On the Apparent Compensation Effect

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It is shown that by linear extrapolation of low temperature Arrhenius lines to $1/T = 0$ a phenomenon resembling the compensation effect is generated because the absolute position of those lines is raised by the entropy of activation energy distribution so that the lines have an intersection point. An equation first derived by O. K. Rice (Activation et Structures des Molécules, p. 304, Paris (1928); O. K. Rice and Ramsberger, *J. Amer. Chem. Soc.* **50**, 617 (1928)) and C. N. Hinshelwood (Kinetics of Chemical Change in Gaseous Systems, 3rd ed., Oxford Clarendon Press (1933)) is used. For a well documented example it is shown graphically that the construction described fits the observations. From the rate equation used an expression is derived which gives for any reaction the number of degrees of freedom contributing to the activation of the critical complex as a function of the limiting activation energies and of the apparent "isocatalytic temperature." It is applied to a number of catalyses by alloys, salts, supported and inverse supported catalysts for a variety of reactions. In all cases values around 10–20 result for the freedom numbers. The conductivity of several doped semiconductors follows the same rule. The results are briefly discussed.

INTRODUCTION

The compensation effect or, as it is also named, the "theta rule" means that in the application of the Arrhenius equation

$$k = k_0 \cdot e^{-q/RT}$$

or

$$\ln k = B - q/RT$$

for rate processes, especially in heterogeneous catalysis, a linear relation holds between the parameters B and q. As a consequence, in comparing several similar reactions over one catalyst, or several similar catalysts for one reaction, a decrease of the activation energy produces an acceleration of the rate and a decrease of the preexponential factor B a retardation. It has been said that in this way "the catalytic trees do not become sky high." The general validity of this relation permits one in the comparison of catalysts to take into account only one of the two parameters B and q, usually the activation energy q.

It can easily be shown that the relation is such that an "isocatalytic temperature" θ exists at which all catalysts of a group show

the same velocity.[1] As an example, in Fig. 1, B has been plotted against q (in kcal/mol) for the dehydrogenation of formic acid vapor over silver alloys (*1*). The linear dependence between the logarithm of the preexponential factor (ln k_0), or B, and q is evident.

Although this effect is encountered very frequently, its basis is not clear. Originally an attempt was made (*2*) to trace this effect to a thermal energy distribution of the active centers at the preparation temperature, supposing that very active centers of low activation energy are rare and that weak centers of high activation energy are numerous. In this case, θ would be the preparation temperature at which the catalysts reached thermal surface equilibrium for the last time. In a review in 1950 many exam-

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[1] A different and trivial "compensation effect" is possible and occurs often in organic chemistry, when several Arrhenius lines of moderate accuracy and different slope are located at random in the narrow temperature interval between the freezing and boiling point of a solvent and are linearly extrapolated to $1/T = 0$. They then *diverge* with rising temperature whereas in the cases treated here they mostly converge into a more or less common intersection point above the region of observation.
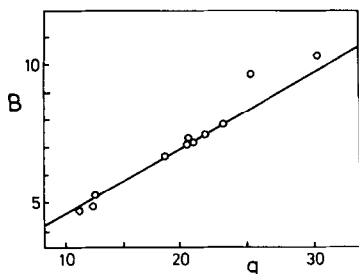
FIG. 1. Compensation effect in the catalytic dehydrogenation of formic acid vapor over α-alloys of silver (1).

ples of such agreement were given (3). However, already by 1955 many counterexamples could be found (4). Hence the isocatalytic temperature could at most be considered a Gaussian scattering parameter, but in view of the wide occurrence of the effect this explanation is not satisfactory. Equally, it would not be satisfying to justify the effect formally by an increase of the activation entropy with increasing activation energy. This involves a (for most examples linear) relationship between the kinetic parameters q and k_0. The Arrhenius equation with its rigid two terms cannot offer such relations. The generally accepted transition state theory introduces into the entropy term k_0 factors of the nature $(2\pi mkT)^{1/2}/h$ and $\exp(h\nu)/kT$, each depending on the respective square term, but not on the total value of q. It is not the place here to examine the effect of selecting certain terms only, but it is evident that this would never give a relationship as general as that treated here (cf. Löffler et al. (5)). Instead we search for a theory which without additional hypotheses gives a positive interdependence of q and k_0. These may be numerous, but the one used in many cases by Hinshelwood (6) and Rice (7) has the additional advantage to inform also on the number of degrees of freedom $s/2$ contributing to the activation of the critical complex in the adsorbate. It is the scope of this investigation to check the application of this formulation for treating the phenomenon

called the "compensation effect" or "Theta rule."

The first step will be to show that this equation is qualitatively suitable to simulate a compensation effect. For this purpose in Fig. 2 the two short lines have been drawn, indicating the law of Arrhenius and designated by 20 and 35 kcal $\cdot$ mol^{-1}. They aim toward $B = 0$ (we omit from here on any temperature independent proportionality factors, in the Arrhenius as well as in the Hinshelwood equation, because we have only to compare chemically equal reactions).

The equation to be tested is

$$k = \frac{(q/RT)^{\frac{1}{2}s-1}}{(\frac{1}{2}s - 1)!} \cdot e^{-q/RT}$$

or

$$\log k = (\tfrac{1}{2}s - 1) \log(q/\mu RT) - \log(\tfrac{1}{2}s - 1)! - q/\mu RT \quad (1)$$

where

$$\mu = 2.303.$$

According to this expression four curves have been drawn, representing $\log k$ vs $10^3/T$ for the activation energies 20 and 35 kcal mol^{-1} and for the values $\tfrac{1}{2}s - 1 = 3$ and 12. At low temperatures $((\tfrac{1}{2}s - 1)RT \ll q)$ their slope deviates very little from the above mentioned Arrhenius energies, but they are
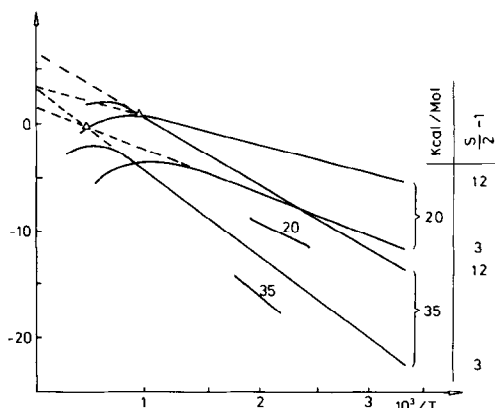

FIG. 2. Simulation of the compensation effect ($\log k$ vs $1/T$).

shifted toward higher probabilities, and this the more so, the higher are the activation energies and the higher the number of degrees of freedom. At very high temperatures, however, these lines curve downward $((\frac{1}{2}s - 1)RT \gg q)$ and would reach $1/T$ asymptotically, although that is outside observation. A linear extrapolation of the rectilinear low temperature branches of these curves is shown by the four interrupted straight lines up to $1/T = 0$. This is the usual way to determine k_0. This would lead to two intersection points of lines with different activation energies (e.g., different catalysts) and equal s. They are designated by triangles in Fig. 2. They would probably be considered as isocatalytic temperature points θ and the respective two pairs of ordinate intercepts as k_0 values increasing with q.

This model shows that indeed both features of a compensation effect, the dependence of k_0 on q and the point θ, can be simulated by an extrapolation of the linear low temperature part of the Arrhenius curve beyond the limit of its validity. This statement does not depend on the special shape of Eq. (1). The only hypothesis made hitherto and maintained in what follows, is that an expression like $\frac{1}{2}s - 1$, related to the activating degrees of freedom, remains constant during the comparison of comparable reactions.
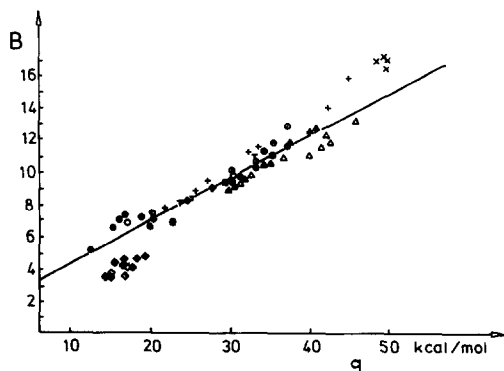

FIG. 3. Dehydrogenation of formic acid vapor over solid alloys of silver and liquid alloys of mercury, lead, bismuth, tin, and thallium (8–12).
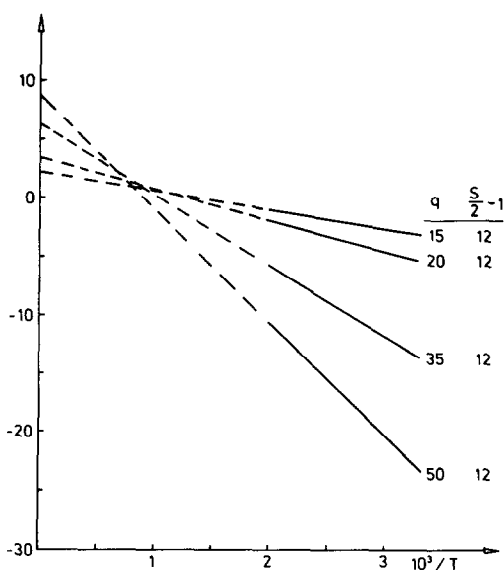

FIG. 4. Graphical representation of intersection and compensation in 19 solid and liquid systems with formic acid vapor (log k vs $1/T$).

It might be added that the effect is not a real physical exaltation of the activity, but is merely fictitious and produced by extrapolation.

The next and second step must be to show whether this approach is also in a quantitative way applicable to a sufficiently broad amount of experimental material. The decomposition of formic acid vapor has been measured (8–12) over different solid alloys of silver and liquid alloys of mercury, thallium, tin, and bismuth in the Arrhenius region. Figure 3 shows that a compensation effect is found in all these cases, $B = \log k_0$ increasing nearly linearly with q for liquids as well as solids (which disproves the old interpretation through active centers).

In Fig. 4 a diagram of log k as a function of $10^3/T$ has been constructed in the following way: the four full lines have the slopes corresponding to the activation energies 15, 20, 25, and 50 kcal · mol^{-1} and extend up to 500 K or $10^3/T = 2$, a region where $(\frac{1}{2}s - 1)RT \ll q$. However, their preexponential term has been taken from Eq. (1) for a temperature of 500 K and for the respective

activation energy. The exponent $\frac{1}{2}s - 1$ has for this example been chosen as 12. From $10^3/T = 2$ to the left these lines have been extrapolated linearly, giving the broken lines. These intersect in the region around $10^3/T = 1$ and their intercepts on the ln k_0 axis are linear functions of the respective q values.

From the average line in Fig. 3 a value of 820 K is calculated, not far from the intersection region of Fig. 4. Hence, the latter is a nearly quantitative representation of the apparent compensation effect for formic acid decomposition over solid and liquid alloys. Figure 4 is but one of a number of similar diagrams with arbitrary parameters s and yet it fits the experiments. This shows that Eq. (1) is indeed a good approximation.

However, it would be desirable to treat the data not, as in this first example, by trial and error, but systematically. For a given set of reactions the upper and lower limit of activation energies and the fictitious isocatalytic temperature θ are the experimental facts, and $\frac{1}{2}s - 1$ is the adaptable parameter.

Let us designate by k the rate coefficient, indifferent whether the point is situated on the full (experimental) or the interrupted (extrapolated, fictitious) part of a line in Fig. 4, with T_a the upper end of the full lines, with the index 1 the upper limit and with the index 2 the lower limit of the measured activation energies. Then at the upper end of every full line in Fig. 4 we have

$$\log k_{T_a} = (\tfrac{1}{2}s - 1) \log(q/\mu R T_a) \\ - \log(\tfrac{1}{2}s - 1)! - q/\mu R T_a.$$

This equation is valid along the whole of the full lines in the form:

$$\log k_T = (\tfrac{1}{2}s - 1) \log(q/\mu R T_a) \\ - \log(\tfrac{1}{2}s - 1)! - q/\mu R T,$$

since in this region $((\tfrac{1}{2}s - 1)RT \ll q)$ the small variation of the slope can be neglected. The extrapolated interrupted lines are represented by the same equation with the same preexponential. Now, at the inter-

section point θ two of these lines intersect and

$$_1k_\theta = {_2k_\theta}$$

or

$$(\tfrac{1}{2}s - 1) \log(q_1/\mu R T_{a_1}) \\ - \log(\tfrac{1}{2}s - 1)! - q_1/\mu R\theta \\ = (\tfrac{1}{2}s - 1) \log(q_2/\mu R T_{a_2}) \\ - \log(\tfrac{1}{2}s - 1)! - q_2/\mu R\theta$$

We may have chosen, as in Fig. 4,

$$T_{a_1} = T_{a_2}.$$

Finally, it follows:

$$\tfrac{1}{2}s - 1 = \frac{\Delta q}{\mu R\theta\Delta \log q}.$$

With this equation it should be possible, at least approximately, to select for a given reaction the best value of $\frac{1}{2}s - 1$ for the simulation of the compensation effect on the ground of the measured set of activation energies and the temperature θ from a collective drawing of log k vs $1/T$.

Provided Eq. (1) can be accepted as an adequate expression for the activation entropy due to the distribution of the activation energy over the degrees of freedom contributing to the activation of the activated complex (containing degrees of the reacting molecule and of part of the catalyst, eventually) this opens a new way to determine the number of those degrees. This was hitherto only possible on the basis of absolute rates, obscured by problems of theory and absolute active surfaces.

This program is important enough to try with a number of typical examples numerically.

Thus Cremer (13) studied the decomposition of ethanol over lanthanide oxides and aluminium oxide and on this occasion made the first observation of an intersection. Also at this time, Grimm and Schwamberger (14) reported on the elimination of HCl from ethyl chloride over inorganic salts, and the present author (15) found in their results again intersections within dif-

TABLE 1

Evaluation of the Degrees of Freedom Parameter ($\frac{1}{2}s - 1$) for Various Reactions

Reactant	Catalyst	kcal/mol		log q_{max}	log q_{min}	θ	Δq	Δ log q	$\frac{1}{2}s - 1$	Ref.
		q_{max}	q_{min}							
HCOOH	TlPb	47		1.673		820	35	0.603	12	(8)
	AgAu		12		1.070					
C_2H_5OH	La_2O_3	32		1.505		910	19	0.391	11.6	(13)
	Al_2O_3		13		1.114					
C_2H_5Cl	$BaCl_2$	39		1.591		639	26	0.477	18.6	(16)
	$BaMnCl_4$		13		1.114					
C_2H_5Cl	$BaCl_2$	21		1.322		493	5.4	0.129	18.6	(14)
	$MgCl_2$		15.6		1.193					
C_2H_5Cl	AgCl	35		1.544		465	10	0.146	22	(14)
	$PbCl_2$		25		1.398					
C_2H_5Cl	CaF_2	24.3		1.386		820	5.5	0.143	18.1	(14)
	MgF_2		17.5		1.243					

ferent catalyst groups. These observations were the origin of the "theta rule" or the "compensation effect." Many years later the author and Karatsas (16) studied the same reaction over three salts which formed in pairs a eutectic, a compound and a mixed crystal. Among these six catalysts only the compound showed a remarkable synergy, but all six had a common intersection point. The fourth example was the dehydrogenation of formic acid, reported already before (8). In Table 1 the equation has been applied to the above mentioned reactions. In every case, the differences were used between the highest and the lowest activation energies. The results of these calculations, in spite of their moderate accuracy (± 2), present some interest. First, they indicate that the number of degrees of freedom is reactant-specific in that halides differ from oxygen-containing organics and, second, it is satisfactory that for ethyl chloride two sets of measurements, made by different authors at different times and places, have given similar results.

The calculation has also been performed for the hydrogenation of ethyl cinnamate over platinum more or less poisoned by diethylsulfide. The respective values (7) are reported in Table 2.[2]

Besides poisoning, a general method of modification of a catalyst is possible in inverse mixed catalysts, i.e., semiconducting catalysts located on an inactive metallic support. Here, the active phase can be modified by manipulating the support or by changing the layer thickness of the catalyst. In the first case studied, oxidation of CO over NiO supported by silver (20), the thickness of the active layer changes from 76 to 15200 Å and the activation energy from 45.6 to 16 kcal · mol^{-1}. In another case, oxidation of SO_2 over Fe_2O_3 supported on silver alloys of different electron concentration, the activation energy varied between 7 and 31 kcal · mol^{-1} (21). These results are also collected in Table 2.

Table 3 shows the values of s, hitherto determined by this method.

Rice (7) has collected and discussed similar values, taken from absolute reaction

[2] In the original paper (7) the observed compensation has been mistaken for a trivial effect like in the footnote to the Introduction, but a common intersection point does in fact exist.

TABLE 2

Degrees of Freedom Parameter for Hydrogenation of Ethyl Cinnamate and Oxidation of CO and SO_2

Reactant	Catalyst	kcal/mol		$\Delta q \times 10^{-3}$	$\Delta \log q$	$\frac{1}{2}s - 1$	θ (°C)
		q_{max}	q_{min}				
$C_6H_5C_2H_4COOEt$	Pt	12.7	6.3	6.4	0.304	13.6	67
$CO + O_2$	NiO	45.6	16.4	29.2	0.444	14	752
$SO_2 + O_2$	Fe_2O_3	31	7	26	0.595	8.7	827

rates. The material is, however, too scarce for correlating it with structural formulas; the only result appears to be that not all the bond vibrations possible contribute to activation. It appears that in heterogeneous catalysis vibrations of the catalyst also contribute.

On the other hand, apparent compensation effects have been observed and described in many physical phenomena, such as evaporation, desorption and electron emission. Another example, thermal semiconductivity, will be mentioned here below.

Schwab and Schmid (17) have modified the p-type semiconductor NiO by doping with Ga_2O_3 or Cr_2O_3. This diminishes the conductivity by consuming positive holes according to

$$Cr_2O_3 + 2e^+ \rightleftharpoons 2Cr(Ni)^+ + 2NiO + \tfrac{1}{2}O_2.$$
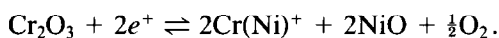
At the same time because of the enthalpy of the above reaction the activation energy of the conduction is modified. On the other

TABLE 3

Collected Values of the Degrees of Freedom Parameter, $\frac{1}{2}s - 1$

Reactant	$\frac{1}{2}s - 1$
HCOOH	12
C_2H_5OH	11.6
C_2H_5Cl	18–22
$C_8H_9CO_2Et$	13.6
CO	14
SO_2	8.7

hand, Meyer and Neldel (18) have modified the n-type conductors TiO_2, Fe_2O_3 and ZnO by oxidative treatment according to

$$\tfrac{1}{2}O_2 + 2e^- \rightleftharpoons ZnO + V_{Zn}^{2-}.$$
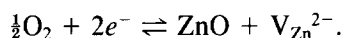
Negative electrons are consumed, and at the same time the enthalpy of the above reaction modifies the activation energy of the conduction, depending on both cases on the amount of the dopant.

In every one of the four cases, the logarithm of the conductivity, extrapolated to $1/T = 0$ according to the Arrhenius law, showed a linear dependence on the energy over 4–8 points and over an energy interval of several electron-volts. The treatment of these data, analogous to that in Table 1, is given in Table 4. This time, the energies are measured in electron-volts, and hence 2.302 R is 1.988×10^{-4} eV · K^{-1} · mol^{-1}.

The remarkable result, indicated in the values of $\frac{1}{2}s - 1$, is that, as in the chemical reactions of chemisorbed molecules, also in the formation of electrons and holes in oxides the activation energy is distributed over a number of (presumably vibrational) degrees of freedom.

The "Theta rule" is valid in semiconductivity also. This explains the well known fact that the Arrhenius plots of semiconductivity tend nearly always to a decrease of slope in the region of very high temperature.

CONCLUSION

The position taken in this article is that the compensation effect and the theta rule

TABLE 4

Evaluation of $(\frac{1}{2}s - 1)$ for the Conductivity of Semiconducting Oxides

Sub-stance	Type	Modifi-cation	eV		log q_{max}	log q_{min}	θ	Δq	$\Delta \log q$	$\frac{1}{2}s - 1$	Ref.
			q_{max}	q_{min}							
NiO	p	Ga-doped	1.12		0.0492		1070	0.72	0.447	7.6	(11)
	p	Cr-doped		0.4		−0.398					
TiO$_2$	n	O$_2$	1.725		0.237		1479	1.375	0.692	6.8	(18)
				0.35		−0.455					
Fe$_2$O$_3$	n	O$_2$	1.175		0.070		910	0.725	0.417	9.6	(18)
				0.45		−0.347					
ZnO	n	O$_2$	1.025		0.0107		1050	0.988	1.4367	3.2	(18)
				0.0375		−1.426					

are artefacts generated by ascribing reality to fictitious lines and fictitious points.

On the other hand, Galwey (19) in an extensive summary tries to classify reasons for the occurrence of a real effect. A reconciling conjecture, which, however, can neither be proven nor rejected, would be the idea that the real high temperature rate curves (through a modification of Eq. (1)) converge or flatten out somewhere at or below θ.

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