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# A New Attempt to Better Understand Arrhenius Equation and Its Activation Energy

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Additional information is available at the end of the chapter

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## 1. Introduction

Activation energy ( $E_a$ ) is strictly combined with kinetics of chemical reactions. The relationship is described by Arrhenius equation

$$k = A \exp(-E_a/RT) \quad (1)$$

where  $k$  is the rate coefficient,  $A$  is a constant,  $R$  is the universal gas constant, and  $T$  is the temperature (in Kelvin);  $R$  has the value of  $8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1}$ ,  $E_a$  is the amount of energy required to ensure that a reaction happens. Common sense is that at higher temperatures, the probability of two molecules colliding is higher. Accordingly, a given reaction rate is higher and the reaction proceeds faster and, the effect of temperature on reaction rates is calculated using the Arrhenius equation. Further reaction rate enhancement is promoted by catalysis. Catalysis is the phenomenon of a catalyst in action. Catalyst is a material that increases the rate of chemical reaction, and for equilibrium reactions it increases the rate at which a chemical system approaches equilibrium, without being consumed in the process [1]. It is applied in small amounts relative to the reactants. Chemical kinetics, based on Arrhenius equation assumes that catalysts lower the activation energy ( $E_a$ ) and the presence of catalyst results in higher reaction rate at the same temperature. In chemical kinetics  $E_a$  is the height of the potential barrier separating the products and reactants. Catalytic reactions have a lower  $E_a$  than those of the thermally activated. This fact enables a chemical reaction not only to proceed faster but also at a lower temperature than otherwise possible. The solid heterogeneous catalyst mechanism that would lower activation energy is still under discussion. It is known that the effect of catalysts is intrinsically connected to the material surface states. However, the connection of catalysts material states to their action is not yet fully clear and specific stimulators of this action are unknown. Few years ago [2] a new approach to  $E_a$  was proposed and a first indirect confirmation was made [3]. Dante et al. [4]

supported the new approach to  $E_a$  by theoretical considerations based on irreversible thermodynamics.

Heterogeneous catalysis provides the link between reactants and products on a reaction pathway which involves simultaneous motion of several to very many atoms [5]. Predictability of the outcome of catalytic reactions is controlled by their molecular mechanisms. Thus, the importance of the activation energy better understanding can not be overestimated. Some forty years ago, work [6] demonstrated that a “chemically stimulated” exo-electron emission (EEE) occurs simultaneously during the partial oxidation process of ethylene. It was also found that the emission rate was proportional to the rate of ethylene oxide formation. Therefore, discussing heterogeneous catalytic reactions, EEE process should also be taken into account, because they involve electro physical phenomena. Additionally, such electrons are of low-energy and are produced from the excited active catalytic surfaces.

## 2. Background and the present work goal

### 2.1. Recent papers focused on the activation energy ( $E_a$ ) new approach

Paper [2] has proposed the new hypothesis concerning kinetics of chemical reactions and  $E_a$ . Shortly the hypothesis was confirmed indirectly [3] by using earlier published results on energy angular distribution of electrons emitted from MIM systems [7] and angular distribution of photoelectrons emitted from solids [8]. The next confirmation step was based on irreversible thermodynamics [4] and, it was demonstrated that the equation of the found reaction rate is also consistent with two different pathways for tribochemical reactions:

$$J_c = \{v_i \exp(-E_a/RT) (1 - e^{-A/RT}) + k [1 - \exp(-J_u c t / T)]\} \prod a_i^{v_i} \quad (2)$$

where:  $J_c$  – reaction rate,  $J_u$  – energy flow towards the reagents due to triboreactions,  $\tau$  – shear stress due to friction,  $A$  – chemical affinity,  $c$  and  $k$  – constants,  $t$  – time,  $a_i$  – activities of reagents,  $v_i$  – stoichiometric coefficient.

The first one is the thermal mechanism, typical for non-friction conditions and, the second concerns the direct transfer of energy from triboelectrons to molecules. The latter one generates special excited or activated molecules, such as radicals or ions which react rapidly to form the products, enhancing the global reaction rate.

### 2.2. Aim of the paper

The major goal of the present paper is to enhance the developed idea and provide it with the better understanding of Arrhenius equation and its activation energy. To make a progress in that field,  $\alpha_i$  model developed by Kulczycki [9] was here applied along with its detailed thermodynamic interpretation. Detailed discussion is focused on the basic Arrhenius equation.

### 3. Thermodynamic interpretation of $\alpha_i$ model

#### 3.1. Theoretical information

The main assumption of  $\alpha_i$  model, described in detail in [9] introduced the **new measure** –  $\alpha_i$  **coefficient** of reagent/lubricating oil or additive **properties / structure** influence on its **reactivity** related to **reaction conditions**. This model was worked out on the bases of the results of tribochemical investigations of different lubricating oils. In relation to tribological processes, **tribochemical reaction conditions** depend on the work done on tribological system - L. The work L is the function of applied load P, which can be treated as the only one variable  $y - L = f(y)$ . The reagents **reactivity** is described by the second function of variable  $y - \phi ( y )$ . Basing on Cauchy theorem the relation between two functions of the same one variable y is as follows:

$$\alpha_i = \{ [f ( b ) - f ( a )] / [ \phi ( b ) - \phi ( a ) ] \} / [f' ( b ) / \phi' ( b ) ] \quad (3)$$

where  $a$  and  $b$  are values of  $y$  parameter. For different reagents value  $b$  is the only one variable (assumption of Cauchy theorem) and  $a$  is constant. Variable  $b$  was related to tribological process conditions – for example applied load P. In  $\alpha_i$  model P is critical value and it relates either to seizure load or weld load. Consequently work done on the system means the work needed to achieve the seizure or weld.

Work done on tribological system can be related to thermodynamic description of tribological process. In the consequence reactivity can be related to the internal energy change  $\Delta u$ , and Eqn. (4) can be written as follows:

$$\alpha_i = [ (L - L_0) / (\Delta u - \Delta u_0) ] \times (d \Delta u / d L) \quad (4)$$

$L = \mu P v t$ ;  $\mu$  - friction coefficient;  $v$  – speed;  $t$  – time;  $P$  – applied load (test result);  
where:  $L_0 = f(a)$ ,  $\Delta u_0 = \phi(a)$

Since it is difficult to define relationship  $\Delta u = \phi (P)$  because  $\Delta u$  is not linear dependence of the applied load P, we can use the first law of thermodynamics L to express it as a function of  $\Delta u$ :

$$L = Q + \Delta u \quad (5)$$

Q is energy dissipated by system during tribological process; mainly it is a dissipated heat, which in relation to tribological process can be described by the following dependence:

$$Q = c_h (T - T_{ot}) \quad (6)$$

$$T = T_b + A P^{0,5} \quad (7)$$

where:  $c_h$  - average specific heat capacity,

$T_b$  – temperature of lubricant out of friction area,  $T_{ot}$  – temperature of environment.

Assuming that both average specific heat capacity and  $T_b$  are constant for different oils, Q can be expressed as

$$Q = A_1 P^{0.5} \tag{8}$$

Consequently

$$\alpha_i = (\mu P_{vt} - \mu P_{0vt}) [(\mu vt dP - A_1 dP^{0.5}) / \mu vt dP] / (\mu vt P - A_1 P^{0.5} - \Delta u_0) \tag{9}$$

### 3.2. Description of the C value as the function of applied load P in terms of Figure 1

It was experimentally found during tribological tests, described in [9], that  $\alpha_i$  is linear function of applied load P. This linear dependence takes place in case the number of lubricants containing additives of different activity, but similar chemical structures were tested in the given tribological test. In this case

$$\alpha_i = (\mu P_{vt} - \mu P_{0vt}) C \tag{10}$$

and for additives of similar chemical structure (for example zinc dithiophosphates) C value is constant. For these additives in the given tribological test

$$C = [(\mu vt dP - A_1 dP^{0.5}) / \mu vt dP] / (\mu vt P - A_1 P^{0.5} - \Delta u_0) \tag{11}$$

The fact that for additives of similar chemical structure (for example zinc dithiophosphates) C value is constant and C is the function of P, which value is different for each additive, requires that C is a harmonic function of P, described by the following dependence:

$$C = A \exp(-ay) / \cos (by + d) \tag{12}$$

where  $y = P$  or  $T$  and  $A, a, b$  and  $d$  are constant value.

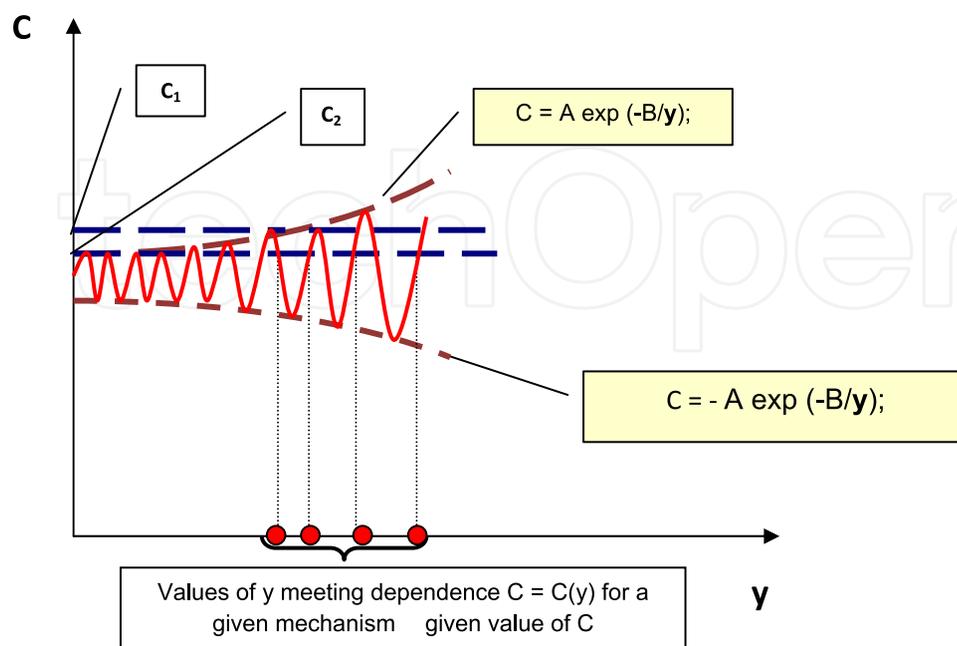


Figure 1. Dependence between C and applied load P

Consequently for the given constant value of  $C$  only some of values  $P$  meet equation (10) and (11). (red points in Figure1.)

What is physical and chemical meaning of those dependences? Answers seem to be also related to tribocatalysis and heterogeneous catalysis. Exponential part of this dependence can be connected with kinetics of chemical reactions by Arrhenius equation:

$$k = A \exp (B - E_a/RT) \quad (13)$$

where temperature  $T$  may be connected with load  $P$  applied in tribological process, as earlier shown in equation (7)

$$T = T_b + \mu P^{0.5} D$$

$D = 10^{-5} V_s P_p^{0.5} (k_1 + k_2)^{-1}$  where:  $V_s$  – sliding speed,  $P_p$  - unit pressure of the metal flow,  $k_1$  and  $k_2$  - coefficients of thermal conductivity of cooperated elements of tribological system [10].

### 3.3. Cauchy`s theorem application to the model

The  $\alpha_i$  model and the equation (12) combine the activation energy delivered to molecules from the energy stream. Considering the energy delivered to molecules for each reaction, the following should be noted:

- Cauchy`s theorem requires the only one variable in functions  $f(y)$  and  $\phi(y)$ ; application of  $\alpha_i$  model to tribochemistry/ tribocatalysis and heterogeneous catalysis this variables can be temperature  $T$  or connected with them applied load  $P$  (tribochemistry/ tribocatalysis).
- To use  $\alpha_i$  model in tribochemical and chemical problems solving it was assumed that variable  $y$  describes critical stage of reaction system, which is equivalent to critical rate of described reactions.
- A critical rate of catalytic reactions or triboreactions is reached at a critical temperature (eg. temperature of catalytic reaction at which there is maximum rate of this reaction) or, equivalently, under a critical load, at which seizure load takes place.
- Connecting critical rate of triboreaction / catalytic reaction with  $C$  in Eqn. 9 and 10 it was concluded that the value of  $E_a$  is the same for different reactants in the case of the same mechanism of triboreactions / catalytic reactions, because  $E_a$  is neither a function of  $T$  nor  $P$  and Cauchy`s theorem does not accept another variables than  $y$ .

Concluding for tribocatalysis:

- $C$  is the function of  $P$  only, so activation energy  $E_a$  has to be constant for different additives / reactants and different values of critical load  $P$ .
- Looking on mathematical analysis for given mechanism there are permitted values of critical load, and consequently permitted values of critical rate of tribochemical reactions.

On the basis of this mathematical model, physical model of tribocatalysis / catalysis was created. The model assumes that mechanical work done on the system (containing liquid

reagents = lubricants), is transformed to internal energy increase and dissipated energy. Internal energy is distributed in the system: one part is distributed to the liquid phase and is responsible for ambient temperature increase of the lubricant ( $T_a$ ), the second part is cumulated in solid body (solid elements of tribological system) and is emitted as electrons or photons by its surface as impulses of high intensity. Energy cumulated in the liquid phase is not sufficient to reach value of  $E_a$ . Energy emitted by surface as impulses can reach value of  $E_a$  and reaction / triboreaction begins to proceed.

Eqn. 10 points that value of  $C$  depends not only on reaction rate constant but on intensity of energy emitted in angle  $\gamma$  from solid body to reaction space. Angle  $\gamma$  can not be another variable in Eqn. 8 and 10 – requirements of Cauchy's theorem, so it should depend on  $T$  or  $P$ . Accordingly, the value of the angle  $\gamma$  depends on the system energy flux. The critical state of a tribological system appears at conditions resulting in destruction of the protective film. It has been observed that for different reactants, the critical rate of reaction leading to protective layer destruction was achieved for different values of energy flux into the system (different values of applied load  $P$ ). The same value of  $C$  obtained for different reactants and different densities of energy streams introduced into the system (characteristic of each reactant) leads to the conclusion that the same critical rate of destruction reaction was achieved and thus for each reactant a different angle  $\gamma$  is connected with the critical rate of reaction (different values of  $T$  or  $P$ ).

Consequently, for each reactant there is a specific value of the energy flux density ( $e_\gamma$ ), where  $e_\gamma = e_0 \cos \gamma$ ,  $e_0$  - intensity of energy stream emitted by the solid/catalyst in normal direction to solid surface ( $\gamma = 0$ ) and the value of activation energy  $E_a$  is constant. Accordingly, it is possible to emphasize that:

- i.  $E_a$  is constant for a given type of reaction and the critical rate of reaction depends not only on the energy quantity added to reactants but on the density of the introduced energy stream (time of the tribological process is constant for each load);
- ii. The catalyst emits pulses of energy flux of high density at an angle  $\gamma$ . The value of emitted in short time energy is equal to the difference between activation energy calculated for reaction without catalyst  $E_a$  and activation energy calculated for catalytic reaction activation energy  $E_{ac}$ ;
- iii. The catalyst collects energy done as mechanical work and emits it as pulses of the high energy density flux, thereby decreasing temperature needed for the reaction initiation or its rate enhancement.

### 3.4. Empirical verification of $\alpha_i$ model and its derivative equation concerning heterogeneous catalysis

#### 3.4.1. Verification of $\alpha_i$ model in tribological tests

Basing on the above dependences and obtained test results the  $\alpha_i$  values were calculated for a number of gear, hydraulic and transmission oils of viscosity at 40 °C in range between 32 to 220 mm<sup>2</sup>/s. Because of the structure of protective layer created by lubricant under

boundary conditions is selected on AW and EP types. The  $\alpha_{AW}$  and  $\alpha_{EP}$  coefficients are assigned to each tested lubricants. The method used in calculation of  $\alpha_{AW}$  and  $\alpha_{EP}$  values on the bases of tribotests results for each lubricant was described in [9].

The  $\alpha_i$  values assigned to those lubricants were related to the results of tribological standard tests. Therefore, it was necessary to find out tribological experimental methods able to provide test results concerning lubricant's ability to create both AW and EP types of the boundary layer. In the already cited work [5], there were selected two different tests carried out using a four ball machine.

The first test was used to determine seizure load  $P_t$  under the following operating conditions:

- rotating speed of upper ball 470 +/- 20 rpm
- load increase continuously from 0 to the seizure load
- seizure load is detected by the friction coefficient measurement.

Following dependence for  $\alpha_{AW}$  determined applying the above described procedure and  $P_t$  values is found:

$$\alpha_{AW} = (0,000086 v_{40} - 0,01) 0,5 \mu P_t^2 v_s v_p^{-1} + 0,2 - 0,00073 v_{40} \quad (14)$$

where:

$v_{40}$  – kinematic viscosity of tested oil at 40 °C

$v_s$  - sliding velocity ( 0,18 m/s )

$v_p$  - speed of load increase ( 45 N/s )

$\mu$ - friction coefficient

This dependence points out that the mechanism of AW type of protective layer formation depends on base oil viscosity.

The  $\alpha_{EP}$  values determined using above procedure were related to the second 4-ball test, where welding load  $P_w$  was the test result. This test was performed under the following operating conditions:

- rotating speed of upper ball 1470 +/- 30 rpm
- stepwise load increase according to Polish Standard PN-76/C-04147 (ASTM D2783: Standard Test Method for Measurement of EP Properties of Lubricating Fluids, Four-Ball Method)
- test duration on each step 10 s

It was found that  $P_w$  values depend on durability of EP type of the boundary layer and was experimentally found the linear dependence between  $\alpha_{EP}$  and  $P_w$ :

$$\alpha_{EP} = 0,48 - 0,00013 P_w \quad (15)$$

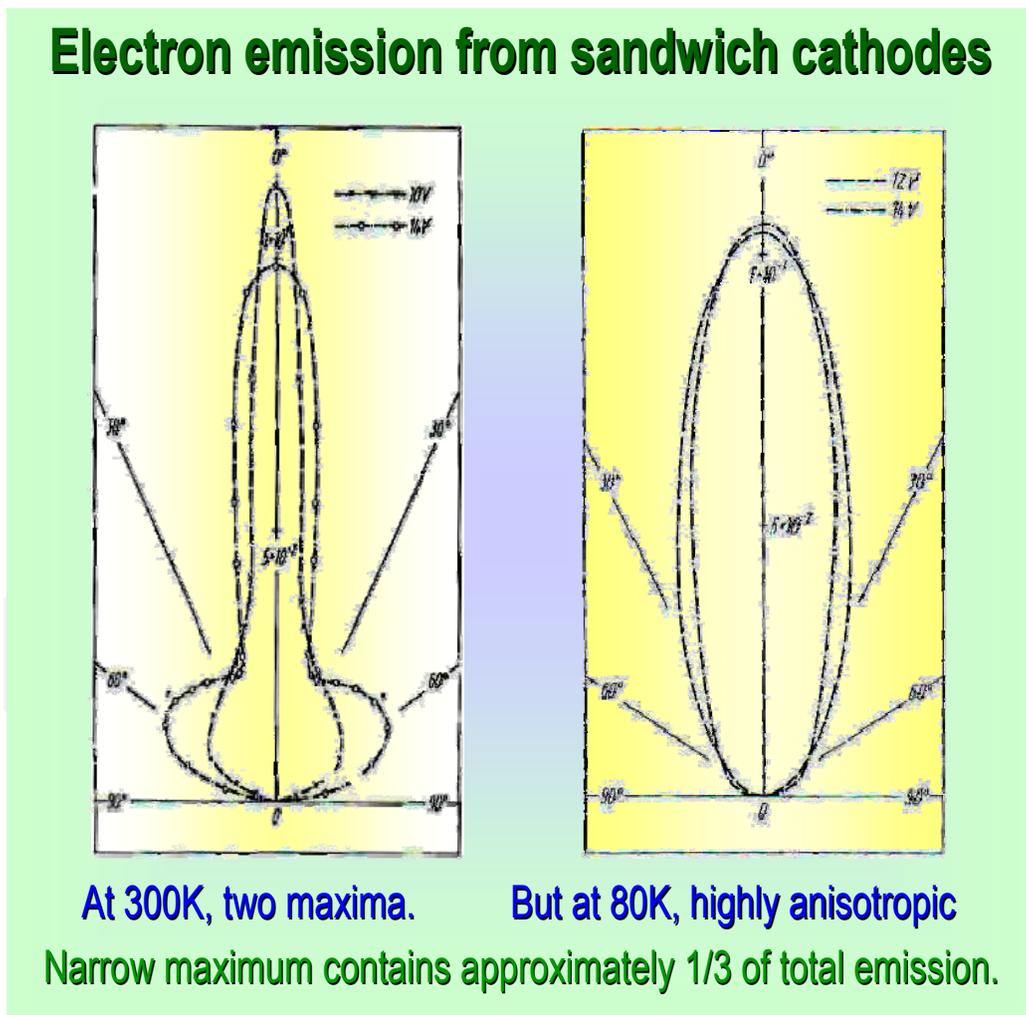
Using both these standard tests the value of  $\alpha_{AW}$  and  $\alpha_{EP}$  can be determined easily and than used to predict the results of another tribological tests (eg. FZG) or analyze the structure of

protective layer created in various machines (participation of AW and EP structure in protective layer).

### 3.4.2. Verification of derivative equation concerning heterogeneous catalysis; electron and photon emission anisotropy

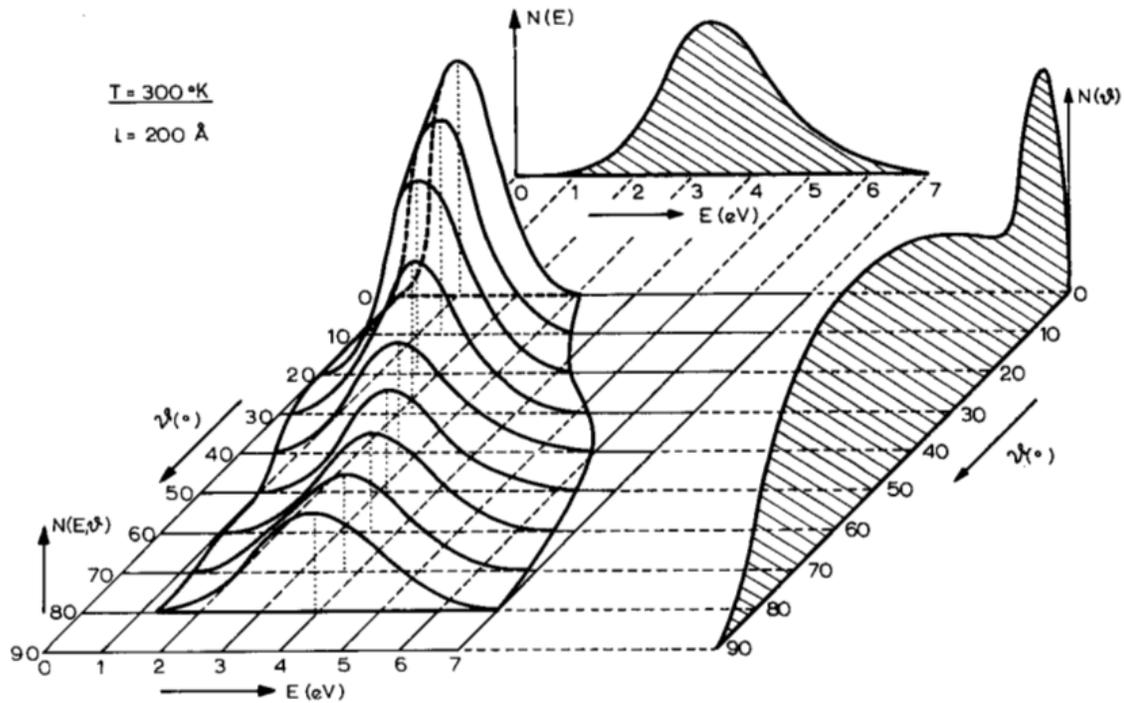
Eqn. 12 ( $C = A \exp(-ay) / \cos (by + d)$ ) leads to conclusion that the emission of energy (electrons and photons) from the surface of solid body is anisotropic one. Exhaustive literature review revealed that there is no data on the angular distribution of triboemitted electrons, but that existing research works on the emission of electrons from cathodes consistently report anisotropic distributions [7, 11-13]. Highly anisotropic distributions with a maximum in the direction normal to the emitting surface were measured.

Figure. 2. illustrates an example of anisotropic electron emission from sandwich cathodes. At the emission temperature of 300K the measured electrons present a quasi-isotropic characteristic. But at a lower temperature of 80K, the isotropic component vanishes.



**Figure 2.** Examples of EE from sandwich cathodes presenting 2 maxima with a maximum in direction normal to the emitting surface, and highly anisotropic EE: based on Hrach research results [7,13]

References [11-12] allow to make an estimate that at room temperature the narrow maximum around the direction normal to the emitting surface contains approximately 1/3 of the total emission. Further work of Hrach [7,13] was of particular significance as he measured the energy characteristics of emitted electrons at different angles by means of a hemispherical collector and the retarding-grid technique. He found that at room temperature (300K) anisotropic energy spectra of emitted electrons were in the range of 0 and 7eV, but for emission angles closer to the normal to the surface the measured energy was between zero and 4 eV. Figure 3. depicts some of these findings.



**Figure 3.** Typical experimental angular and energy distribution of electrons emitted from Al-Al<sub>2</sub>O<sub>3</sub>-Au sandwich cathode structures. Temperature: 300K, applied voltage: 10V [13]

Reference [3] includes more detailed information concerning figures 2 and 3. More recent study [14] was on the angular distribution of thermo-stimulated exoelectron emission (TSEE) from alpha-Al<sub>2</sub>O<sub>3</sub>. Anisotropic angular distributions were strongly directed normally to the surface; the energy of the emitted electrons was in the range of 0 to 4 eV. Jablonski and Zemek [8] found highly anisotropic distribution similar to one of electron-type for the photon emission from X-ray-irradiated thin polycrystalline aluminum foils.

### 3.5. Discussion on the basic Arrhenius equation

In Arrhenius equation  $T$  equals  $T_a$ , ( $T = T_a$ ) and it relates to ambient temperature of reaction mixture. Conclusions from  $\alpha_i$  model are as follows:

- When catalyst is used ambient energy  $RT_a$  is less than energy in space near catalysts particles surface =  $RT_s$ .  $T_s$  is the calculated temperature near catalyst surface and it should be higher than ambient temperature of reaction mixture.  $RT_s$  is real energy acted

to the molecules of reactants and this energy should be introduced into Arrhenius equation.

$$k = A \exp (B - E_a / RT_s) \quad (16)$$

Relation between  $RT_a$  and  $RT_s$  is as follows:

$$\exp (B - E_a / RT_s) / \exp (B - E_a / RT_a) = 1 / (e_o \cos \gamma) \quad (17)$$

$$E_a / RT_s = E_a / RT_a + \ln (e_o \cos \gamma) \quad (18)$$

When  $(e_o \cos \gamma) > 1$  the real energy near catalyst surface is less than ambient energy ( $RT_s < RT_a$ ) – reaction inhibition, when  $(e_o \cos \gamma) < 1$  the real energy near catalyst surface is higher than ambient energy ( $RT_s > RT_a$ ) – catalytic effect, for  $(e_o \cos \gamma) = 1$  there is no catalytic nor inhibitor effect.

In case the same value of reaction rate constant for reaction without and with catalyst is compared using Arrhenius equation, there should be noticed difference between activation energy for reaction with catalyst ( $E_{ac}$ ) and without catalyst ( $E_a$ ). The hypothesis based on  $\alpha_i$  model is that this difference is equal to energy emitted by solids surface in angle  $\gamma$ .

$$\Delta E_a = 40 \text{ kJ/mol} = 240 \times 10^{22} \text{ eV/mol} = 4 \text{ eV / molecule}$$

Empirically determined energy emitted by solid surface is in the range 3 to 7eV and it is the range of value of  $\Delta E_a$ .

The results of these calculations are in line with hypothesis based on  $\alpha_i$  model saying that catalytic effect is due to energy emission from catalysts surface in the form of electrons / photons stream, additional energy of which makes possible to reach the same reaction rate in lower ambient temperature or increase the reaction rate in the same ambient temperature. This hypothesis is described by C in Eqn. 8: C is the quotient of reaction rate constant described by Arrhenius equation and the stream of energy emitted by the surface of catalyst in angle  $\gamma$ .

Concluding the general dependence (1):

$$\alpha_i = \{ [f(b) - f(a)] / [\phi(b) - \phi(a)] \} / [f'(b) / \phi'(b)] \quad (1)$$

can be shown as follows:

$$\alpha_i = (L - L_0) A [\exp (B - E_a / RT_a)] / e_o \cos(\gamma) \quad (19)$$

therefore, it is concluded that:

$$\begin{aligned} \{ [f(b) - f(a)] / [\phi(b) - \phi(a)] \} / [f'(b) / \phi'(b)] &= \\ &= (L - L_0) A [\exp (B - E_a / RT_a)] / e_o \cos(\gamma) \end{aligned} \quad (20)$$

Function  $f(y)$  represents the stream of energy introduced into the system, function  $\phi(y)$  is connected with catalytic / tribocatalytic reaction critical rate, which is represent by the ratio

of reaction rate constant described by Arrhenius equation and the stream of energy emitted by catalysts surface in angle  $\gamma$ . This ratio points that to the equation describing reaction rate constant (Arrhenius equation) should be added denominator describing the stream of energy emitted by catalysts surface. The reaction rate constant described by the above ratio leads to another explanation of the mechanism of catalytic effect than, based on Arrhenius equation, decreasing of the value of activation energy.

### 3.6. Practical significance of the new ( $E_a$ ) approach in tribo- and mechano-chemistry

Mechanochemistry is the coupling of the mechanical and the chemical phenomena on a molecular scale and includes mechanical breakage, chemical behaviour of mechanically-stressed solids (e.g., stress-corrosion cracking), tribology, polymer degradation under shear, cavitation-related phenomena (e.g., sonochemistry and sonoluminescence), shockwave chemistry and physics, and even the burgeoning field of molecular machines. Mechanochemistry can be seen as an interface between chemistry and mechanical engineering. A smart method was proposed recently, in order to measure the energy involved during mechanical transformations. Displacement reactions between a metal oxide and a more reactive metal can be induced by ball milling. In some cases the reaction progresses gradually and a metal/metal-oxide nanocomposite is formed. Ball milling may also initiate a self propagating combustive reaction. The information available about these processes is reviewed. It is argued that the gradual or combustive nature of the reaction depends on thermodynamic parameters, the microstructure of the reaction mixture, and the way they develop during the milling process.

Baláž, et al. [15] investigated the mechanochemical treatment of solids which lead to a positive influence on the solid – liquid kinetics. They used Arrhenius equation for activation energy analysis. The breaking of bonds in the crystalline lattice of solids brings about a decrease ( $\Delta E^*$ ) in the activation energy and an increase in the rate of leaching

$$(\Delta E^*) = E - E^* \quad (21)$$

$$k^* = k \exp (\Delta E^*/RT) \quad (22)$$

where  $E$  is the apparent activation energy of the non-disordered solid,  $E^*$  is the apparent activation energy of the disordered solid,  $k$ ,  $R$  and  $T$  stand for the rate constant of leaching for the non-disordered solid, (the pre-exponential factor) gas constant and reaction temperature, respectively;  $k^*$  is the rate constant of leaching for the disordered solid. If  $E > E^*$ , then  $\exp (\Delta E^*/RT) > 1$  and thus it follows from Eqn. (18) that  $k^* > k$ , i.e., the rate of leaching of a disordered solid is greater than that of an ordered mineral.

Thermodynamic methods are essentially macroscopic by origin and nature. They appear in the analysis of macroscopic engineering systems. They have been reliably validated in numerous macroscopic experiments and observations. Most probably there can be found areas that permit analysis of mechanochemical systems by means of relatively simple

thermodynamic methods. From the purely thermodynamic point of view, the central problem of mechanochemistry is the exchange of energy between the (long-range) elastic energy and the (short-range) energy accumulated in individual bonds.

There is no clear theory which could be adapted to mechanochemistry, however the most recent approach [16] should be mentioned here. The  $\alpha_i$  model applied for tribochemical applications can also be adapted to mechanochemistry. This model can be helpful in general dependences formulation, related to kinetics of mechanochemical reactions and to mechanical forces used for reactions activation. The theory based on  $\alpha_i$  model assumes that mechanical energy introduced into solid body – reagent or catalyst, is accumulated in it and then emitted as low energy electrons or photons of energy equal or higher than activation energy of the reaction. The general Eqn. (19) can be used to determine quantitatively relationship between mechanical stress ( $L$ ), the possibility of solid body to accumulate and then emit energy ( $e_0 \cos \gamma$ ) and kinetics of mechanochemical reaction.

Mechanochemistry, especially results of investigations shown above can be explained by hypothesis based on  $\alpha_i$  model. On the other hand the positive effect of mechanical stress on catalyst efficiency confirms this hypothesis. However the reason of this effect can be mechanically (eg. during milling) produced changes of catalysts surface.

Rodriguez et al. [17] found out the influence of ultrasound radiation on catalysts effectiveness. They tested a new advanced method for dechlorination of 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzenes in organic solvent catalysed by palladium on carbon support and solid hydrazine hydrochloride yields benzene in short reaction times. The catalyst system can be efficiently reused for several cycles. Ultrasound radiation of the heterogeneous catalyst reaction increases remarkably the rate of dechlorination. Moreover, Rodriguez found that there is optimum energy of ultrasound radiation which results maximum catalysts efficiency. This effect is not seen when ultrasound radiation act liquid reactants. Rodriguez results confirm thesis that energy, in this case of ultrasound radiation is useful in reaction rate increasing when solid body – particles of catalyst are present in reaction mixture. This energy is cumulated by catalyst and emitted to the space near catalyst surface, what is the reason of reaction rate increasing. This effect can not be explained by the changes of the structure of catalysts surface, like in other mechanochemical effects (eg. during milling) so the only one probably mechanism is emission of cumulated in solid catalyst energy to reaction space.

The concept of mechanochemistry to modify molecular reactivity has a rich history for a long time. For instance Kauzmann and Eyring as early as 1940 [18] suggested that the mechanical perturbation of diatomic molecules could alter the reaction coordinates combined with their homolytic dissociation.

The chemical kinetic quantitatively describes homogenous reactions, where the rate of reaction depends only on heat introduced to reaction system. Kinetic equations concern reagents concentration, and according to Arrhenius equation: temperature of reaction mixture as well as activation energy.

These kinetic equations used in heterogeneous catalytic reactions description concern no one parameter characterizing catalyst. Consequently the effect of catalyst action can be explained only by the decreasing of activation energy value – the only one calculated parameter in kinetic equations. It is the reason that all theories of catalysts action try explain the mechanism of activation energy decreasing.

The  $\alpha_i$  model, particularly equation (19) describes catalytic and tribocatalytic reactions by dependence concerning parts, which quantitatively characterizes:

- all kinds of energy introduced into the reaction system, including mechanical energy - L in eqn. (19)
- properties of catalyst, explained by energy emitted from its surface to reaction space –  $e_0 \cos \gamma$ .

Resulted from the  $\alpha_i$  model concept of the mechanism of heterogeneous catalysis and tribocatalysis, shown above, is confirmed partly by tribochemistry and mechanochemistry. This mechanism should be directly confirmed, particularly by materials engineering, which should explain:

- the role of support in catalysts activity,
- the possibility of energy storage by different materials
- the influence of catalyst surface structure on the electrons / photons emission

Most recent work [19] emphasizes that while the detailed mechanisms by which different mechanochemical phenomena arise are not always well understood, mechanical forces are capable of effecting novel reactivity. Additionally, it strengthens that using force, one can effectively shepherd a chemical reaction down specific reaction pathways, for instance *by selectively lowering the energy of a transition state*. At this point it is of note, that the field of polymer mechanochemistry, has also the potential to change this paradigm by revolutionizing the way chemists think about controlling chemical reactions [19].

In recent years the mechanochemistry field approach has found a renaissance, and different techniques have been applied to activate chemical reaction [20-22] and thereby to lower their activation energy.

#### 4. Conclusions

- i. The  $\alpha_i$  model put forward in this paper attempts to correlate mechanical work performed on a solid with its catalytic activity. This model was worked out on the basis of tribological tests results and was dedicated to tribochemistry.
- ii. The analysis of basic dependences resulted from  $\alpha_i$  model lead to the conclusion that the mechanism of catalysis related to tribological processes can be adapted to heterogeneous catalysis including mechanochemical reactions.
- iii. The reactants molecules energy resulted from ambient temperature of reaction mixture is enhanced near solid surface by additional energy – emitted electrons / photons. Due to the additional energy the reaction can reach a critical rate.

- iv. The energy emitted from surface as pulses ranges 3–5 eV and can reach the value of activation energy ( $E_a$ ) and the triboreaction process starts to proceed or reaches the critical rate.
- v. Based on the discussion concerning the  $\alpha_i$  model, thermionic emission, and the NIRAM approach it is concluded that for both thermochemical heterogeneous reactions and catalyzed heterogeneous processes, the same activation energy ( $E_a$  value) is needed to initiate the reaction process.
- vi. The hypothesis, based on  $\alpha_i$  model is that the mechanical work done on the reaction system is transformed to internal energy increase.
- vii. The internal energy is distributed into a liquid / fluid phase bringing about ambient temperature increase ( $T_a$ ), and a part of introduced energy is accumulated in solid machine elements of tribological systems and, catalyst particles in catalytic processes.
- viii. This accumulated energy is emitted by solid surface to reaction space as electrons / photons. The electron / photon emission is anisotropic one. There is a specific angle  $\gamma$  at which emitted energy is suitable to activate reactant molecules.

In the summary it can be said that the problem of Arrhenius equation adaptation to heterogeneous catalysis as well as tribocatalysis might be solved using  $\alpha_i$  model. Instead of Arrhenius equation in reaction rate description should be used the quotidian of reaction rate constant according to Arrhenius equation and the stream of energy emitted by the surface of catalyst in angle  $\gamma$ . The reaction rate constant described by the above ratio leads to another explanation of the mechanism of catalytic effect than, based on Arrhenius equation, decreasing of the value of activation energy. This effect is due to addition portion of energy emitted by catalysts surface to the reaction space. At this point it should be emphasized that equation (19) describes both catalytic and tribocatalytic reactions. This equation quantitatively characterizes all kinds of energy introduced into the reaction system, including mechanical energy and properties of catalyst, explained by energy emitted from its surface to reaction space.

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### 5. References

- [1] Bond G.C. *Heterogeneous Catalysis: Principles and Applications*. Oxford: Clarendon Press, 1987.

- [2] Kajdas C.K, Kulczycki A. A New Idea of the Influence of Solid Materials on Kinetics of Chemical Reactions. *Materials Science – Poland* 2008, 26, 787 - 796. [http://materialsscience.pwr.wroc.pl/bi/vol26no3/articles/ms\\_2008\\_375.pdf](http://materialsscience.pwr.wroc.pl/bi/vol26no3/articles/ms_2008_375.pdf)
- [3] Kajdas C.K, Kulczycki A, Kurzydłowski K.J, Molina G.J. Activation Energy of Tribochemical and Heterogeneous Catalytic Reactions. *Materials Science-Poland* 2010, 28, 523-533. [http://materialsscience.pwr.wroc.pl/bi/vol28no2/articles/ms\\_15\\_2009-373kajdas.pdf](http://materialsscience.pwr.wroc.pl/bi/vol28no2/articles/ms_15_2009-373kajdas.pdf)
- [4] Dante R.C, Kajdas C.K, Kulczycki A. Theoretical Advances in the Kinetics of Tribochemical Reactions. *Reaction, Kinetics Mechanisms and Catalysis* 2010, 99, 37 – 46.
- [5] Klier K. The Transition State in Heterogeneous Catalysis, *Topics in Catalysis* 2002, 18, 3-4, 141 -156.
- [6] Sato N, Seo M. Chemically Stimulated Exo-emission from a Silver Catalyst. *Nature* 1967; 216(Oct) 361-362. DOI:10.1038/216361a0
- [7] Hrach H. Energy Angular Distribution of Electrons Emitted from MIM Systems. *Thin Solid Films* 1973, 15, 65-69. [http://dx.doi.org/10.1016/0040-6090\(73\)90204-6](http://dx.doi.org/10.1016/0040-6090(73)90204-6)
- [8] Jablonski A, Zemek J. Angular Distribution of Photoemission from Amorphous and Polycrystalline Solids. *Physical Review B*, 1993, 48, 4799-4805. DOI:10.1103/PhysRevB.48.4799
- [9] Kulczycki A. The Correlation Between Results of Different Model Friction Tests in Terms of an Energy Analysis of Friction and Lubrication. *Wear* 1985, 103, 67-75.
- [10] Hebda M, Wachal A. *Trybologia*, Warszawa: Wydawnictwa Naukowo-Techniczne, 1980.
- [11] Hrach R, May J. Electrons Emitted from MIM Structures. *Physica Status Solidi (a)*, 1977, 1, 637-642.
- [12] Gould R.D, Hogarth C.A. Angular Distribution Measurements of Electrons Emitted from Thin Film Au-SiO<sub>x</sub>-Au Diode and Triode Structures. *Physica Status Solidi (a)*, 1977, 41, 439-442. DOI: 10.1002/pssa.2210410212
- [13] Hrach R. Emission of Electrons from MIM Systems: Discussion of Processes in the Cathode. *Czechoslovak Journal of Physics B*, 1973, 23(2), 234-242. <http://link.springer.com/article/10.1007/BF01587248?null>
- [14] Fitting H.-J, Glaefcke H, Wild W, Lang J. Energy and Angular Distribution of Exoelectrons. *Physica Status Solidi (a)*, 1977, 42, K75-K77.
- [15] Baláž P, Choi W.S, Fabian, M, Godocikova E. Mechanochemistry in the Preparation of Advanced Materials. *Acta Montanistica Slovaca* 2006, 11(2), 122-129. <http://actamont.tuke.sk/pdf/2006/n2/5balaz.pdf>
- [16] Hiratsuka K, Kajdas C. Mechanochemistry as a Key to Understand the Mechanisms of Boundary Lubrication, mechanolysis and Gas Evolution during friction. *Proc. IMechE Part J: J. Engineering Tribology*, 2012 (submitted for publication).
- [17] Rodriguez J.G, Lafuente A. A New Advanced Method for Heterogeneous Catalysed Dechlorination of 1,2,3-, 1,2,4-, and 1,3,5 – Trichlorobenzenes in Hydrocarbon Solvent. *Tetrahedron Letters* 2002, 43, 9645 – 9647. <http://144.206.159.178/ft/1010/73973/1269348.pdf>

- [18] Kauzmann W, Eyring H. The Viscous Flow of Large Molecules. *Journal of American Chemical Society* 1940, 62, 3113-3125.
- [19] Wiggins K.M, Brantley N, Bielawski C.W. Polymer Mechanochemistry: Force Enabled Transformations. *American Chemical Society Macro Letters* 2012, 1, 623-626. DOI: 10.1021/mz300167y
- [20] Beyer M.K, Clausen-Schaumann H. Mechanochemistry: the Mechanical Activation of Covalent Bonds. *Chemical Reviews* 2005; 105(8) 2921-2948. DOI:10.1021/cr030697h
- [21] Caruso M.M, Davis D.A, Shen Q, Odom S.A, Sottos N.R, White S.R, Moore J.S. Mechanically-Induced Chemical Changes in Polymeric Materials. *Chemical Reviews* 2009, 109, 5755-5798. DOI: 10.1021/cr9001353
- [22] Kaupp G. Mechanochemistry: the Varied Applications of Mechanical Bond-Breaking, *The Royal Society of Chemistry, CrystEngComm* 2009, 11, 388-403. DOI: 10.1039/b810822f

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