

## THE COMPENSATION EFFECT REVISITED

*M. P. Suárez, A. Palermo and C. M. Aldao*

Institute of Materials Science and Technology (INTEMA) Universidad Nacional de Mar del Plata - CONICET, Mar del Plata, Argentina

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### Abstract

It is generally accepted that the compensation effect arises when a linear relation between  $\ln A$  and  $E$  is detected for a simple reaction taking place over different catalysts or for different reactions over one catalyst. For a perfect linear relation between  $\ln A$  and  $E$  representation of the reaction rate constant in an Arrhenius plot results in a series of straight lines which intersect in a single point. The importance is stressed of defining unambiguously what is meant by the compensation effect, and it is shown how the scatter in the values of  $\ln A$  is translated into Arrhenius plots.

**Keywords:** compensation effect, kinetics

### Introduction

In many reports of kinetic studies, it is stated that a group of rate processes exhibits a compensation effect. Although several theoretical explanations for this effect have been presented, many researchers consider it to be an empirical observation, while others are absolutely skeptical as to its existence and implications. Indeed, numerous reports on the compensation effect may arise because the available data refer to catalysts of similar activities, the similar temperature range widely used in experimental kinetic studies, the exclusion of inactive systems, scatter of the data, or computational artifacts [1-9].

The Arrhenius equation has been widely used to fit the experimental rate data as a function of temperature for both homogeneous and heterogeneous reactions. The Arrhenius equation is expressed as

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

or

$$\ln k = \ln A - E/RT \quad (2)$$

where  $k$  is the reaction rate constant,  $A$  the pre-exponential factor,  $E$  the activation energy, and  $T$  the absolute reaction temperature.  $A$  and  $E$  sometimes display a relationship for a series of related reactions, this being called the compensation effect (Fig. 1). This effect is such that if  $E$  increases, so will the pre-exponential factor, so that the product of the latter and the exponential factor does not vary too much. An increase in  $A$  at constant  $E$  implies a higher rate, while an increase in  $E$  at constant  $A$  implies a lower rate, and a simultaneous increase or decrease in  $E$  and  $A$  tends to compensate the reaction rate.

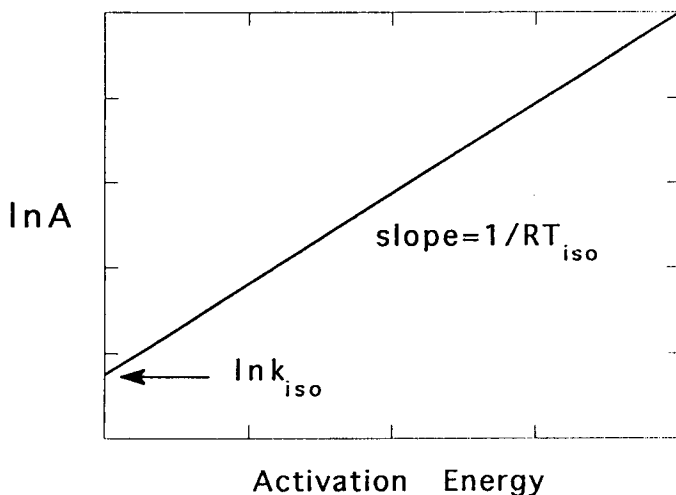


Fig. 1 The compensation effect as generally accepted

Figure 2 represents the variation in activity through a catalyst series as a function of temperature; Bond refers to this as an activity pattern [6]. The decreasing sequence of catalyst activity for temperatures greater than  $T_{iso}$  is  $abc$ , whereas for temperatures below  $T_{iso}$  the sequence is exactly the opposite. There are two common ways to evaluate relative activities: by comparing the temperatures required to achieve a certain rate of conversion and by comparing the rates at certain representative temperatures. The second comparison is preferred for practical reasons and because it permits the temperature dependence of the activity sequence to be assessed directly.

For a linear relation between  $\ln A$  and  $E$ , as shown in Fig. 1, we can write

$$\ln A = a + bE \quad (3)$$

combination of this with Eq. 2 leads to  $a = \ln k_{iso}$  and  $b = 1/RT_{iso}$ , where  $k_{iso}$  is the isokinetic rate constant and  $T_{iso}$  the isokinetic temperature. Indeed, if Eq. (3) is satisfied for either a reaction taking place over various catalysts or several reac-

tions on a given catalyst, the Arrhenius plot yields a family of straight lines which show a concurrence such as that displayed in Fig. 2 [2]. It would be expected that the isokinetic temperature could be easily estimated from the experimental results.

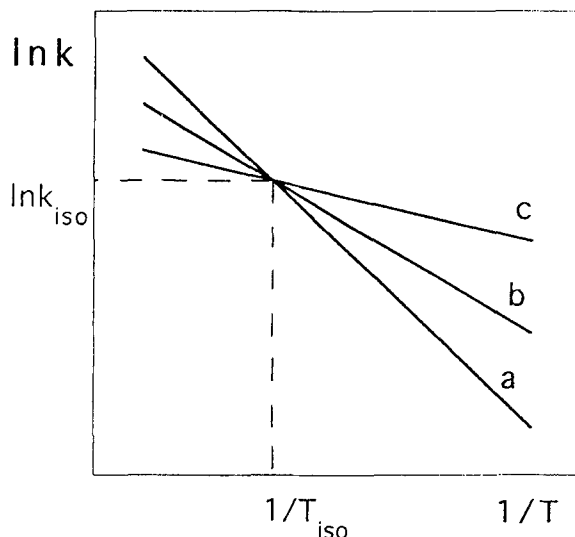


Fig. 2 Arrhenius diagram in the existence of an isokinetic temperature

In our own discussion, we realized that we did not know what the compensation effect actually meant. It was even more surprising when we found that the views of many researchers in the field do not agree concerning this issue [10]. We were then motivated to establish what we should understand when we talk about the occurrence of a compensation effect. After an overview of the most common interpretations for the compensation effect, we will analyze the consequences of experimental errors in a very simple but enlightening approach.

### Interpretation of the compensation effect

Numerous explanations for the compensation effect have been reported. These models often rely on the specific process under consideration, which severely limits their range of applicability. The first approach was due to Constable, who considered an energetically heterogeneous surface and showed that the reaction must proceed almost exclusively on the most active sites, where the activation energy is minimal [1]. Since the activation energy appears as a positive

exponent in the pre-exponential factor, a higher activation energy will be accompanied by a larger factor  $A$ .

In many cases of heterogeneous catalysis, a linear relationship may exist between enthalpy ( $H$ ) and entropy ( $S$ ) changes in chemisorption over a series of catalysts. From the absolute theory of reaction rates, the reaction rate constant can be written as [3]

$$k = (\kappa T/h) \exp(\Delta S^*/R) \exp(\Delta H^*/RT) \quad (4)$$

where  $\kappa$  is the Boltzmann constant,  $h$  the Planck's constant, and  $\Delta S^*$  and  $\Delta H^*$  the differences between the values for the activated complex and those for the reactants. Compensation occurs if an increase in  $\Delta H^*$  is associated with an increase in  $\Delta S^*$ .

The above interpretation has been suggested in slightly different forms by several authors [2, 3]. Everett affirms that the vibrational entropy of the adsorbed molecule arising from the translational motions (normal and parallel to the surface) depends on the curvature at the minimum in the potential energy curve, increasing with the depth of the minimum [4]. Similarly, entropy contributions arising from rotation of the adsorbed molecule are likely to be the more restricted, the greater the strength of adsorption. Proportionality between the heat and entropy of adsorption is therefore to be expected. In the interpretation due to Cremer, the compensation effect is explained through the temperature dependence of the activation energy and the pre-exponential factor [3].

Sosnovski suggested that two types of active sites with differing activation energies could explain the phenomenon [5]. Variation of temperature changes the relative number of sites compensating the change in the average measured activation energy. Bond deduced an expression for the reaction rate constant in terms of the free energy [6]. It appears that the equation for the compensation effect is merely a means of expressing the fact that  $\Delta G$  has the same value for all catalysts at the isokinetic temperature. Therefore, complete compensation is possible only at this temperature, and the difference between the logs of the rates over any two catalysts at any other temperature will be proportional to the difference between the reciprocal temperatures and the difference between the free energies of activation at that temperature.

In a review article, Galwey concluded that the most common explanations are surface heterogeneity and the occurrence of two or more concurrent reactions, and that no simple theoretical explanation for the compensation behaviour has been recognized as having general application [7]. More recently, Curtis Conner presented a possible general explanation for the compensation effect by relating the entropy of the transition to the change in the energy level

of the transition state [9]. The compensation effect has also been attributed to experimental error, inaccuracy or poor experimental techniques [8].

Ranganathan and coworkers investigated the use of the compensation effect in evaluating catalysts [11]. They showed how the compensation effect could be used to differentiate the effects of surface properties (e.g. surface area, pore volume, particle size, crystalline size, etc) from 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 could be correlated with  $\ln k_{\text{iso}}$ , while for the correlation of surface properties, the use  $E$  and  $A$  was recommended.

### Analysis of scatter in experimental data

We have already seen that it is accepted that the compensation effect arises when a linear relation is observed between the logarithm of the pre-exponential factor ( $A$ ) and the activation energy ( $E$ ), in the form  $\ln A = a + bE$ . The compensation effect can also be detected in an Arrhenius plot of the type  $\ln k$  vs.  $1/T$ , where straight lines for a series of catalysts intersect in a single point. We will show in this section how scatter in the values of  $\ln A$  is translated into the Arrhenius relation.

The Arrhenius equation for two different catalysts or reactions is given by

$$\ln k_1 = \ln A_1 - E_1/RT \quad (5)$$

$$\ln k_2 = \ln A_2 - E_2/RT \quad (6)$$

The intersection of these straight lines determines the isokinetic point, i.e.

$$1/T_{\text{iso}} = (\ln A_1 - \ln A_2)R/(E_1 - E_2) \quad (7)$$

If a displacement,  $\Delta \ln A$  is assumed, Eqs (5) and (6) can be rewritten as

$$\ln k_1 = \ln A_1 - E_1/RT + \Delta \ln A_1 \quad (8)$$

$$\ln k_2 = \ln A_2 - E_2/RT + \Delta \ln A_2 \quad (9)$$

and, as above, the intersection of these curves can be found by equating them. The temperature for the resulting intersection point will be given by

$$1/T = (\ln A_1 - \ln A_2 + \Delta \ln A_1 - \Delta \ln A_2)R/(E_1 - E_2) \quad (10)$$

In the most unfavourable case, the displacements  $\Delta \ln A_1$  and  $\Delta \ln A_2$  have opposite signs. For simplicity, it will be considered that the same mistake is being made in the evaluations of  $A_1$  and  $A_2$ , and that  $\Delta \ln A_1$  and  $\Delta \ln A_2$  will have the same absolute value  $\Delta \ln A$ . Then, Eq. (10) becomes

$$1/T = (\ln A_1 - \ln A_2 + 2\Delta \ln A)R/(E_1 - E_2) \quad (11)$$

From this result and the Arrhenius equation, we can write

$$\ln k - \ln k_{iso} = \Delta \ln A - 2\Delta \ln A E_1 / (E_1 - E_2) \quad (12)$$

Therefore, the intervals of maximum error in the evaluation of  $\ln k$  and  $T$  are

$$\Delta \ln k = 2\Delta \ln A + 2E_1 / |E_1 - E_2| \quad (13)$$

$$\Delta (1/T) = 4R\Delta \ln A / |E_1 - E_2| \quad (14)$$

These intervals of maximum error in the evaluation of the isokinetic constant and temperature determine a parallelogram. This figure contains all the possible intersection points of the Arrhenius plot. The scatter of the experimental points in the original figure  $\ln A$  vs.  $E$  is translated into various intersection points of the straight lines  $\ln k$  vs.  $T$ , but all of these points lie inside a parallelogram (Fig. 3).

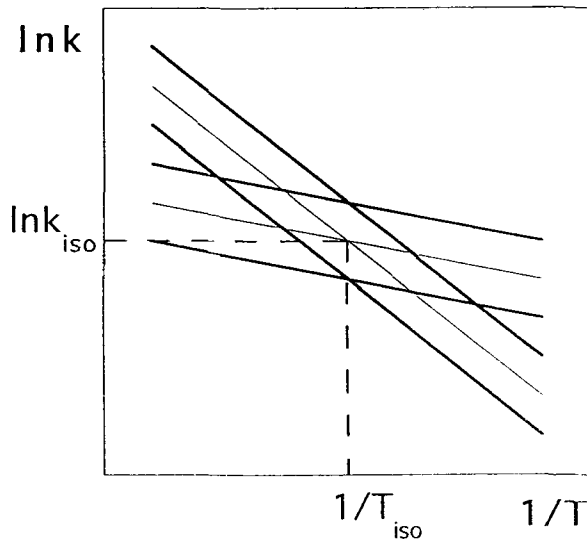


Fig. 3 Arrhenius relation with scatter in  $\ln A$  for two reactions

## Discussion

If all the experimental points lie on a straight line in a  $\ln A$  vs.  $E$  plot, then there will be a single intersection in the Arrhenius plot. The isokinetic parameters with no error can be calculated for this case only. As may be seen in Eq. (13), the error in the determination of the rate constant depends on the values of the pre-exponential factor, the activation energy, and the difference between the activation energies corresponding to two experimental points. This error increases with the scatter in  $\ln A$  and the activation energy, and becomes smaller as the difference in slopes increases.

Before it is established whether the compensation effect actually exists, a clear definition is needed. On the one hand, if we consider that the compensation effect is the linear relation between the logarithm of the pre-exponential factor and the activation energy, then a compensation effect is present in spite of some scattering in the experimental points. On the other hand, if we call the compensation effect the existence of an isokinetic temperature, then the scatter in the experimental points can imply the absence of this effect. Consider the case when all points lie on a straight line in a  $\ln A$  vs.  $E$  plot, except for one point which is very close to that line but has the same activation energy as another point. (Note that an excellent fit can be achieved with a correlation coefficient as close to 1 as is desired.) According to the first definition a compensation effect is clearly detected, while according to the second one a compensation effect cannot be established.

As an example from the literature, let us examine the pyrolysis of cellulosic materials studied by Chornet and Roy [12]. The plot of  $\ln A$  as a function of the activation energy shows a linear relation between them, with  $\Delta \ln A = 1.8$  for a 95% confidence level, suggesting the existence of a compensation effect (Fig. 4). However, if the Arrhenius equation for the experimental data is plotted, there is no single point of concurrence, so the isokinetic parameters are not determined (Fig. 5).

The first criterion to establish the existence of a compensation effect, i.e. a linear relation between  $\ln A$  and the activation energy, has been considered by Agrawal to lead to a false compensation effect [10]. Indeed, this is the case if we consider the existence of a single point of concurrence in an Arrhenius plot to be absolutely needed. Many researchers have erroneously inferred an isokinetic temperature from a linear  $\ln A$  vs.  $E$  plot. However, it should be pointed out that a very small error in the  $\ln A$  vs.  $E$  plot might determine a large uncertainty in the isokinetic parameters.

To clarify the consequences of some dispersion in the experimental data, we will analyze the effects of scatter in  $\ln A$  ( $\Delta \ln A = 1$ ) in the evaluation of the iso-

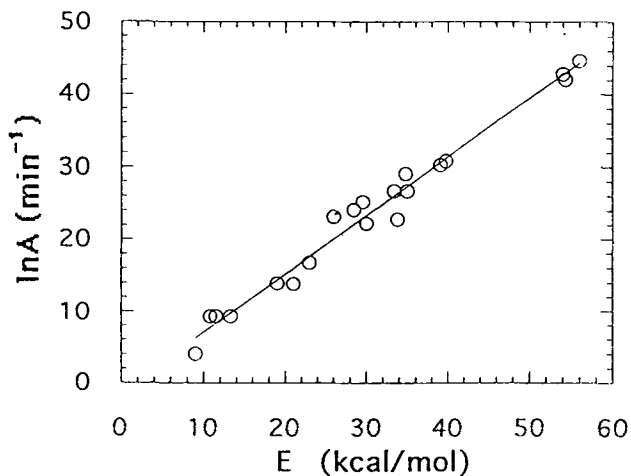


Fig. 4  $\ln A$  vs. activation energy in pyrolysis of cellulosic materials from Ref. [11]

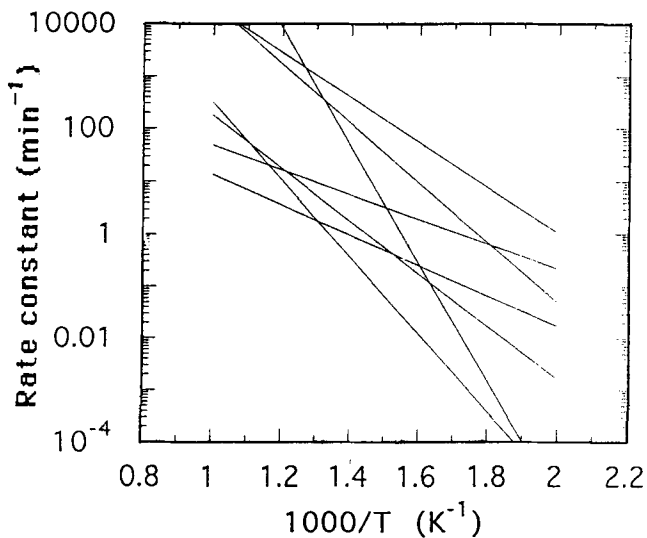
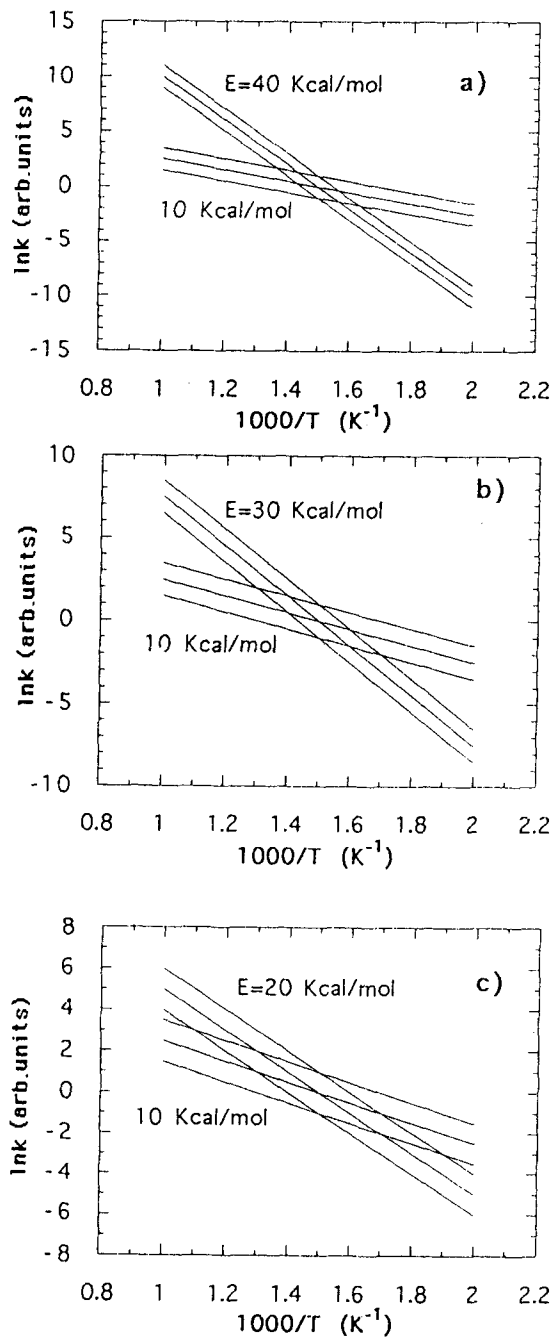


Fig. 5 Arrhenius plot for some points of Fig. 3 showing the non existence of an isokinetic temperature

kinetic parameters for different  $\Delta E$  between two consecutive activation energies. Figure 6 reveals that the error in the determination of the isokinetic parameters increases as the difference in  $E$  decreases. It may be seen that, even for an acceptable error in  $\ln A$  and with quite different consecutive values of  $E$ , the





**Fig. 6** Arrhenius plots with scatter in  $\ln A$  which shows how the uncertainties in the isokinetic temperature and isokinetic rate constant increase as the difference in activation energies decreases

straight lines do not show a single point of concurrence and the uncertainties in determining the isokinetic temperature are large.

## Conclusions

The compensation effect can be useful in kinetic research. Thus, before the occurrence of a compensation effect, can be established it must be defined what will be accepted as a compensation effect: a linear relation between  $\ln A$  and  $E$ , or the existence of a single point of concurrence in an Arrhenius plot.

The above discussion indicates the necessity of exercising great caution when a linear relationship between the coefficients  $\ln A$  and  $E$  is given before inferring the existence of isokinetic parameters. This caution should be even greater when the difference between two consecutive values of activation energy is small.

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**Zusammenfassung** — Es ist allgemein anerkannt, daß der Kompensationseffekt auftritt, wenn zwischen  $\ln A$  und  $E$  eine lineare Korrelation für eine einfache Reaktion bei verschiedenen Katalysatoren oder für verschiedene Reaktionen mit dem gleichen Katalysator beobachtet wird. Für eine perfekte lineare Beziehung zwischen  $\ln A$  und  $E$  ergibt die Darstellung der Reaktionsgeschwindigkeitskonstante in einer Arrheniusschen Darstellung eine Serie von Geraden, die sich alle in einem Punkt schneiden. Es wird die Bedeutung unterstrichen, eindeutig zu definieren, was mit dem Kompensationseffekt gemeint ist und es wird gezeigt, wie die Streuung der Werte für  $\ln A$  in die Arrheniussche Darstellung übertragen wird.