

# Normalization of kinetic equations for thermostimulated processes

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**Abstract** The article introduces a new approach to construction of kinetic equations where the system variable—concentration of reactants—is substituted by relative dimensionless value. It offers the canonical form of kinetic equations and their approximated expressions revealing some general characteristics of thermally actuated processes. Necessity and expediency of building kinetic equations on the basis of relative dimensionless variables have been proved theoretically and also confirmed with original experimental research. Some aspects of experimental investigation of thermally stimulated exoelectron emission phenomenon also are described.

**Keywords** Kinetic analysis · Kinetics order · Frequency factor · Reaction rate · Exoelectron emission

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## Abbreviations

EE Exoelectron emission  
TSEE Thermally stimulated exoelectron emission  
TSL Thermally stimulated luminescence  
TE Thermionic emission

## Introduction

The development history of kinetics as discipline consists of several branches, what did not promote formation of careful generalizing concepts. In chemical kinetics some properties of non-equilibrium processes are well described by Arrhenius empiric equation, where dominated such parameters as reactants concentration and characteristic kinetic constants: activation energy, kinetics order and frequency factor (triplet), which should unequivocally describe system properties of observable object. At construction of generalizing theories for interpretation of observable processes it is important to carefully differentiate intensive and extensive properties of under investigation system. While the activation energy is quite comprehensible intensive physical property (i.e. constant not depending on amount of elements forming system) for non first order reactions the reaction rate constant allegedly depends on initial quantity of substance. So this constant fall within extensive class of properties, what looks doubtful (even its dimension defined differently for various kinetics order, this is mentioned even in textbooks about chemistry on this we abstain from concrete references besides corresponding information given also in any encyclopedia). For removing of such uncertainty and revealing of common characteristics we offer new approach to construction of kinetic equations containing certain generalization.

Exploration of considered systems (taking into account their energy-wise binding) is more effective by probing of their properties with variation of temperature, so we shall consider so-called thermostimulated processes where alterations controlled simultaneously by time and variation of temperature.

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### Substitution of system variable

For simplicity of our statement we shall consider the prevalent form of differential kinetic equation most frequently used in the practical purposes

$$-\frac{dn}{dt} = S \cdot n^\gamma \exp\left(-\frac{E}{kT}\right) \quad (1)$$

where  $t$  is the time,  $T$ -absolute temperature,  $k$ -Boltzmann's constant,  $\gamma$ -kinetics order,  $E$ -activation energy,  $S$ -frequency factor. Under  $n$  concentration of some reagent usually is meant. Our doubts are just connected to its definition. Kinetic processes inherently are supervised by energy parameters and configuration (combinatorics, symmetry) of system formation (or disintegration). The physical size or distance here is not regulating factor, on this  $n$  cannot express absolute concentration. From our point of view  $n$  should reflect only relative dimensionless numbers (the amount or concentration, already it is not important). Such inoffensive replacement practically cause nothing if  $\gamma = 1$  however in other cases changes are essential. The matter is that according to the usual interpretation of Eq. 1 the absolute concentration of elements making system should qualitatively influence process (compare Eqs. 2 and 3).

$$-\frac{dn}{dt} = \frac{S \cdot \exp\left(-\frac{E}{kT}\right)}{\left[n_0^{1-\gamma} + (\gamma-1)S \int_0^t \exp\left(-\frac{E}{kT}\right) dt\right]^{\frac{\gamma}{\gamma-1}}} \quad (2)$$

$$-\frac{dn}{dt} = \frac{S \cdot \exp\left(-\frac{E}{kT}\right)}{\left[1 + (\gamma-1)S \int_0^t \exp\left(-\frac{E}{kT}\right) dt\right]^{\frac{\gamma}{\gamma-1}}} \quad (3)$$

Certainly for example increase in concentration should intensify process however it should remain within the limits of superposition principle and don't cause anomalous distortions. Below we shall return to the clarification of changes following to suggested substitution but before we shall consider some general characteristics of processes obeyed the Eq. 1 and proceeding in a linear thermostimulation mode. Let

$$T = T_0 + \mu t \text{ and } n = \frac{N}{N_0} \quad (4)$$

where  $N$  and  $N_0$  are the absolute numbers (or concentration it doesn't matter) at the current moment and at any conditionally initial moment respectively (memorylessness according to Markov chain),  $T_0$  temperature at conditionally initial moment,  $\mu$ -heating rate.

Taking into account the condition of an extremum from the Eq. 1 follows:

$$\frac{E\mu \exp\left(-\frac{E}{kT_m}\right)}{kST_m^2} = \gamma + (1-\gamma) \int_0^\infty \frac{\exp\left(-\frac{1}{y}\right)}{\left(y + \frac{kT_m}{E}\right)^2} dy \quad (5)$$

valid for any  $\gamma$  including one ( $m$ -indexes point magnitudes at maximum). The parametrical integral [1, 2] included in the right side of Eq. 5 always is less than one and in cases interesting to us ( $10kT < E$ ) is very close to it. In this area with accuracy better than 0.2% it can be replaced with expression

$$\int_0^\infty \frac{\exp\left(-\frac{1}{y}\right)}{\left(y + \frac{kT}{E}\right)^2} dy = G\left(\frac{kT}{E}\right) \approx \frac{1}{1 + 2\frac{kT}{E} - \exp\left(-\frac{E}{2\sqrt{kT}}\right)} \quad (6a)$$

or

$$G\left(\frac{kT}{E}\right) = G \approx 1 - 2\frac{kT}{E} + \exp\left(-\sqrt{\frac{E}{kT}}\right) \approx 1 \quad (6b)$$

It means that for the moderate thermostimulation regimes sufficiently well obeyed the condition:

$$\frac{E\mu_m \exp\left(-\frac{E}{kT_m}\right)}{kST_m^2} \approx 1 + (\gamma-1) \left[ 2\frac{kT_m}{E} - \exp\left(-\sqrt{\frac{E}{kT_m}}\right) \right] \quad (7)$$

For  $\gamma = 1$  the Eq. 7 is exact, for other possible values of  $\gamma$  criterion of an extremum varies insignificantly because the right part of (7) always is close to 1. This is a very important property of considered regularity because at presence of processes with transitive values of  $\gamma$  experimental results will appear not as stepwise alteration or arising of several peaks, but as one peak with respective alteration of its symmetry. This term has been involved [3] in kinetics for estimation of responsible process order. The vertical through a maximum, which dividing peak on two parts, accepted as an axis of symmetry (Fig. 1).

In case of first order at the moment of maximum passage the majority of a resource is already spent, on this the right

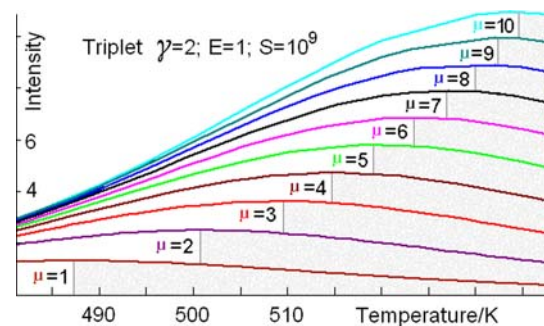


Fig. 1 Simulated heating rate variation

slope is more abrupt. At  $\gamma > 1$  the peak is more symmetric (Fig. 2). As against of  $E$  and  $S$  the temperature of a maximum is not the system constant, it depends on a heating rate (Fig. 1), however practically this dependence is not so crucial. While the order is responsible for a glow curve shape [4], the peak width and its place on a temperature scale adjusted by activation energy and frequency factor together (Fig. 2).

The reasons of such dependence can be tracked by the approximated representation of canonical equation. For illustration of process we substitute constant  $S$  by  $T_m$ , which, as marked above, weakly depends on heating rate and at the fixed values of  $E$  indirectly, but completely corresponds to certain  $S$  (Application of  $T_m$  as iteration parameter also facilitates process of calculation and simulation). So for  $\gamma \neq 1$

$$\frac{dn}{dt} = \frac{\frac{E\mu}{kT_m^2} \exp\left(\frac{E}{kT_m} - \frac{E}{kT}\right)}{\gamma + (1-\gamma)G_m} \left[ 1 + \frac{T_m^2}{T^2} \frac{(\gamma-1)G}{(1-\gamma)G_m} \exp\left(\frac{E}{kT_m} - \frac{E}{kT}\right) \right]^{\frac{\gamma}{\gamma-1}} \quad (8)$$

and for  $\gamma = 1$

$$\frac{dn}{dt} = \frac{\frac{E\mu}{kT_m^2} \exp\left(\frac{E}{kT_m} - \frac{E}{kT}\right)}{\exp\left[\frac{T_m^2}{T^2} G \exp\left(\frac{E}{kT_m} - \frac{E}{kT}\right)\right]} \quad (9)$$

$G_m$  --- represents particular value of function  $G$  (defined above by Eq. 6a, b) at  $T = T_m$ .

At  $T < T_m$  in all equations prevail same exponential factor (exponent in numerator), this circumstance justifies one of the methods for calculation of activation energy by an "initial rise" [5]. After passage of a maximum ( $T > T_m$ ) for  $\gamma = 1$  linked up powerful double exponential factor and process sharply falls. At  $\gamma < 1$  decay is even more bluff as the second summand of brackets in denominator of the Eq. 8 inverts polarity and after  $T_m$  sharply achieve 1 in consequence of that process pass away. In other cases the negative moderate degree of this positive sum provides

relatively slow decay. And at last from (8) and (9) it is possible to determine relative height of peaks:

$$\left(\frac{dn}{dt}\right)_m = \frac{E\mu}{kT_m^2} f_\gamma = \frac{E\mu}{kT_m^2} \frac{\gamma^{\frac{\gamma}{1-\gamma}}}{[\gamma + (1-\gamma)G_m]^{\frac{\gamma}{1-\gamma}}} \quad \forall \gamma \neq 1 \quad (10)$$

$$\left(\frac{dn}{dt}\right)_m = \frac{E\mu}{kT_m^2} \exp[-G_m] \quad \forall \gamma = 1 \quad (11)$$

In Table 1 factor containing  $\gamma$  was calculated for most actual value of a ratio  $E/kT_m = 25$  and shows that peaks with low order can be expressed more brightly, what is obvious as the area under peak (integral quantity) should precisely correspond to full initial number and it is usual that observance of this condition demands increase in height at tighten of a peak.

Now for comparison we should reveal similar formulas adequate to Eq. 2 written for accepted earlier concentration

$$\frac{E\mu \exp\left(\frac{E}{kT_m}\right)}{kST_m^2} = \frac{\gamma + (1-\gamma)G\left(\frac{kT}{E}\right)}{n_o^{1-\gamma}} \quad (12)$$

As against of the Eq. 7 in the right side of (12) presented denominator containing the initial concentration in power  $(1-\gamma)$ , what means significant dependence of peak arrangement (on a temperature scale) from magnitude of initial concentration. The formula (12) mathematically most brightly expresses that essential distinction which corresponds to substitution of absolute concentration by relative ( $n_o \gg 1$  in contrast to  $n_o = 1$  in Eq. 12). If in objective reality kinetics really would be controlled by absolute concentration the change of initial concentration would be lead to such rearrangement of peaks on a temperature scale as it is shown on Fig. 3.

Except for it such dependence would allow researchers to determine precisely absolute concentration by the numerical analysis (only proportional values are usually measured in real physical experiments). Initially just with this purpose we have carried out the experimental investigation described below, however in fact the variation of initial concentrations does not result neither displacement of peaks on a temperature scale nor disproportional change of peaks height what confirms our assumption, that the kinetic equations should be constructed only for relative alterations. One more significant condition confirming our assumption is necessity of kinetic equation balancing at  $\gamma \neq 1$  which demand to include in  $S$  without any logic

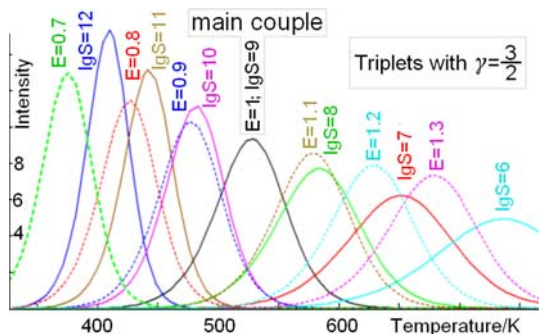
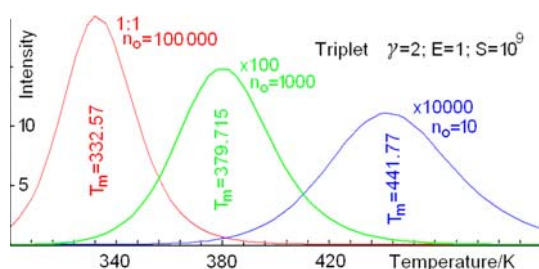


Fig. 2 Simulated variation of  $E$  and  $S$ . Above each peak specified only that parameter which is changed in the main couple

Table 1 Approximated numerical values of  $\gamma$  containing factors— $f_\gamma$  in (10)

$\gamma$	0.5	1	1.5	2	2.5	3
$f_\gamma$	0.5	0.395	0.257	0.203	0.165	0.137



**Fig. 3** Variation of initial concentration. Above each peak the initial concentration and multiplication factor involved for visualization of figure is specified

substantiation certain components counterpoising it to dimension of concentration in  $(1-\gamma)$  power.

Investigation of kinetics in chemical reactions is complicated by technical awkwardness of direct monitoring of reactants quantity. Situation is another at observation of such phenomena as Thermally Stimulated Luminescence (TSL) and/or Thermally Stimulated Exoelectron Emission (TSEE) where it is possible high-sensitive direct electronic measurements with high-precision. Besides processes with non first order kinetics mainly observed when solid surface appears as one of reagent of elementary interaction (catalysis).

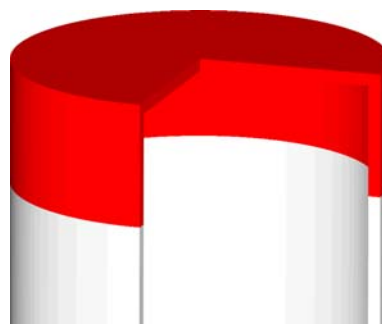
### Experiment, hardware and technology

Experimentally was investigated TSEE from X-ray irradiated Copper. Experimental results were carried out in the following conditions:

The vacuum  $10^{-5}$  Pa was achieved by mercury diffusion pump, preexperimental treatments comprise heating (about 700 K) of all vacuum chamber (stainless steel) and liquid nitrogen traps. Sample holder also heated and his temperature always (except of intentional exclusions) was higher then the other parts of installation. The substrate (oxygen less technical Copper *M0*) had form of hollow cylinder (Fig. 4), in which was placed chromo nickel strip electrical heater.

After treatment (up to 1,000 K) the substrate was cooled down to room temperature in a natural way. For the further cooling before an excitation the inner hollow of substrate filled up by liquid nitrogen. The design of the vacuum chamber allowed moving a substrate under various windows (Detector-Secondary Electron Multiplier-SEM, roentgen tube, or optical window).

The X-ray radiation was used as an EE exciter (mainly 50 kV, 12 mA, 6 min. Dose about  $10^4 R$ ). The emission current was measured by common way amplification of a SEM signal and through the digital converter passed to the target storage device.



**Fig. 4** Substrate. The hollow copper cylinder (*top*) connected with the stainless steel tube by vacuum diffusion welding

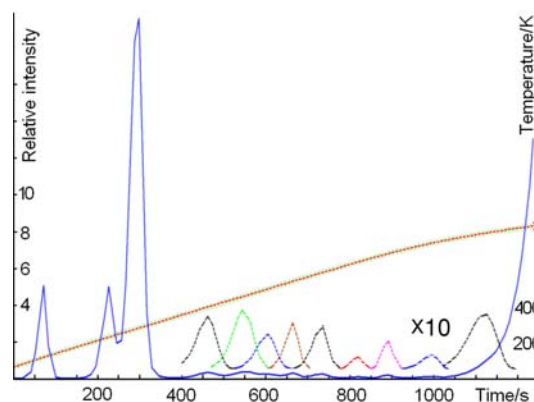
Temperature of the substrate was measured by caulked in it chromo nickel thermocouple heat sensor of digital voltmeter which transferred measured data to the same multichannel recorder. Changes of residual gases pressure in the measuring chamber also was fixed similarly. Regularly was conducted calibration and monitoring of the full measuring path.

Maintained two so-called blank cycles without sample and, or excitation, in which all other conditions are kept.

After an irradiation the substrate was heated up at constant power of the heater, or with the special heating rate gradually augment device (dotted curve on Fig. 5).

During the heating through every 10 s the target device fixed average value of an emission current and temperature of substrate that makes up so-called TSEE spectrum (blue continuous curve on Fig. 5).

In a range 800–1,000 K was measured well known thermionic (TE) emission what allowed in addition to calibrate measuring chain and to check up work function of the Copper substrate at initial low temperature stage of its TE.



**Fig. 5** TSEE Glow curve of annealed copper substrate. Continuous line—experimental data; dotted line—temperature course; dashed line—computer deciphering of overlapped processes (multiplied for better visualization)



The key factor in the physical phenomena under investigation is the temperature. Usually measurement of temperature seems to be simple, but in discussed experiments required especial accuracy. In our conditions the temperature was measured in one local site of a substrate. Despite of good translucency of copper, really the temperature is somehow distributed around the sample. Temperature distribution (temperature field [6]) is influenced by such factors as geometry of a substrate and a heater, power of a heater, thermal sink, etc. On the other hand the notion of temperature implies in itself some averaging, on this for the kinetic analysis of the received results we used some averaging by mathematical approximation revealed as least square fit of experimental data of temperature course in whole interval.

## Results and discussion

After all accessible precautions for maintenance of measurements accuracy we have obtained the results on the basis of which became possible sufficiently authentic numerical processing of experimental data.

We are not going to discuss experimental results indicating interrelation between catalytic properties of copper and its exoemissive activity, for substantiation of our proposition it is quite enough kinetic analysis of some part of obtained TSEE spectra.

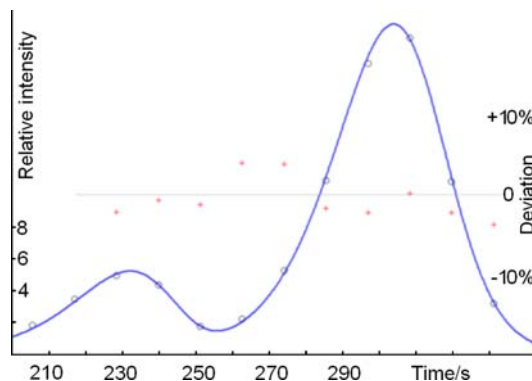
Well-reproducible TSEE spectrum of a copper substrate is shown on Fig. 5. On an ordinates axis plotted relative intensity because in real experiments can be measured signal only proportionate to that velocity of process which is analytically expressed in the above-stated kinetic equations.

Some peaks (including most strongly expressed one near to 0 °C) have fractional order of kinetics ( $4/3$ ) as it was revealed by quantitative analysis (Fig. 6).

With the purpose to investigate the dependence of TSEE response on an irradiation doze we have carried out a cycle of measurements in which the applied irradiation doze was changed for three orders. It is obvious that each case caused corresponding changes of integral (identical with initial) amount of exoactive reagents. This was revealed in appropriate changes of peaks height, but for all that there were no temperature shifts of the maximum or anomalous change of peaks height. Arrangement of peaks also remained stable at alterations of initial quantities by chemical inhibition of exoactive centers.

So we have two rigorous experimental facts:

- 1 Kinetics order of observable process differs from one;
- 2 Variation of initial concentration is not accompanied by displacement of this emissive peak on the temperature scale.



**Fig. 6** Experimental and simulated peaks. Red cross + points indicate relative distinction between direct measurement (plotted as black rings) and simulation—continuous blue curve

Jointly these two results actually confirm our assumption, i.e. really absolute concentration of reagents cannot play the role of a limiting variable for the description of the discussed kinetic process.

We have found out the similar regularity investigating TSEE spectra of technical stainless steel and gold plates (99.9%).

We consider this result as experimental confirmation of the above mentioned assumptions.

There are various ways for deciphering of kinetic parameters from experimental data [7]. Many of them have lost an importance with the advent of computer means of modeling. Each of the known methods has its own advantages and deficiency. In not isothermal experiments frequently used variation of heating rate. At processing of measuring results we usually used computer modeling with the data obtained within one experiment cycle however for the greater authenticity of results we rechecked everything with different heating rates. By computer modeling not only numerical values of triplets were varied, but also probable mixing of some physical processes with nearby kinetic parameters also was examined. However the best coincidence between experimental data and computer model was obtained with the fractional kinetics order. On the basis of such deepened analysis we were convinced, that the conclusion mentioned above as main experimental fact is quite authentic.

So we consider that the offered approach to construction of kinetic equations with relative dimensionless system variables is proved theoretically and also confirmed by the results of some special experimental researches. However there are numerous categories of physical and chemical phenomena where additional examination of suggested replacement would be possible. We do not have technical means to carry out such investigation. We hope that after these publication researchers of other branches will pay

attention to these aspects and accordingly confirm or disprove our statements.

It seems very interesting that common normalized equation can describe processes with transitive kinetics order. The shape of such simulations would not so appreciably differ from usual curves. Maybe it was just for this reason that such occurrences remained unnoticed.

One more important branch of kinetics is investigation of crystal growth, phase transitions, and processes of crystalline systems disintegration. The degree of conversion [7, 8] is used in this area as a system variable that certainly is the relative value, what automatically satisfying the principle which we have discussed in the present paper.

Improvement of kinetic analysis for physical and chemical processes implies significant potential for further development of so actual Nanoscience and Soft Condensed Matter as well, because in formations with minimum quantity of atoms (molecules) all refinements of formation or disintegration of energetically self-bonded systems should be brightly expressed. In this respect the method of TSEE possesses significant resources.

## Conclusions

The offered normalization of kinetic equations for thermostimulated processes specifies the general approach to construction of formal kinetics equations because in accordance with it they can describe only relative alterations. The particular result of the suggested substitution of system variables emerged in validation of reaction rate constants for non first order kinetic processes. The proper

quantity of the frequency factor, according to our statement, always should have the same dimension irrespective of the reaction order (obtained earlier numerical results should be corrected accordingly). Only after such definition full set of kinetic parameters (triplets) unequivocally describing the certain physical object can be constructed. It makes possible more correct comparison of different investigation results and formation of kinetic characteristics complement data bank for various physical objects what can promote efficiency of kinetic analysis for elaboration or perfection of generalizing laws.

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