

# Thermodynamic Aspects in Heterogeneous Initiated Catalysis

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## To cite this article:

Talyshinsky Rashid. Thermodynamic Aspects in Heterogeneous Initiated Catalysis. *International Journal of Pharmacy and Chemistry*. Vol. 8, No. 4, 2022, pp. 44-47. doi: 10.11648/j.ijpc.20220804.12

**Received:** September 3, 2022; **Accepted:** September 17, 2022; **Published:** September 27, 2022

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**Abstract:** The aim of this work is to develop the fundamental foundations of initiated heterogeneous catalysis. In the classical concept, it was assumed that the catalytic system was reduced to the concept of a catalyst. Further, this concept expanded to the simultaneous action of a catalyst with a reaction medium, and then the action of an inductor or initiator was connected. Since the addition of an initiator to the catalytic system ensures the operation of the catalytic system, unlike a catalyst that does not perform work, remains unchanged during the catalytic cycle, it made sense to analyze the thermodynamic basis for the initiation of heterogeneous catalysis. A modern phenomenology of initiated heterogeneous-catalytic processes is proposed, based on the thermodynamics and kinetics of chemical reactions, taking into account the chemical coupling of individual stages and routes. A chemical evaluation of the synergism resulting from the combination of catalytic and induction interaction of reagents with a catalyst is given. A fundamental difference is shown between the thermodynamic and kinetic effects of chemical reactions, between the action of a catalyst and an initiator. The possibilities of using carbon monoxide and synthesis gas in conjugated reactions using an initiator are noted. The presence of dynamic compensation effects in catalysis, expressed by a simultaneous decrease in the activation barrier and an increase in the intensity of interaction of reagents, indicates non-additive phenomena, the nonlinearity of the reaction mechanism, as well as possible autocatalysis or autoinitiation. The basis for the proposed phenomenology in the field of initiated catalysis is not only heterogeneous-catalytic, but also homogeneous-catalytic processes, in particular, the discovered effect on the catalysis of benzoic acids during the conversion of phenyloxirane. Thus, the presence of an initiator in the catalytic system is the rule rather than the exception, which makes it possible to extend the proposed phenomenology of initiated catalysis to all its manifestations in nature.

**Keywords:** Thermodynamics, Kinetics, Induction, Initiation, Catalysis, Synergism

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## 1. Introduction

The rate of reactions occurring during heterogeneous catalytic processes is controlled by the selection of catalysts and optimization of regulatory parameters (temperature, pressure, concentration of reagents and initiators). The theoretical basis for mathematical modeling of processes in this case is their thermodynamic and kinetic foundations.

For the management of multi-route reactions, the stoichiometric basis of the final routes and mathematical expressions of the dependence of the velocities on the concentrations of reacting substances are of particular importance [1]. The form of the velocity equations is consistent with the stage scheme for the selected slow

reactions. The numerical values of the velocity constants are described by the classical Arrhenius equation reflecting their dependence on temperature [2]. The Arrhenius equation makes it possible to estimate the contribution of kinetic factors to the rate of reactions occurring in a heterogeneous catalytic system. This equation includes the so-called activation energy [3], the formal decrease of which reflects the functional capabilities of the catalytic system.

With a more meaningful analysis of the activation energy, it can be decomposed into a number of components, in particular, into free energy, bound energy, chemisorption bond energy with the catalyst, the energy of particle

migration on the surface of the catalyst, etc. If we assume such an additive position with linear addition of the components, then it would be necessary to allocate free energy, as an isobaric-isothermal potential, assuming that in the catalysis does not change its numerical value.

A catalytic system is commonly understood from a modern point of view [4] as a combination of a catalyst, initiator and reaction medium. The catalyst accelerates the achievement of chemical equilibrium in the slow stages of the process. The initiator (or inductor) performs work on the interaction between the catalyst and the reagents (or on the transformation of the catalyst surface), and the reaction medium modifies the catalyst. In general, a synergistic effect is achieved, reducing the energy barrier with an acceleration of the interaction between the reagents and the catalytic surface.

In the theory of active collisions, in our opinion, it is more correct to understand not literally the collision of molecules of reacting substances (which is unlikely), but the interaction of shock waves during the oscillation of electronic shells. According to the authors [5], the result of just such an interaction is resonance, which actually determines the essence of the catalytic action.

The foundations of the resonance theory were laid, in particular, by Semenov, Shilov and Voevodsky in the works on the study of radical chain transformations [6], used by practice later in [7-11].

Compensation effects in catalysis are manifested when modifying catalysts of a given type or when initiating catalytic processes. In the latter case, there may be a sharp increase in the intensity of the interaction with a simultaneous decrease in the energy barrier of the reaction. This phenomenon was observed in particular when studying the chemistry of the conversion of ethanol to 1,3-butadiene in the presence of hydrogen peroxide. In this paper, an attempt is made to explain the mechanism of initiation of the process from the standpoint of thermodynamics, using a classical analysis based on the theory of active interactions with the expansion of the range of reactions aimed at obtaining the main monomers of synthetic rubber.

## 2. Discussion

Dynamic compensation effect (DCE) differs from the well-known kinetic compensation effect in that the response to the initiator's action leads, when the activation barrier decreases, not to a proportional decrease in the "the intensity factor of the interaction  $K_0$ ", but, on the contrary, to its sharp increase due, for example, of branched radical chain reactions [11, 12].

In this aspect, the question of the actual change of the energy barrier under the influence of catalysis becomes debatable. The energy barrier, along with kinetic parameters, should objectively include a thermodynamic component.

In this position (with a fixed value of the activation energy of the reaction and a given initiator in stationary conditions), the discussion of the results of work on kinetic compensation

effects should be revised.

Figure 1 shows the geometric relationship between the classical thermodynamic characteristics.

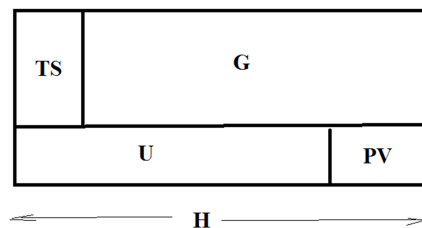


Figure 1. The relationship between thermodynamic characteristics.

$$G = U + PV - TS$$

$$H = U + PV$$

$$dG = -SdT + VdP$$

$$dG = -SdT + VdP + \mu dN,$$

where  $\mu$  is the chemical potential, which can be defined as the energy that must be expended to add another particle to the system. In a branched-chain process, this potential is multiplied by the degree of branching.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -RT \ln K_p$$

Equilibrium pressure constant

$$K_p = k_1/k_{-1}$$

Let's take internal energy as a function of volume and temperature:

$$U = f(V, T)$$

Let's write down the full differential of this function

$$dU = (\partial U / \partial V) dV + (\partial U / \partial T) dT$$

As a result, the activation energy consists of two thermodynamic components that have no direct connection with the nature of the catalyst, but depend on the action of the inductor or initiator in the system. Hence, the reaction rate is determined by the temperature and the number of mobile particles. During the transition from kinetics to dynamics, the number of mobile particles may change during the process, and we observe an externally reduced reaction barrier due to changes in entropy. Note also that the interaction of mobile particles is carried out through a reaction medium. These positions significantly change the views on the nature of catalysis.

It is known that

$$\Delta H - T\Delta S = \Delta G.$$

Indeed, the activation energy is reduced to a change in the Gibbs free energy when the initial substances are converted into reaction products. Since in the absence of a catalyst and

initiator, the enthalpy change  $\Delta H$  is the difference between the enthalpy of the starting substances and the reaction products  $H_2 - H_1$ , the initial and final values of the heat of the substances involved in the reaction are equal:



According to the theory of the transition state, the formation of an intermediate activated complex is characterized by entropy and Gibbs energies (free energy):

$$H = TS + G$$

In a bimolecular reaction, one molecule of an activated complex ( $AK^*$ ) is formed from two gas molecules, therefore, for bimolecular reactions, the entropy factor  $\exp(\Delta S^\ddagger/R)$  is interpreted as a steric multiplier in accordance with the theory of active interactions [2]:

$$k(t) = \frac{kT}{h} e^{\frac{\Delta G}{RT}} = \frac{kT}{h} e^{\frac{\Delta S}{RT}} \frac{kT}{h} e^{-\frac{\Delta H}{RT}}$$

$$\Delta S^* = S_{AK^*} - S_{\text{reagent}}$$

$$\Delta H^\ddagger = \Delta H^\ddagger_{\text{product}} - \sum \Delta H^\ddagger_{\text{reagent}}$$

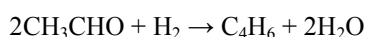
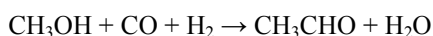
$$\Delta E^\ddagger = \Delta H^\ddagger + RT$$

In the works [11-15], the issues of coupling in chemical kinetics and dynamics of oxidative catalytic processes occurring mainly by a radical chain mechanism are analyzed. Dynamic aspects in heterogeneous catalysis are noted.

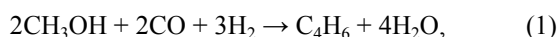
Based on the above, multiplicity of stationary states concepts are become clearer and more explicable [16].

Currently, catalytic reactions using CO and syngas are becoming the most widespread, allowing to strengthen the production rules for the synthesis of synthetic rubber monomers.

By linear combination of routes



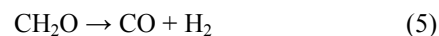
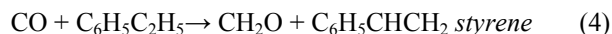
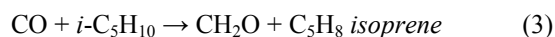
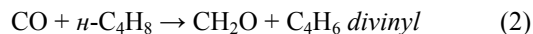
the final stoichiometric gross equation is obtained



which reflects the course of the reaction of the interaction of methanol and synthesis gas with the formation of divinyl. Second product is acetic acid, formed in the well-known reaction of the industrial process of oxosynthesis.

The possibility of implementing the final equation (1) is proved by the thermodynamic possibility of implementing combined routes [17]. This reaction may be of interest from a practical point of view in enterprises where there is an excess of the synthesis gas resource.

Another universal approach is the use of carbon monoxide in the oxidative dehydrogenation of n-butenes, isoamylenes and ethylbenzene into divinyl, isoprene and styrene, respectively:



with the return to the reaction cycle of CO.

If isobutylenes are present in the raw material in bimolecular reaction (2), there is a probability of their interaction with formaldehyde by a known reaction with the formation of isoprene. Hence, there is a possibility of complex processing of C4-C5 olefins into isoprene with the participation of synthesis gas, which can eventually be considered as a gaseous catalyst for the dehydration of olefins into the target product – isoprene. Such a path would be an elegant continuation of the concept of using CO in C1 chemistry.

### 3. Conclusions

In the presence of a catalyst, there is an influence of additional values of chemisorption enthalpies on the one hand and the influence of the initiator on the other, which leads to the need to adjust the Arrhenius equation taking into account chemisorption enthalpies and resonant values of free energy. It follows that in most cases the activation energy ceases to be a constant value and dynamically changes during the process.

Thus, the reaction rate is determined by the temperature and the number of mobile particles. During the transition from kinetics to dynamics, when the number of mobile particles changes during the process, we observe an external decrease in the reaction barrier due to a change in entropy. Note also that the interaction of mobile particles is carried out through a reaction medium. These positions significantly change the views on the nature of catalysis, allowing us to find common positions characteristic of enzymatic, homogeneous and heterogeneous catalysis, which was unacceptable using classical approaches.

As a result, the description of the speed of the catalytic process objectively reduces not to kinetic, but to dynamic equations. The description of the stationary state of a catalytic system is an exception to the rule rather than the rule.

Resonant phenomena in catalysis associated with the influence of initiators were also noted in [18], in which the enthalpy and entropy kinetic compensation effect was analyzed. Benzoic acids seem to initiate the conversion of phenyloxirane. The initiating effect in catalysis in this case can be explained by the presence of conjugated chemical stages.

### Gratitude

*The work was carried out in accordance with the State task of the INHS RAS.*

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