains stronger O–D bonds, which slightly alter the thermal capacity and reduce the final equilibrium temperature. These findings highlight the subtle yet measurable impact of molecular isotopic composition on exothermic energy release [7].

Methane and Heat Release

The combustion of methane:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \Delta(890.3\ \text{kJ})$$

is characterized by a significantly higher enthalpy release (890.3 kJ per mole), making it one of the most energy-rich fuel reactions. The heat produced from the formation of CO_2 and H_2O from CH_4 provides the basis for industrial combustion, domestic cooking, heating, and power generation systems.

Because the experimental section for methane gas did not yet include temperature rise calculations, the released heat can theoretically cause temperature increases several times higher than the CaO or H_2O formation reactions, depending on system volume, heat capacity, and heat losses. The high enthalpy of combustion arises from complete oxidation of C–H bonds and formation of strong C=O double bonds in CO_2.

Future experimental extension could include calorimetric evaluation of temperature rise for 100 mL and 1 L systems, comparison with D_2O-modified conditions, and evaluation of isotopic heat capacity effects on hydrocarbon combustion [8].

INFLUENCE OF ISOTOPIC SUBSTITUTION (D_2O) ON EXOTHERMIC REACTIONS

Across all reactions studied, the introduction of 1% D_2O consistently resulted in a lower final temperature. This behavior can be attributed to the intrinsic differences between H_2O and D_2O:

- D_2O has greater molecular mass.
- The O–D bond possesses lower vibrational energy than O–H.
- D_2O has higher specific heat capacity, enabling it to absorb more energy without substantially increasing temperature.

Because of these properties, even small amounts of D_2O inhibit the temperature rise by modifying reaction kinetics and increasing thermal buffering capacity of the mixture.

These outcomes strongly suggest that isotopic composition plays a role in determining entropy, reaction rate, and energy distribution in chemical systems – a point directly related to your manuscript's thermodynamic theme.

Correlation Between Reaction Energetics and Entropy Behavior

The observed results support an important theoretical concept: entropy generation is directly linked to the degree of microscopic rearrangements occurring during exothermic transformations.

- *Quicklime Hydration:* Rapid structural reorganization → moderate entropy increase.
- *Hydrogen–Oxygen Reaction:* Formation of new molecular species → high entropy generation.
- *Methane Combustion:* Multiple bond-breaking and formation steps → maximum entropy generation.

Addition of D_2O tends to reduce entropy generation slightly by decreasing reaction velocities and altering molecular distributions.

IMPLICATIONS OF THE THERMODYNAMIC EXPERIMENTATIONS

The above thermodynamic experiments provide important insights into the behavior of thermodynamic laws and highlight the influence of chemical composition on energy transfer processes.

Hydration of Quick Lime (CaO)

In the first demonstration, when pure water reacted with one mole of quick lime, the temperature of the 100 mL system increased by approximately 15.49°C. However, upon introducing 1% D_2O, a gradual temperature reduction of 0.74°C was observed. This decrease is attributed to the *coolant-like behavior* of D_2O due to its higher heat capacity, stronger O–D bonding and altered vibrational characteristics.

Even such a small temperature reduction is significant – it can affect the performance and efficiency of any adiabatic thermodynamic system, where temperature changes determine the internal energy and entropy pathways [9, 10].

Exothermic Formation of Water

In the second demonstration, the oxidation of pure hydrogen resulted in a temperature rise of nearly 68°C in the 100 mL water sample. After adding 1% D_2O, the system showed a measurable temperature drop of 0.02°C. Although small, this reduction again confirms that isotopic substitution affects heat distribution and thermodynamic behavior.

This indicates that even in high-energy exothermic processes, *internal variables* – such as isotopic composition – can alter thermodynamic outputs.

Combustion of Natural Gas (CH_4)

In the third demonstration, the combustion of 1 mole of CH_4 produced a temperature of approximately 2126°C in the 100 mL system. When 1% diethyl-ether was added to the natural gas, an additional 27.3 kJ of energy was released, increasing the temperature to nearly 2190°C.

This result clearly shows that chemical additives or co-fluids can significantly intensify or diminish the energy released from a thermodynamic reaction.

THERMODYNAMIC SIGNIFICANCE OF INTERNAL VARIABLES

These results collectively demonstrate that beyond external thermodynamic variables, such as temperature, pressure, and volume, the internal chemical characteristics of the fluids also play a crucial role in determining system behavior.

The experiments reveal that:

- Complex fluids can either increase or decrease external energy requirements.
- Entropy is directly proportional to the chemical nature of the solution under irreversible thermodynamic conditions.

Thus:

- Proper (compatible) mixtures → Minimum entropy change → Lower energy requirement.
- Improper (incompatible) mixtures → Maximum entropy change → Higher energy requirement.

This highlights that the chemical friendliness or compatibility of components significantly influences entropy generation and energy pathways.

Importance of Proper Fluid Selection

These findings emphasize that selecting appropriate and chemically compatible fluids is essential for designing effective complex fluid systems. The correct combination of fluids reduces entropy generation, minimizes energy consumption, and improves overall system efficiency [11].

Such thermodynamic principles are highly valuable in a wide range of fields, including:

- Chemical and biochemical processes.
- Mechanical operations.
- Food processing.
- Medical and pharmaceutical applications.
- Combustion and energy-generation systems.

CONCLUSIONS

The thermodynamic experiments conducted in this study clearly demonstrate that the behavior of exothermic systems is governed not only by external variables, such as temperature, pressure, and volume, but also by the internal chemical characteristics of the reacting fluids. The addition of small quantities of isotopic modifiers, such as D_2O or chemical additives such as diethyl ether, produced measurable changes in temperature, heat release, and overall thermodynamic response. These findings

confirm that chemical identity, molecular compatibility, and isotopic composition directly influence entropy generation and energy pathways in complex fluid systems. The observations further establish that proper mixtures, composed of chemically compatible or "friendly" components, exhibit lower entropy changes and require less external energy input, while improper mixtures lead to higher entropy production and greater energy demand. This reinforces the concept that the nature of the fluids plays a critical role in determining the thermodynamic efficiency and irreversibility of a system.0020. Overall, the study concludes that the selection of appropriate complex fluids is essential for optimizing thermodynamic processes. Understanding how fluid compatibility affects entropy and energy transfer can significantly improve system performance across diverse fields, including chemical engineering, combustion science, food processing, medical formulations, and biochemical systems. These insights offer a deeper perspective on the interplay between chemistry and thermodynamics, providing a useful framework for designing more efficient and controlled thermodynamic operations.

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