ON THE COMPENSATION EFFECT

Ravindra K. Agrawal

CHEMICAL TECHNOLOGY DIVISION, ARGONNE NATIONAL LABORATORY, 9700 SOUTH CASS AVENUE, ARGONNE, ILLINOIS 60439, U.S.A.

Arrhenius equation is popularly used to relate the change in the rate constant with temperature. The linearized form of Arrhenius equation has often been used to establish a relation between ln A and E for a series of related reactions. Occurrence of such a compensating behavior between ln A and E has been widely reported in the literature. The validity of the compensation effect has been heatedly debated. Compensation effect can arise from computational artifact or can arise from various chemical factors. This depends entirely on the data set used to establish the compensation behavior. This article stresses the importance of statistical analysis and the use of simple Arrhenius plots to draw conclusions regarding the occurrence of compensation effect. With the help of a few examples, some checkpoints to draw conclusions regarding the occurrence of true or false compensation effect are suggested.

The Arrhenius equation is widely accepted in homogeneous reaction kinetics as a useful tool for predicting a change in the reaction rate constant as a function of temperature. The Arrhenius equation is expressed as:

$$k = A \exp(-E/RT) \tag{1}$$

where k is the reaction rate constant, A is the frequency factor, E is the activation energy, and T is the absolute reaction temperature. In a typical homogeneous gas phase reaction, E represents the amount of energy in excess of the average energy level which the reactants must have in order for the reaction to proceed. A is related to the frequency of vibration of these molecules. In view of the tremendous success of the Arrhenius equation in the gas phase reaction kinetics its usage has crept into the field of solid state reaction kinetics. For solid state reactions there is no definition for a "mole of solid," hence, in such a base both A and E have little physical significance. Though the true energy barrier may be related to the calculated value of E in the solid state reaction kinetics, its true relationship will not be clear until a definition or the significance for a "mole of solid" is established.

Hence, in order to avoid confusion and to distinguish the difference between gas phase and solid state reactions, A should be called the pre-exponential factor and E called the apparent activation energy.

Sometimes $\log A$ and E exhibit a linear relationship for a series of related reactions. This relation is then referred to as the "compensation effect" or "isokinetic effect" or the θ rule. The linear relation may be obtained from the Arrhenius equation and is expressed as:

$$\ln A = \ln k_{iso} + \frac{E}{RT_{iso}} \qquad (2)$$

where k_{iso} is the isokinetic rate constant and T_{iso} is the isokinetic temperature. Evidence for such a compensating behavior was first reported in catalysis studies [1]. Such an occurrence of compensation effect has now been reported in numerous other fields [2–7]. Recently compensation effect has been reported in the pyrolysis of pitch [8] and cellulosic materials [9–10]. Since pyrolysis mechanism of cellulosic materials is complex [11–17], it is of interest to investigate and see if compensation effect provides further insight into the reaction mechanism.

Several theories that predict such linear compensation behavior have been reported [3, 18–24]. These theories suggest that the occurrence of compensation effect is probably due to enthalpy-entropy relationship; tunneling effect; relation between entropy of transition and change in the energy levels of the transition state; simultaneous occurrence of reactions on surface centers involving different activation energies; and, due to existence of interrelated kinetic behavior within a group of rate processes [2–4, 20, 24]. The isokinetic temperature has been suggested to characterize the temperature of onset of reaction; to signify a temperature at which relative reaction rates within the group of related reactions undergo an inversion; or to represent the temperature at which rate constants of all reactions of the series have the same value [2, 3, 5, 20].

The existence of compensation behavior in heterogeneous reactions has been debated. Several authors have suggested that compensation effect arises due to computational artifact from experimental errors in rate constants from which the Arrhenius parameters are calculated [25–29]. Since the two Arrhenius parameters are derived from the same kinetic data, the relation between these two dependent variables is questionable. In the literature reviewed the occurrence of compensation effect has been most cited in nonisothermal studies or from Arrhenius parameters derived from kinetic data in narrow temperature range. Inaccurate temperature measurement and occurrence of large temperature gradients within the sample [30–32] tend to support the theory that compensation behavior arises from computational artifacts from experimental errors in rate coefficients. Some investigators have, in fact, suggested that Arrhenius equation is perhaps unsuitable

for such thermoanalytical studies [33–35]. Some others have detailed statistical procedures to correctly treat the data for detecting the linear compensation behavior [3, 27, 28, 36–39]. Unfortunately these procedures have been rarely followed to draw conclusions regarding compensation effect.

Illustrating examples of true and false occurrence of compensation effect, this paper will attempt to highlight the importance of statistical analysis and the use of simple Arrhenius plots to draw conclusions regarding the occurrence of compensation behavior within the given data set. As suggested by Exner [27, 28, 36] it is emphasized that plots of $\ln k$ vs. inverse temperature rather than $\ln A$ vs. E should be examined if the investigator wishes to detect the occurrence of compensation effect. Establishing the occurrence of true compensation effect is necessary before any speculation of the reaction mechanism is made. A few checkpoints to draw conclusions regarding the occurrence of true or false compensation effect is also suggested.

Results and discussion

Numerous occurrences of compensation behavior have been reported in the literature by correlating $\ln A$ with E. Equation (2) suggests that a plot of $\ln A$ vs. E is a straight line with a slope of $1/RT_{iso}$ and an intercept of $\ln k_{iso}$ (see Fig. 1). Unfortunately, the error of estimates of the slopes and intercept is rarely reported. As seen later, the linear relation between $\ln A$ and E does not imply the occurrence of true compensation effect. An alternate and more reliable method to detect
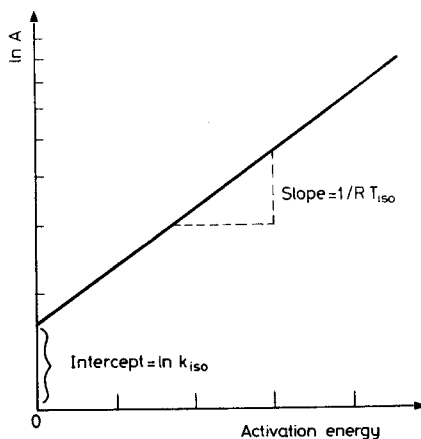

Fig. 1 A plot generally accepted to establish the existence of compensation effect

compensation behavior is shown in Fig. 2. Figure 2 is an Arrhenius plot of ln k vs. inverse temperature. It can be seen from Fig. 2 that occurrence of true compensation effect suggests the existence of some characteristic temperature, T_{iso}, at which all rates are equal. The arrows in Fig. 2, show that an increase in E causes an increase in ln A and a decrease in E results in a lower value of ln A. Hence
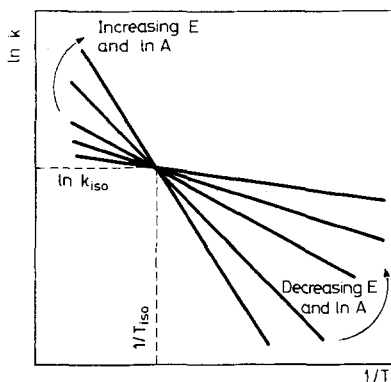

Fig. 2 Arrhenius plot displaying a single point of concurrence. Such a plot generally indicates the occurrence of true compensation effect

compensation effect may simply be an odd effect of the data treatment. If the isokinetic temperature is the average of the temperature range covered by the measurements, or if T_{iso} is an unrealistic large value (Fig. 3a), then the compensation behavior may simply be an artifact due to nonnegligible experimental and computational errors. If Arrhenius plots display no such concurrence at a single point (Fig. 3, a to c), then the reacting system exhibits no compensation effect. If a series of reaction displays Fig. 1, but fails to display a single point of concurrence (Fig. 2) and instead show trends as suggested in Fig. 3, then the system exhibits a false compensation effect. Such a trend may occur when an investigator compares ln A and E varying the "order of reaction" n; or when nonnegligible experimental errors such as large temperature gradient within the sample; or errors due to various mathematical approximation of rate equation. All these factors result in an inaccurate estimate of ln K_{iso}. For establishing true kinetic compensation effect it is suggested that the condition ln k_{iso} or log k_{iso} $\neq$ 0, should be satisfied within the experimental and computational errors.

Perhaps one of the best known occurrences of compensation effect has been reported for the decomposition of formic acid on magnesite that had been previously heated to the temperature specified in the temperature range of 370 to 800° (Fig. 4 [4, 40]). The Arrhenius plot clearly indicates a concurrence. Such a concurrence must be detected for a linear compensation effect to be due to chemical
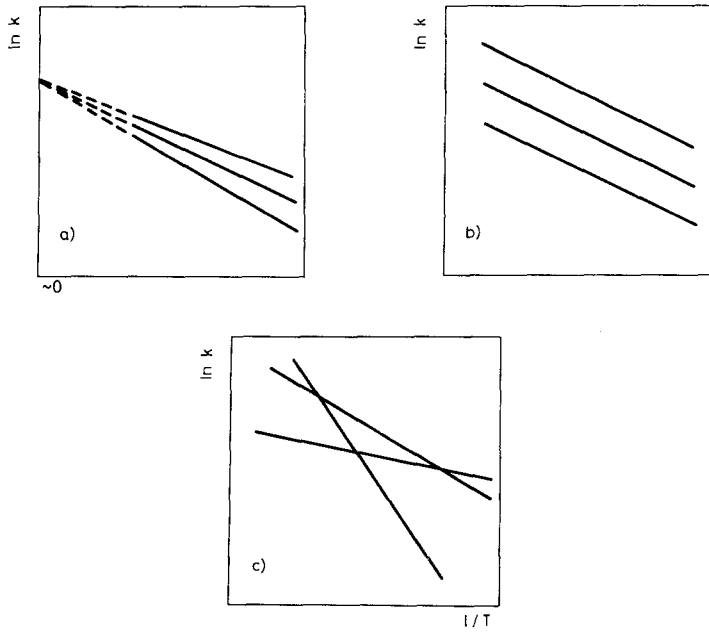
Fig. 3 Arrhenius plots representing no compensation effect. A series of related reactions indicating trends of Figures 1 and 3 exhibit the occurrence of "false compensation effect"
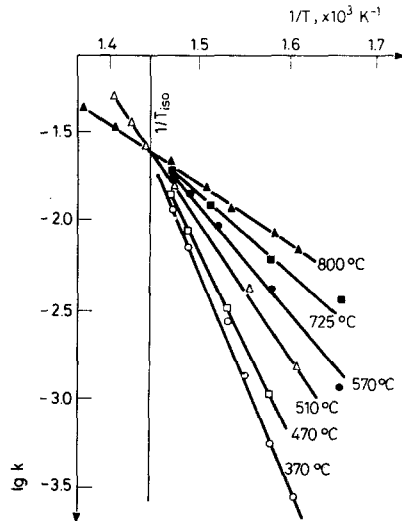

Fig. 4 Arrhenius plots for decomposition of formic acid over magnesite ($MgCO_3$—MgO) [4, 40]

effects rather than due to propagation of experimental errors. The plot also suggests the existence of a temperature (T_{iso}) at which all related reactions proceed at the same rate. Above T_{iso} the faster reaction has higher activation energy and below T_{iso} the faster reaction has the lower activation energy. The plot also aids in speculating the change in reaction pattern if magnesite was preheated to temperatures other than those used in the study.

Recently Fairbridge et al. [9] and Chornet and Roy [10] have reported the existence of compensation effect in the pyrolysis of cellulosic materials. Chornet and Roy [10] made a detailed statistical analysis of nonisothermal data reported in the literature using pseudo first-order reaction treatment. Table 1 summarizes the data used by Chornet and Roy [10] to draw conclusions regarding the existence of compensation effect in pyrolysis of cellulosic materials. Their plot (Fig. 5) suggests the existence of compensation effect. Fitting the data as suggested by Eq. (2) results in the following expression:

$$\ln A = -1.0484 \ (\pm 1.8287) + 0.8106 \ (\pm 0.0530) \ E \qquad (3)$$

Table 1 Data used by Chornet and Roy [10] in establishing the compensation effect for pyrolysis of cellulosic materials

| Material	T range, °C	E, kcal/mol	A, min^{-1}	Symbols in Figs 5 and 6
Wood	280–325	23.0	1.9×10^7	a
Wood	325–350	54.0	3.9×10^{18}	b
Lignin	280–344	21.0	9.9×10^5	c
Lignin	344–435	9.0	5.6×10	d
Lignin	280–300	34.8	4.3×10^{12}	e
Lignin	360–500	33.8	7.6×10^9	f
Cellulose	300–420	54.3	1.8×10^{18}	g
Cellulose	280–360	39.8	2.4×10^{13}	h
Cellulose	250–1000	33.4	4.0×10^{11}	i
Cellulose	230–400	30.0	4.2×10^9	j
Cellulose	275–360	56.0	2.4×10^{19}	k
Hemicellulose	240–350	29.6	8.7×10^{10}	l
Hemicellulose	220–280	28.5	2.9×10^{10}	m
α-cellulose	240–308	35.0	3.9×10^{11}	n
α-cellulose	308–360	56.0	2.4×10^{19}	k
α-cellulose	230–560	13.3	1.1×10^4	o
α-cellulose	240–580	11.5	1.1×10^4	p
α-cellulose	280–700	19.0	1.0×10^6	q
Filter paper	160–380	39.1	1.4×10^{13}	r
Filter paper	280–400	10.8	1.1×10^4	s
Peat	100–800	26.0	1.1×10^{10}	t
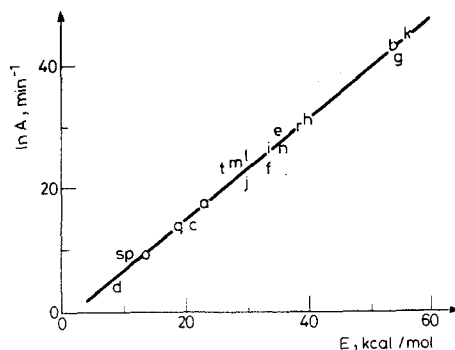
Fig. 5 A plot indicating an occurrence of "false compensation effect" in pyrolysis of cellulosic materials. For a key to the symbols see Table 1

with a correlation coefficient of 0.982. The figures in brackets represent error limits at 95% confidence for the reported parameters. Chornet and Roy [10] claim that these results imply the existence of compensation behavior as $\sigma_1/RT_{iso} < 0.03 \ E$. Earlier Galwey [3] had suggested that there is evidence for the existence of a compensation effect when $\sigma_1/RT_{iso} < 0. \ 1 \ E$. Chornet and Roy [10] suggest that the existence of compensation effect might be due to an exponential energy site distribution. As discussed earlier, if true compensation effect exists, then the Arrhenius plot should indicate a common point of concurrence. However, such a plot (Fig. 6) indicates no such point of concurrence. An examination of Eq. (3) suggests that $\ln k_{iso}$ cannot be determined within the accuracy of the data. In this case, since $\ln k_{iso}$ is not significantly different from zero, the linear relation between $\ln A$ and E is due to false compensation effect. The cause for false compensation may be due to nonnegligible experimental errors such as inaccurate temperature measurement; or due to the existence of temperature gradient within the sample; or due to errors resulting from various mathematical approximations; but certainly not due to any chemical factors. Hence, the relation in this case has no physical significance.

In their studies on decomposition of $CaCO_3$, Zsakó and Arz [5] reported an occurrence of compensation effect. In their analysis they used values of A and E estimated by using the following orders of reaction: 0, 1/3, 2/3, and 1. Since manipulation of order of reaction has no physical significance, for this study, data obtained for the first order system is used to detect the existence of compensation effect. Table 2 lists the data reviewed by Zsakó and Arz [5] for first order systems only. Linear statistical analysis between $\log A$ and E suggests the following relationship:

$$\log A = -1.1950 \ (\pm 2.1950) + 0.1922 \ (\pm 0.0104) \ E \qquad (4)$$
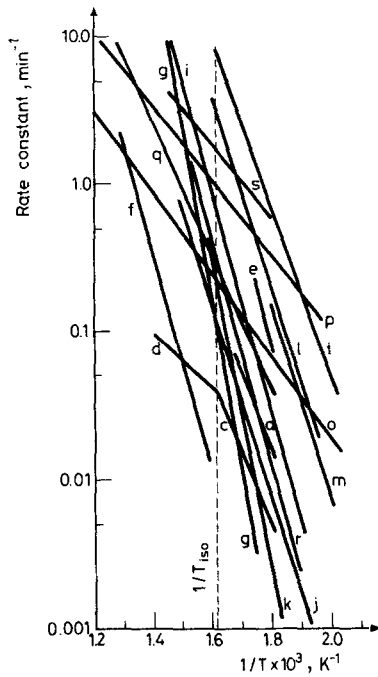
Fig. 6 Arrhenius plot showing no single point of concurrence for pyrolysis of cellulosic materials. Line k overlaps with lines b and h (not shown), and line r overlaps with n (not shown). Symbols are identical to those in Figure 5 and Table 1
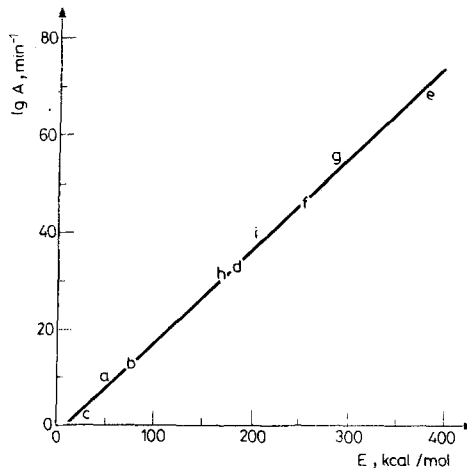

Fig. 7 A plot indicating an occurrence of "false compensation effect" in the thermal decomposition of $CaCO_3$. For a key to the symbols see Table 2

Table 2 Data used by Zsakó and Arz [5] in establishing the compensation effect for thermal decomposition of $CaCO_3$ ("order of reaction" = 1)

Atmosphere	p, mm Hg	q, °C/min	E, kcal/mol	$\log A$, min^{-1}	Symbols in Figs 7 and 8
Air	760	3	58.7	10.0	a
Air	760	10	75.5	12.9	b
Air	760	10	26.3	2.2	c
Air	760	10	177.3	33.5	d
CO_2	200	0.83	377.5	68.9	e
CO_2	75	1.22	251.7	47.3	f
CO_2	43	0.43	289.4	55.7	g
CO_2	23.5	2	169.3	32.2	h
CO_2	23.5	0.93	201.3	39.2	i

with a correlation coefficient of 0.998. The figures in brackets represent error limits 95% confidence of the estimated values. Figure 7 is a plot of $\log A$ vs. E and shows an excellent correlation as suggested by Eq. (4). However, the Arrhenius plot (Fig. 8) shows no single point of concurrence. Also $\log k_{iso}$ is not significantly different from zero within 95% confidence limits. Hence, this relation is due to an artifact of computational and experimental errors and not due to any chemical factors. This
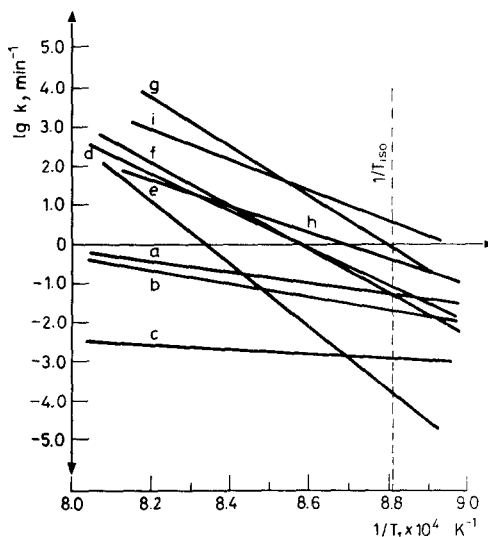

Fig. 8 Arrhenius plot showing no single point of concurrence for the thermal decomposition of $CaCO_3$. Symbols are identical to those in Figure 7 and Table 2

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data set does not imply the existence of true compensation effect. Inputting the results from various orders of reaction does not change this conclusion.

Alvarez et al. [4] have reported the existence of compensation effect for the decomposition of $(CH_3NH_3)_2 \cdot MnCl_4$. Table 3 lists the parameters used by

Table 3 Data used by Alvarez et al. [41] in establishing the compensation effect for the decomposition of $(CH_3NH_3)_2 \cdot MnCl_4$

Method	"Order of Reaction"	E, kcal/mol	A, min^{-1}	Symbols in Fig. 9
Horowitz–Metzger	0.45	18.19	3.25×10^7	a
Coats–Redfern	0.45	15.05	1.04×10^6	b
Satava	—	30	1.66×10^{12}	c
Max. point	0.45	18.93	2.6×10^8	d
Freeman–Carroll	4.15	30.20	4.74×10^{13}	e
Ratio	0.61	20.77	4.60×10^8	f

Alvarez [4] to report the occurrence of compensation effect. The correlation between ln A and E was made using the results obtained from various theoretical schemes proposed by numerous investigators. Equation (5) represents the results from linear least square analysis between ln A and E

$$\ln A = -1.3226 \, (\pm 5.6325) + 1.0369 \, (\pm 0.2455) \, E \qquad (5)$$

with a correlation coefficient of 0.986. The figures in the brackets represent error limits for the parameters at 95% confidence. Based on a plot of ln A vs. E (Fig. 9),
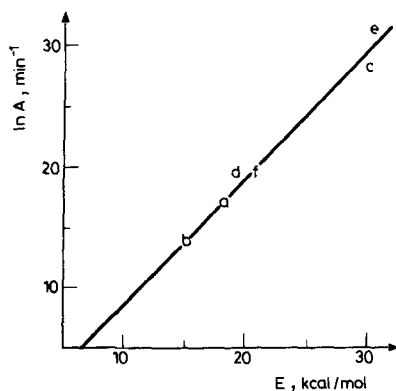

Fig. 9 A plot indicating an occurrence of "false compensation effect" in the decomposition of $(CH_3NH_3)_2 \cdot MnCl_4$. For a key to the symbols see Table 3

Alvarez et al. [41] claim the existence of compensation effect in their system. However, in Fig. 10, a plot of ln k vs. inverse temperature show no single point of concurrence. Also, ln k_{iso} is not significantly different from zero within 95% confidence limits. In other word, ln k_{iso} cannot be determined within reasonable error limits. The relation between ln A and E is due to a negligible value of ln k_{iso}. Figure 10 also demonstrates that comparison of ln A vs. E for parameters derived from different mathematical approximation has no physical significance. The relation in Fig. 9 is due to computational artifact resulting from various mathematical approximations.
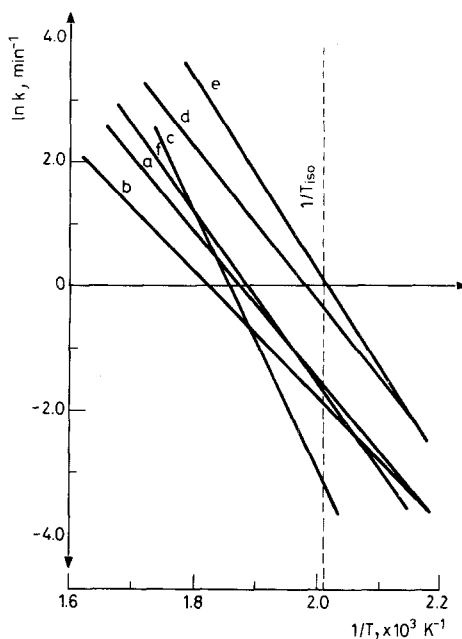

Fig. 10 Arrhenius plot showing no single point of concurrence for the decomposition of $(CH_3NH_3)_2 \cdot MnCl_4$. Symbols are identical to those in Figure 9 and Table 3

An examination of the literature reviewed showed other occurrences of such false compensation effect. Since there is an enormous amount of literature with little data reported, it is almost impossible to trace all such occurrences of false compensation effect. It is recommended that investigators wishing to establish compensation effect in their system show a plot of ln k vs. inverse temperature instead of ln A vs. E. This will aid in eliminating skepticism. It will also lead to a better understanding of the compensation effect. Investigators should avoid manipulating the "order of reaction," "frequency factor," and "activation energy," to fit their data. One

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should also be cautious trying to establish a relation between $\ln A$ and E obtained from different mathematical treatments. False compensation effect results primarily from inaccurate temperature measurement, temperature gradients within the sample, and due to nonnegligible computational errors introduced by various mathematical approximations.

Appendix

Statistical Formulas used in the Linear Least Square Regression Analysis. The linearized Arrhenius equation may be written as

$$\ln A = \ln k_{iso} + \frac{E}{RT_{iso}}$$

through 'n' number of data sets (E_1, $\ln A_1$; E_2, $\ln A_2$; ...E_n, $\ln A_n$) available in each series of related reactions. The values of slope ($1/RT_{iso}$), intercept ($\ln k_{iso}$) and correlation coefficient was obtained as follows:

$$\text{Slope} = \frac{1}{RT_{iso}} = \frac{n \sum E_i \ln A_i - \sum E_i \sum \ln A_i}{n \sum E_i^2 - (\sum E_i)^2}$$

$$\text{Intercept} = \ln k_{iso} = \frac{\sum \ln A_i - (1/RT_{iso}) \sum E_i}{n}$$

$$\text{Correlation coefficient} = \frac{(1/RT_{iso})\sigma_E}{\sigma_{\ln A}}$$

Standard error about the fitted regression line = SE.

$$SE = \sqrt{\frac{(\sum (\ln A_i)^2 - \ln k_{iso} \sum \ln A_i - (1/RT_{iso}) \sum E_i \ln A_i)}{n-2}}$$

$$\text{Standard deviation of slope} = \sigma_{1/RT_{iso}} = \frac{SE}{\sqrt{\sum (E_i - \bar{E})^2}}$$

$$\text{Standard deviation of intercept} = \sigma_{\ln k_{iso}} = SE \left[\frac{1}{n} + \frac{\bar{E}^2}{\sum (E_i - \bar{E})^2} \right]^{1/2}$$

Nomenclature

A = frequency factor or preexponential factor
E = activation energy or apparent activation energy
k = rate constant
R = gas constant
T = absolute temperature

Greek ᵎ
σ = standard deviation

Subscript
iso = isokinetic

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Zusammenfassung — Die Arrhenius-Gleichung wird gewöhnlich zur Beschreibung des Zusammenhanges zwischen Geschwindigkeitskonstante und Temperatur benutzt. Die linearisierte Form der Arrhenius-Gleichung wurde dazu benutzt, eine Beziehung zwischen ln A und E für eine Reihe von Reaktionen des gleichen Typs aufzustellen. Ein solches Kompensationsverhalten von ln A und E wurde in der Literatur beschrieben, die Realität des Kompensationseffektes war jedoch Gegenstand heftiger Debatten. Ein Kompensationseffekt kann durch ein Rechenartefakt vorgetäuscht oder aber durch verschiedene chemische Faktoren bedingt sein. Dies hängt ausschließlich von der für den Nachweis des Kompensationsverhaltens aufgestellten Datenfolge ab. Dieser Artikel unterstreicht die Wichtigkeit der statistischen Analyse und die Verwendung einfacher Arrheniusgeraden für sich auf das Vorliegen eines Kompensationseffektes beziehende Schlußfolgerungen. An Hand einiger Beispiele werden einige Kontrollmöglichkeiten zur Unterscheidung tatsächlicher und vorgetäuschter Kompensationseffekte aufgezeigt.

Резюме — Уравнения Аррениуса широко используется для связи изменения константы скорости реакции с температурой. Линейная форма уравнения была использована для определения связи между ln A и E в ряду родственных реакций. Случай такого компенсационного влияния между *ln A* и E был приведен в литературе. Справедливость этого компенсационного эффекта горячо обсуждалась. Компенсационный эффект может возникать как вследствии ошибок вычислений, так и различных химических факторов. Это всецели зависит от набора данных, используемых при установлении компенсационного поведения. В статье делается ударение на важность статистического анализа и использования простых аррениусовских графиков, чтобы сделать заключения, касающихся случая компенсационного эффекта. На нескольких примерах показаны некоторые проверочные точки для определения случаев истинного или фальшивого компенсационного эффекта.