THE COMPENSATION EFFECT:
A FACT OR A FICTION

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In this article, the facts and fictions surrounding the compensation effect is explored. False compensation effect occurs mainly due to: propagation of computational and experimental errors resulting in inaccurate estimates of the Arrhenius parameters; and, the natural compensation between $\ln A$ and E. Since Arrhenius parameters are sensitive to errors in temperature; the errors due to uncertainty in temperature should be minimized to eliminate false compensation effect. Increasing the experimental temperature range is helpful in minimizing errors due to uncertainty in temperature. A point of concurrence in a plot of $\ln k$ and $1/T$ establishes the occurrence of true compensation effect. True compensation effect has been shown to be a useful tool in chemical research for: identifying the governing reaction mechanism; predicting the effects of various reaction parameters; and, correlating and reducing experimental data.

The compensation effect (c.e.) is one of the more controversial areas of chemical research. Although the occurrence of c.e. has been widely reported in the literature, most authors do not attempt to identify the theoretical and/or mechanistic implications for their observation and their discovery of c.e. is passed over with little or not discussion. Thus, the lack in understanding the usefulness of c.e. has not helped quench the controversy either.

c.e. is based on the Arrhenius equation:

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

where k = rate constant, A = pre-exponential factor, E = activation energy, R = gas constant, and T = temperature. c.e. is defined as the linear relation between $\ln A$ and E for a series of related reactions or for the same reaction carried out in a series of different conditions. In mathematical terms, c.e. is expressed as:

$$\ln A = \ln k_{iso} + E/RT \tag{2}$$

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where k_{iso} = rate constant at the isokinetic temperature. Recently, Agrawal [1] stressed the importance of statistical analysis and the use of Arrhenius plots to draw conclusions regarding the occurrence of c.e. To understand the significance of c.e., Agrawal [1] divided c.e. into two sets: one arising from "chemical" factors (factual or true c.e.) and the other from computational and experimental artifacts (fictional or false c.e.). Chemical factors include chemical reactions, surface reactions, catalytic reactions, diffusion controlled reactions, and other physical reactions such as phase transformation, nucleation, crystallization etc. The computational and experimental artifacts include computational errors (non-unique results, inappropriate mathematical equations, etc.), instrumental errors (bouyancy and aerodynamic effects, etc.) and experimental errors (inaccurate temperature measurement, temperature gradients, inaccurate weights, calibration errors, etc.). Agrawal [1] also suggested the criteria, $\ln k_{iso} \neq 0$ to distinguish between two types of c.e. and that: (a) for "true" c.e. a series of related reaction yields a linear correlation between $\ln A$ and E and a plot of $\ln k$ vs. $1/T$ (k = rate constant and T = temperature) for the same series of reaction displays a point of concurrence; and, (b) for "false" c.e., the plot of $\ln A$ vs. E is linear but the plot of $\ln k$ vs. $1/T$ does not show a point of concurrence. Šesták [2], commenting on the work of Agrawal [1], suggests tha the occurrence of c.e. can be explained as an odd effect of the data treatment based on the flexible Arrhenius equation. In view of this argument, the limitations of the Arrhenius equation is explored in this paper.

If correctly analyzed, c.e. can prove to be a powerful tool in chemical research for: speculating and understanding the governing reaction mechanism; predicting the effects of various parameters on reactions; predicting the reaction rates and Arrhenius parameters when limited data is available; differentiating the effects of surface and bulk properties; and, in correlating and estimating heat of formation of catalyst oxides, metallic radii, periodic number, etc. Therefore, the occurrence of *all* types of c.e. should not be discarded as an artifact of data treatment. Instead the nature of c.e. should be established before any decision regarding its significance is made. Following up on the previous work [1], this paper furthers the discussion on c.e. and explore facts and fictions surrounding the c.e.

Discussions

Limitations of the Arrhenius equation

Šesták [2] suggests that occurrence of c.e. can be due to: (a) use of inappropriate form of kinetic equation, and/or, (b) a small angle of intersection of $\ln A$ and E in Hilbert space. The literature contains many citations for c.e. arising from use of an apparently appropriate kinetic model $F(a)$ [3]. This has to be explained before c.e.

can be discarded as an artifact. Further, Šesták [2] cites the work of Pysiak [4] and Militký [5] to suggest that ln A is superfluous and hence unnecessary parameter for correlating data in a narrow temperature range. However, replacing A by $k_9 \exp(E/R9)$ (9 = reference temperature and k_9 = rate constant at the reference temperature) may not resolve the problem. If the data is scattered and it is difficult to fit the data to a linear equation, then using the value of k_9 (which is assumed to be accurately known) to estimate the value of the rate constant at some other temperature may be helpful in eliminating some error. However, since the value of E cannot be determined a priori, one still has to force a linear correlation to estimate the slope $(-E/R)$ from a plot of ln k vs. $1/T$. If the temperature range is narrow and as the experimental data contains large scatter, E is bound to be erroneous. In such a case, it is inappropriate to discard the value of intercept, ln A, as superfluous and unnecessary. It is also inappropriate to use such a data to show a relationship between ln A and E. Instead the whole data should be discarded or additional experiments should be performed.

Šesták [2] and Garn [6] have suggested that c.e. arises from the deficiencies in the Arrhenius equation. Arrhenius equation has been successfully used to describe the temperature dependence of the reaction rate constant (see Agrawal [7] for more discussion on the validity of the Arrhenius equation). Since A and E in the Arrhenius equation are usually determined from the intercept and the slope of a plot of ln k vs. $1/T$, it is natural that ln A and E exhibit c.e. The linking of A and E can be best visualized in Fig. 2 in Reference [1]. Though the linear relation between ln A and E may be due to computational and experimental artifacts, a single point of concurrence in a plot of ln k and $1/T$ for a series of related reaction is certainly not due to these artifacts. This concurrence point delinks c.e. from ln A and E. Therefore, it is because of this concurrence point that c.e. cannot be discarded as an artifact.

Šesták [2] suggested that Arrhenius equation can exhibit nonlinear relation depending on various possible values of E; $E > 2RT$, $E < 2RT$ or $E \doteq 2RT$. However, the use of Arrhenius equation to explain the temperature dependence of the reaction rate constant is valid as long as $E > 2RT$ or $k < Ae^{-2}$. In most cases of solid decomposition or solid-gas reactions, the maximum reaction temperature at which the chemical reaction rate ceases to be dominant is about 1300 K. Beyond this temperature, the reaction is diffusion limited. This implies that $E > 5.2$ kcal/mol for a chemical reaction to be the rate limiting step. Typically for a chemical reaction, $A > 10^6$ min^{-1}, this implies $k < 140{,}000$ min^{-1} (or ln $k < 11.8$ ln(min^{-1}) for the Arrhenius equation to be applicable. Thus the Arrhenius equation will exhibit a linear behaviour as long as $E > 5.2$ kcal/mol and ln $k < 11.8$ ln(min^{-1}). Šesták [2] also suggests that the Arrhenius relation can describe non-linear relation depending on the value of the pre-exponential factor. However, for unique results, the pre-

exponential factors has to be derived from the experimental data and cannot be chosen at will due to the c.e. [8].

Estimation of the desirable experimental temperature range

Based on Voňka [9] results, Šesták suggests that

$$\theta_{rad} \approx 2(T_f - T_0)/(T_f + T_0) \tag{3}$$

provided $(T_f + T_0) \gg (T_f - T_0)$. θ = angle in which 1 and $1/T$ meet each other in the Hilbert space. Šesták [2] further proposed that for mathematically justifiable results the temperature range should be greater than 25 K and 80 K for experimental temperature of 300 K and 900 K, respectively, based on the assumption of an angle below 5°.

For reliable determination of Arrhenius parameters, k's should be measured over a wide temperature range. This temperature range is a function of the accuracy with which the temperature of the sample can be measured and the temperature gradient across the sample. By taking the derivative of the Arrhenius equation with respect to temperature:

$$\frac{d \ln k}{dT} = \frac{dk/k}{dT} = \frac{E}{RT^2} \tag{4}$$

dk = incremental change in k resulting from an incremental temperature change dT. dk/k is the corresponding fractional change in k. Thus, E/RT^2 gives an estimate of the relative change in k for one degree temperature change. To examine the errors introduced in E by uncertainities in the temperature, a knowledge of the temperature range is also necessary. The activation energy, E, can be determined from a knowledge of the rate constants, k_1 and k_2, measured at two different temperatures, T_1 and T_2. The Arrhenius equation may be written as:

$$E = \frac{RT_1 T_2}{T_2 - T_1} \ln\left(\frac{k_2}{k_1}\right) \tag{5}$$

If errors in T_1, T_2, k_1 and k_2 are random, the relative error in activation energy, $\Delta E/E$, is [10]

$$\left(\frac{\Delta E}{E}\right)^2 = \left(\frac{T_2}{T_2 - T_1}\right)^2 \left(\frac{\Delta T_1}{T_1}\right)^2 + \left(\frac{T_1}{T_2 - T_1}\right)^2 \left(\frac{\Delta T_2}{T_2}\right)^2$$

$$+ \left[\frac{1}{\ln\left(\frac{k_2}{k_1}\right)}\right]^2 \left[\left(\frac{\Delta k_1}{k_1}\right)^2 + \left(\frac{\Delta k_2}{k_2}\right)^2\right] \tag{6}$$

where Δx = error in parameter x, and $\Delta x/x$ = relative error in x. Thus, the relative error in E is strongly dependent on the size of the temperature range chosen. Decreases in the size of the temperature range greatly increases the uncertainity in E because it not only increases the contributions of the first two terms, but also simultaneously increases the contribution of the last term, as the term $\ln(k_2/k_1)$ in the denominator approaches zero as k_2 approaches k_1. For estimating the desirable temperature range, if it is assumed that: the errors in k is negligible (i.e. assuming $\Delta k_1 \approx \Delta k_2 \approx 0$, this assumption is also consistent in case of non-isothermal reactions where k is not determined directly from the experimental data); the error in E is strongly dependent on T; and, T_1 and T_2 are close together in value so that $T_1 \approx T_2 \approx T$ and $T_{\text{range}} = T_2 - T_1$; Eq. (6) reduces to:

$$\frac{\Delta E}{E} = 1.414 \; \frac{\Delta T}{T_{\text{range}}} \tag{7}$$

Equation (7) indicates that $\Delta E/E$ is proportional to the errors in T and inversely proportional to the temperature range. Therefore by increasing the temperature range, the errors in E can be significantly reduced. Equation (7) also indicates that the error in E is not a function of reaction temperature. Šesták's proposal that the temperature ranges should be greater than 25 K at 300 K and greater than 80 K at 900 K, therefore appears to be inconsistent with this theory. Clearly, the disagreement indicates additional work may be needed to resolve the issue.

Realistically, the uncertainty in temperature (ΔT) is about 3 to 5 K (this value depends on the heating rate) from reliable non-isothermal experiments and it is less than 1 K for isothermal experiments. Therefore, for ΔT = 5 K and 10% error in E (i.e. $\Delta E/E$ = 0.1), according to Eq. (7) the temperature range is about 70 K. For isothermal experiments the desirable temperature range will be significantly lower than 70 K. Since the accuracy of the temperature measured in isothermal studies is generally less than 1 K, the temperature range of 70 K, implies a relative error in E of 2%. Thus, for Arrhenius parameters derived from the same temperature range, E's determined from isothermal experimental will be generally more reliable than those determined from non-isothermal studies. Further, A calculated from the Arrhenius equation via

$$\frac{d(\ln A)}{dE} = \frac{1}{RT} \tag{8}$$

implies that any error in E will be reflected in A as an apparent compensation. Since the accuracy of E is a strong function of the error in temperature and, the error in A is in turn a function of error in E, a linear relation in a plot of $\ln A$ versus E could also result due to errors. This reason along with the natural dependence of A and E on each other are the probable causes for false c.e. c.e. due to errors in E can be

eliminated by plotting $\ln k$ versus $1/T$. Thus the error analysis further strengthens the earlier finding that the plot of $\ln k$ versus $1/T$ rather than $\ln A$ and E be used to demonstrate the existence of c.e. [1]. After the existence of true c.e. is established, investigators could then examine plots of $\ln A$ and E for the significance and implications of c.e.

From the previous discussions, it can be concluded the linear relationship between $\ln A$ and E can arise due to chemical factors (true c.e.) or artifacts (false c.e.). A single point of concurrence in a plot of $\ln k$ versus $1/T$ is due to true c.e. This concurrence will be likely to be observed if $\ln k_{iso} \neq 0$ [1]. Unfortunately, little efforts have been directed towards understanding the significance of true compensation. Most authors simply report the existence of c.e. and do not attempt to identify the cause or the probable mechanism for c.e. This has given rise to many controvercies and consequently the usefulness of c.e. is underrated in the literature.

Usefulness of compensation effect

Ranganathan et al. [11] were perhaps one of the few researchers who investigated the use of c.e. in evaluating catalysts. They showed how c.e. could be used to differentiate the effects of surface properties (e.g. surface area, pore volume, particle size, crystalline size, etc.) and bulk properties (e.g. metallic radius, heat of formation of catalyst oxides, latent heat of sublimation and the chemical properties which characterize the catalyst). They found that the bulk properties of catalysts such as heat of formation of catalyst oxides, metallic radii and periodic group number could be correlated with $\ln k_{iso}$. They also reported that catalysts having different bulk properties had different $\ln k_{iso}$. However, catalysts having similar bulk properties but having different surface properties exhibited the same $\ln k_{iso}$. Also, $\ln k_{iso}$ was reported to be least susceptible to changes in physical structure or method of preparation of catalyst. Therefore, they suggested that $\ln k_{iso}$ can be used to correlate bulk properties but not the surface properties; and, for correlation of surface properties the use of E or A was recommended. For the decomposition of hydrogen peroxide, irrespective of the bulk and surface property, T_{iso} was the same and could be considered as unique for a reaction. Constant values for T_{iso} have been reported for various other reactions: hydrogenation of ethylene, decomposition of formic acid, oxidation of methane [11]. Therefore, the use of T_{iso} to characterize reactions should be explored.

Decomposition of hydrogen peroxide. Deren et al. [12] studied the decomposition of hydrogen peroxide over chromic oxide gel which was previously annealed at various temperatures between 100 and 700°. They reported that catalysts annealed up to 350° had the same $\ln k_{iso}$ and the catalysts annealed above 400° exhibited another $\ln k_{iso}$. Samples annealed up to 350° were found to be amorphous chromic

acid ($Cr_2O_3 \cdot CrO_3$) whereas the samples annealed at 400° and higher were found to be crystalline Cr_2O_3 samples. Ranganathan et al. [11] analyzed the data of Deren et al. [12] and reported that the differences in surface changes for the catalysts with the same bulk properties exhibited the same $\ln k_{iso}$. Thus it was the differences in the bulk properties (such as heat of formation of catalyst oxides and metallic radii) that resulted in two different $\ln k_{iso}$. Irrespective of the catalyst annealing temperature, the decomposition of hydrogen peroxide exhibited the same T_{iso}. Therefore it can be seen that c.e. can be useful in reducing the data, explaining the experimental observations and characterizing and establishing the governing reaction mechanism.

Hydrogenation of ethylene. Doring et al. [13] studied the hydrogenation of ethylene in presence of platinum/silica catalysts with different crystallite sizes. The catalysts were impregnated in chloroplatinic acid, dried and then reduced at different temperatures, thus the amounts of residual chlorine were different. The chlorine content decreased with increasing reducing temperatures, i.e. for reducing temperatures of 80°, 210° and 500°, residual chlorine content were 0.16, 0.13 and 0.034, respectively. Doring et al. [13] found it difficult to separate the catalytic activity due to chlorine promotion (change in bulk property) and the changes in average crystallite sizes (changes in the surface property). Ranganathan et al. [11] showed how c.e. could be used to separate these effects. Ranganathan et al. [11] found that catalysts reduced at different temperatures had different bulk properties (i.e. different amounts of residual chlorine) and exhibited different $\ln k_{iso}$. All catalysts reduced at one temperature but having different surface properties exhibited the same $\ln k_{iso}$. Therefore it was shown that the governing mechanism was catalytic activity due to chlorine and not due to differences in crystallite size. Thus Ranganathan et al. [11] successfully demonstrated how c.e. can be effectively used to separate the effects of surface and bulk properties. Again, T_{iso} was found to be constant for the reaction irrespective of bulk and surface property.

Decomposition of formic acid. Cremer [14] has reported c.e. for the decomposition of formic acid over magnesite ($MgCO_3/MgO$) that had been pretreated to various specified temperatures. The results of Cremer's study indicates that by increasing the magnesite pretreatment temperature, the rate constant for the decomposition of formic acid can be increased. However, at temperatures over 690 K (isokinetic temperature), there is a reversal in the reaction and the reaction rate decreases as the magnesite pretreatment temperature is increased. Since $\ln k_{iso}$ and T_{iso} are the same irrespective of the pretreatment temperature, it is the differences in surface properties which may have resulted in c.e. Therefore, one can speculate that the increase in the reaction rate (due to an increase in the pretreatment temperature at reaction temperatures below 690 K) may be due to active sites on catalyst surface (such as reactive MgO sites from the less reactive $MgCO_3$) created by pretreatment

and participation of the active sites to remove CO_2, which enabled formic acid to decompose more readily. Since the E decreases due to enhanced catalysis, as the reaction temperature is increased beyond 690 K, there is a reversal in the reaction. Thus c.e. can help understand the governing reaction mechanism. Further, c.e. can also aid in estimating the reaction rate constants if magnesite were pretreated to a different temperature. Based on the requirements and economics, the reaction conditions could be optimized and the design engineer could actually estimate the effects of heat pretreatment at other pretreatment temperatures without actually doing additional experiments. Also in designing a system for the decomposition of formic acid, if the desired reaction temperature is less than 690 K, pretreatment of magnesite can prove to be advantageous due to enhanced catalytic activity. However, if the reaction temperature was greater than 690 K, pretreatment is not desirable. Thus c.e. can prove to be a tool to predict rates, understand the reaction mechanisms and optimize process design.

Conclusions

The Arrhenius equation appears to be applicable for most chemical reactions as long as $E > 5.2$ kcal/mol and $k < 1.4 \times 10^5$ min^{-1}. The accuracy of the Arrhenius parameters derived from experimental data is a strong function of error in temperature measurement and the temperature range. Depending on the uncertainity in the measured reaction temperature, the desirable temperature range should be at least 70 K. The desirable temperature range is not a function of the experimental temperature. Since errors in E will be reflected in A, the occurrence of c.e. must be examined closely for possible artifacts. To establish the occurrence of true c.e., besides showing a linear relation between $\ln A$ and E, a point of concurrence in a plot of $\ln k$ versus $1/T$ should be shown. After the true c.e. has been established, plots of $\ln A$ and E can be examined to identify the mechanistic implications of c.e. True c.e. can prove to be useful in chemical research for: identifying the governing reaction mechanism; predicting effects of various parameters on reactions; predicting Arrhenius parameters when limited data is available; separating the effects of surface and bulk properties; and, optimizing process design. $\ln k_{iso}$ can be used to correlate bulk properties of catalysts such as: heat of formation of catalyst oxide; metallic radii; and, periodic group number. Since T_{iso} is independent of bulk and surface properties, T_{iso} can be used to characterize catalysts and/or reactions. Clearly the significance of true c.e. is highly underrated and it is insufficiently utilized. Investigators should avoid reporting the occurrence of c.e. merely for the purpose of discovery but should test their data for the occurrence of true c.e. and attempt at establishing the theoretical and/or mechanistic implications of true c.e. in their system.

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Zusammenfassung — In dieser Mitteilung werden Fakten und Vorstellungen betreffs des Kompensationseffektes untersucht. Falsche Kompensationseffekte werden hauptsächlich verursacht durch: eine ungenaue Ermittlung der Arrheniusparameter durch die Fortpflanzung von rechnerischen und experimentellen Fehlern sowie dem natürlichen Kompensationseffektes zwischen ln A und E. Das Arrheniusparameter gegenüber Fehler im Temperaturwert sehr empfindlich sind, sollten Temperaturungenauigkeitsfehler zur Vermeidung eines falschen Kompensationseffektes minimalisiert werden. Zur Verminderung der aus der Temperaturungenauigkeit resultierenden Fehler ist es von Nutzen, den Temperaturbereich des Experimentes zu erweitern. Ein wahrer Kompensationseffekt wird durch einen Schnittpunkt in einem ln $k - 1/T$ Diagramm angezeigt. Es wird gezeigt, daß der wahre Kompensationseffekt ein nutzvolles Mittel in der chemischen Forschung darstellt: zur Feststellung des dominierenden Reaktionsmechanismus, zur Vorhersage der einflüsse verschiedener Reaktionsparameter und zur Aufarbeitung und Schlußfolgerung von bzw. aus experimentellen Daten.

Резюме — В статье изучены факты и домыслы, касающиеся компенсационного эффекта. Ошибочный компенсационный эффект наблюдается вследствии наличия расчетных и экспериментальных ошибок, приводящих к неточному определению аррениусовских параметров, а также вследствии естественной компенсации между ln A и E. Поскольку аррениусовские параметры чувствительны к ошибкам определения температуры, которые следует свести до минимума, чтобы избежать ошибочного компенсационного эффекта. Одним из таких способов является увеличение экспериментального интервала температур. точка совпадения на графике ln $k - 1/T$ определяет местонахождения истинного компенсационного эффекта. Показано, что компенсационный эффект является полезным в химических исследования для установления определяющего механизма реакции, определения влияния различных параметров реакции, установления различных соотношений и уменьшения экспериментальных данных.