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Review

Hess Law Applicability to Heterogeneous Combustion Reactions Resulting to Non-Monotonicity of Enthalpy Distribution in Them

I. A. Filimonov[1*], **I. I. Filimonova**[2]

[1]Merzhanov Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Academician Osipyan str., 8, Chernogolovka, Moscow Region, 142432, Russia
[2]Gubkin Russian State University of Oil and Gas (National Research University), Leninskii av. 65, build 1, Moscow, 119991, Russia
Email: e_filimonov61@inbox.ru

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Abstract: The definition of reaction irreversibility (reversibility) available now in literature does not allow for determining this reaction peculiarity before a practice. Moreover, in mathematical terms, such a definition is not universal and leads actually to the denial of any similarity in physicochemical processes, in particular in combustion waves. We have considered the irreversibility of reactions from the mathematical viewpoint as independence of a reaction rate on the concentration of products directly. As a result, in terms of Le_i numbers, we have formulated conditions sufficient for the enthalpy of reagents to be a complete differential (or a thermodynamic potential) and independent of the reaction path. And conversely, the conditions necessary for that enthalpy of reagents are significantly dependent on the reaction path ($Le \cong 1$). A comparison of the conclusions we obtained with the data from experiments available in the literature showed a good agreement with them and put an edge on the question of determining the irreversibility (reversibility) of reactions in the scientific community. We have shown that the small values of the diffusion coefficients of reagents D_i compared to the thermal diffusivity coefficient κ, and with them, the corresponding small Lewis numbers ($Le_i = D_i/\kappa \ll 1$) for the most heterogeneous combustion synthesis systems, are the sufficient conditions for the enthalpy of reactions (H) to be a complete differential of the systems states and, vice versa, a strong similarity appears between the enthalpy and concentration fields at $Le \cong 1$.

Keywords**:** potential enthalpy, independence on reaction way, diffusion coefficients, Lewis numbers

1. Introduction

In accordance with the definition [1], the reversibility (or irreversibility) of a chemical reaction is determined just by the sequence of phase transformations accompanying the reaction. The corresponding sequences of the reversible and irreversible transformations are illustrated in Figure 1. Enthalpy independence on reactions ways is illustrated on Figure 2. Figure 3 presents enthalpy dependence on concentrations at $Le \cong 1$. One can easily generalize the definition [1] to any number of corresponding chemical transformations exceeding the double scraps of irreversible reaction sequences or the triple reversible chain of reactions presented in Figure 1. Such a definition is based solely on experimental data and does not allow judging the reversibility or irreversibility of reactions in advance of any practice. Nevertheless, irreversibility,

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as an option in reaction properties, may be formulated mathematically much easier than the definition accepted in [1]. Authors [1] have considered the SHS processes in which the combustion time (t_{comb}) is significantly shorter than the time of heat removal (t_{hr}): $t_{\text{comb}} \ll t_{\text{hr}}$ Therefore, in fact, they looked solely at isolated systems whose entropy grows monotonically with time. Respectively, they concluded that all SHS reactions are irreversible [1]. However, this conclusion does not concern, for example, Belousov-Zhabotinskii reactions (BZR) [2], which reveal the characteristic times comparable with that of heat removal. BZR is a double sequence of reversible reaction transformations. The same ($t_{\text{comb}} \approx= t_{\text{hr}}$) concerns spiral spin combustion [3] and combustion synthesis of ZnS [4]. As a result, the enthalpy distribution in these cases has a non-monotonic wrong-way temperature behavior by definition [1].

2. Alternative definitions of reaction irreversibility (reversibility)

In contrast to the definition [1], the irreversibility of a reaction can also be alternatively expressed in mathematical terms through the function of reaction rate. The reaction is irreversible if the reaction rate does not directly depend on the concentration of products, but, for example, is determined solely by temperature and concentrations of an initial reagent. The modern theory of thermal explosion [5]-[8] is developed precisely for irreversible reactions corresponding to the alternative definition [1] of the irreversibility concept. Implicitly, such reactions whose entropy grows monotonically over time are considered as the reactions of correct temperature behavior [9], [10]. Following [11], the reason for wrong-way temperature behavior during self-ignition of hydrocarbon and hydrocarbon-air mixtures by the Pd catalysts versus Pt wires (as catalysts) is the fact, that Pd forms thermally stable intermediate oxide product on the wire surface, which disrupts the thermal and mechanical contact of the gas with the catalyst and leads to non-monotonic temperature distributions (hot spots) on the Pd surface. Vice versa, PtO_2 on the surface of the platinum catalyst is thermally unstable and does not affect the thermal and mechanical contact.

3. Background

The first law of thermodynamics or Hess law was discovered by Germain Henri Hess (1802-1850). The law establishes the interrelation of a way of chemical reaction with changes of the enthalpy at each point of this way. By analogy with potential fields, such as the field of weight and a stationary electric field, it is claimed that the enthalpy increment doesn't depend on a form of a reaction way: $\Delta H_{13} \equiv \Delta H_{12} + \Delta H_{23}$ (1), see Figure 1. The enthalpy serves as a potential of the reaction rate, i.e., the enthalpy of the reacting system as height in the field of weight or electric potential, is a potential too and her increment from the point of start (1) to the point of the finish (3) determines the rate of chemical transformation at points 1-3. Unfortunately, the widest and universal use of the law of Hess in the various textbooks in chemistry has prevented the rational and critical attitude towards him among its users. Therefore, neither in education nor in scientific literature, the question of limits of applicability of a ratio (1) wasn't raised and hasn't yet been considered. Let's consider reactions of the "gas-solid" type producing probably charged species or intermediate reactants.

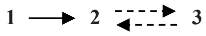

Figure 1. Sequences of irreversible (solid arrows) or reversible (solid + dashed arrows) transformations during chemical reactions.

We will prove that, dependent on values of the Lewis numbers, the enthalpy field of products and initial or intermediate reactants may be completely different: from a purely potential one up to a completely linear or vortex field. Figure 1 illustrates reversible and irreversible sequences [1] of phase transformations during a chemical reaction.

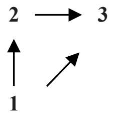

Figure 2. Independence of reagent enthalpy on a heterogeneous reaction way at $Le_i \ll 1$: $H_{13} \equiv H_{12} + H_{23}$.

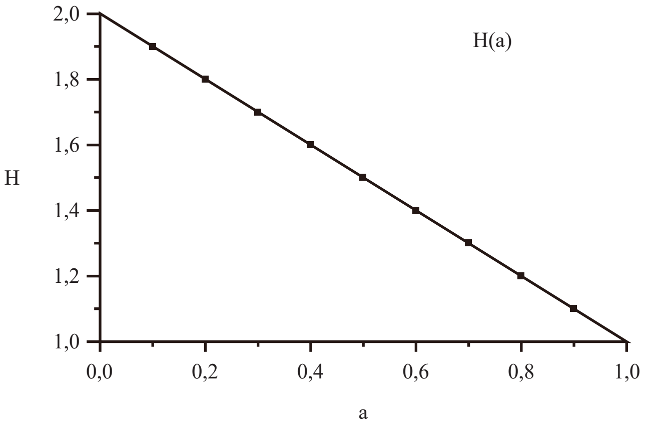

Figure 3. Enthalpy linear dependence on concentrations of reagents of a reaction at $Le_i \approx= 1$. A similarity of the fields of enthalpy (temperature) and reagent concentrations.

The current theory of thermal explosion (TE) [4]-[7] has been developed preferably for concentrated systems only (point explosions or ideally stirred reactors). No distributions of temperature or reagent concentrations are taken into account. In such a formulation, the theory of TE retains the form of the theory of TE developed by N. N. Semenov [8] (Semenov theory of TE).

4. Basic expression for reaction enthalpy

Let's consider the basic expression for enthalpy of an irreversible heterogeneous reaction [3]:

$$\rho \mathbf{u} \cdot (H + Qa) - \frac{\lambda}{c}\left(\frac{\mathrm{d}H}{\mathrm{d}x} + Le \cdot Q \frac{\mathrm{d}a}{\mathrm{d}x}\right) = \rho \mathbf{u} H_0 = const \qquad (1)$$

Where H is the reaction enthalpy, a is the reagent initial concentration, Q is the reaction heat release, **u** is the velocity of a 1D combustion wave supported by the reaction, and x is the space coordinate.

As one may easily conclude from eq. (1), the equation solution has the form:

$$H = H_0 + Q \cdot [1 - a] \qquad (2)$$

which is the first integral of the one-dimensional diffusion-thermal problem [3].

At $Le \ll 1$, one may see from eqs (1, 2) that the reaction enthalpy does not depend on the reagent concentrations and consequently on the reaction rate as well as on the reaction way. While at $Le_i >\cong 1$, corresponding to the limit of gas flames or granulated initially mixtures of reacting powders, the reaction enthalpy function is related linearly with the reagent concentration and there is a well-known similarity between the fields of enthalpy and that of concentrations, i.e., instead of two variables: H, a. One has to find just one of them reducing the number of equations to be solved finally.

5. Ambipolar diffusion estimates during combustion synthesis of zinc sulfide

Let's estimate the coefficients of the ambipolar charge carrier's diffusion to see if low diffusion coefficients, as well as low Lewis numbers, correspond actually to a real combustion synthesis. We are going to evaluate the coefficients and numbers in the same way as it was done in [5]. The formation of zinc cations in the metal lattice occurs reversibly: $Zn^X = Zn^{2+} + 2e^-$. Nevertheless, due to the difference in the coefficients of mobility and diffusion, we have: $\mu_e \gg \{\mu_{h+}, \mu_{S^{2-}}, \mu_{Zn^{2+}}\}$, $\mu_{h^+} \ll \{\mu_{S^{2-}}, \mu_{Zn^{2+}}\}$; $D_{h^+} \ll \langle D_{S^{2-}}, D_{Zn^{2+}}\rangle$, $D_e \gg \langle D_{h^+}, D_{S^{2-}}, D_{Zn^{2+}}\rangle$. Therefore, ambipolar diffusion of the Zn cations and electrons, as well as sulfur ions and electron holes, is carried out in pairs: faster particles in a pair (electrons, for example) slow down, but run forward and accelerate slower particles. As a result, slow charge carriers accelerate and diffuse with ambipolar diffusion coefficients, approximately equal to twice of the coefficients of slow particles: $D_{a,e} = \frac{\left(\mu_e D_{Zn^{2+}} + \mu_{Zn^{2+}} D_e\right)}{\left(\mu_e + \mu_{Zn^{2+}}\right)} \cong 2D_{Zn^{2+}} \ll D_e$. For the ZnS synthesis in argon, one may find the following ambipolar coefficients:

$$2.98\times10^{-4}\,\mathrm{mm}^2/\mathrm{s} < \mathrm{D}^{\mathrm{arga}}_{\mathrm{Zn}^{2+}} \le 2\times10^{-3}\,\mathrm{mm}^2/\mathrm{s},\ \text{i.e.,}\ Le^{\mathrm{arga}}_{\mathrm{Zn}^{2+}} \cong 0.01.$$

$$Pe^{\mathrm{arga}}_{\mathrm{Zn}^{2+}} =\cong 0.745\times10^3 \div 0.5\times10^4 = 745 \div 5000 \gg Pe_{\mathrm{T}}$$

where $Pe_T = 10 \div 100$. And one may see that the ZnS combustion synthesis in argon is mainly determined by thermal diffusion.

Various attempts to provide an accurate, clear, and final definition of the irreversibility of reactions in the combustion community arise from the very beginning of the formation of the science of combustion and still do not stop up to now. A lot of people have contributed to this question. Almost all of them tried to solve the problem kinetically just by restricting or prescribing kinetic schemes themselves [1], [2], [4], [6]-[10]. Nevertheless, one has to note that in contrast to them we are the first who has pointed out and proved numerically that the definition mentioned above strongly depends also on the transport phenomena directly involved in combustion, i.e., on reagents diffusion and heat transfer. Due to the small values of diffusion coefficients in heterogeneous systems that are natural for them the enthalpy of such systems turns out to be an additive value and a real thermodynamic potential, independent of the reaction path. This is a characteristic of the majority of all SHS reactions [6]-[9].

The above estimates of diffusion coefficients, as well as of Peclet and Lewis numbers, are consistent with experimental data not only on zinc sulfide synthesis but also on other heterogeneous systems [11], [12]. Therefore, we believe that relationships are a necessary and integral attribute of the concept of the irreversibility of reactions. In practice, the estimated values of the diffusion coefficients led to non-monotonic and so-called "wrong-way" temperature distributions [13] in combustion waves [13].

From the point of view of formal logic or chemical kinetics, the irreversibility and potential of a reaction path are completely independent concepts. However, as we have shown, they are interconnected in fact. The potentiality includes irreversibility in some of this part since there is no potential without irreversibility of reaction rates.

5.1 *Potential inequalities and ratios*

One way to prove that large changes in Gibbs potential as the well-known attribute of reactions irreversibility is completely equivalent to the above-mentioned approximation of a constant initial potential (reaction rate):

$$\mu_{\mathrm{i}} - \mu_{\mathrm{f}} = \frac{\mathrm{G_i}}{\mathrm{N_i}} - \frac{\mathrm{G_f}}{\mathrm{N_f}} = \frac{\mathrm{N_f}\cdot\mathrm{G_i} - \mathrm{G_f}\cdot\mathrm{N_i}}{\mathrm{N_f}\cdot\mathrm{N_i}} = \frac{\mathrm{G_i}}{\mathrm{N_i}} - \frac{\mathrm{G_f}}{\mathrm{N_i} - \Delta\mathrm{N}} = \frac{\mathrm{G_i}}{\mathrm{N_i}} - \frac{\mathrm{G_f}}{\mathrm{N_i}}\cdot\left[1 - \frac{\Delta\mathrm{N}}{\mathrm{N_i}}\right]^{-1} \cong \frac{\Delta\mathrm{G}}{\mathrm{N_i}} >> 1 \tag{3}$$

i.e.,

$$\mu_i - \mu_f \cong \Delta G / N_i, \tag{4}$$

at $\Delta N \ll N_i$, where μ_i is a chemical potential of the reaction's initial state and μ_f is a chemical potential of the reaction's final state.

N is the number of gas moles. One may see from relation (1) that, at the large changes of G, i.e., $\Delta G \gg \Delta G^* = N_i$, the ratio equivalent to (1) is $\mu_i \gg \mu_f$. ΔN is a change of gas moles consumed by the reaction, $\Delta N \ll N_i$. Subscript i denotes values related to the initial state, subscript f denotes values related to the final state, and superscript * denotes the critical value of Gibbs potential changes during the reaction.

If the final state potential has been chosen as that of a small equilibrium value: $\mu_f = o(1) \cong 0$, then the initial state potential greatly exceeds both the final potential and the potential unity: $\mu_i \gg 1$, μ_f. At a limited rate of the potential changes: $\left|\frac{\partial \mu_i}{\partial t}\right| \leq \text{const} \ll \infty$, the potential changes during reactions need an infinite time that, in other words, means the reaction irreversibility, i.e., the initial chemical potential has to be much greater than the potential of a final reaction state, or of the equilibrium at $\Delta G \ll N_i$.

The most direct and simplest proof of the reaction irreversibility may consist in the positivity of the system-specific thermal capacity [14], i.e., $C_p = T \cdot \left(\frac{\partial S}{\partial T}\right)_p > 0$ and $C_V = T \cdot \left(\frac{\partial S}{\partial T}\right)_V > 0$. Due to positive values of temperature T, these expressions mean that, for reactions as closed thermodynamic systems the following inequality is valid: $dS > 0$. This inequality directly means the irreversibility of a reaction way.

6. Conclusions

As a result, we can conclude, that the sufficiently small diffusion coefficients of reagents as well as the small Lewis numbers are completely sufficient to consider enthalpy as a thermodynamic potential during irreversible heterogeneous reactions.

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Conflict of interest

The authors declare that there is no personal or organizational conflict of interest with this work.

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