Note

COMPENSATION AND THE SMITH–TOPLEY EFFECTS

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The occurrence of a compensatory relationship between the logarithm of A, the Arrhenius factor, and E_a, the activation energy, in the kinetic equation

$$k = A \exp(-E_a/RT)$$

has been widely reported for many and diverse heterogeneous reactions[1]. In the particular case of the thermal decomposition of solids, several publications have appeared recently[2-4]. The relationship is usually linear, the increase in log A being offset by an increase in E_a expressed as

$$\log A = a + bE_a$$

During this time, publications have appeared that have questioned the assumption of chemical causation for the existence of the linear compensation effect[5-7]. This paper is concerned with the reversible solid state chemical reaction of the type

$$\text{solid (A)} \rightleftarrows \text{solid (B)} + \text{gas (C)}$$

where the reaction exhibits the Smith–Topley effect. The purpose is to see whether a compensation effect exists in this case.

The Smith–Topley effect has been a puzzling phenomenon. It occurs during the dehydration of solid hydrates over a range of fixed environmental vapor pressures. Here, the rate constants exhibit two extrema so that in this restricted range an increase in the vapor pressure may yield an increase in the dehydration rate. Dollimore and co-workers[8, 9], have investigated this effect using thermogravimetry to study the dehydration rates of calcium oxalate monohydrate. The kinetics were carried out isothermally at various pressures of water vapor. Though the reaction rate for dehydration decreased sharply with increasing water vapor pressure up to 0.067 kNm^{-2}, beyond this value the rate of dehydration increased to a somewhat higher value followed then by a steady fall. Thus, the rate constants exhibited a minimum and
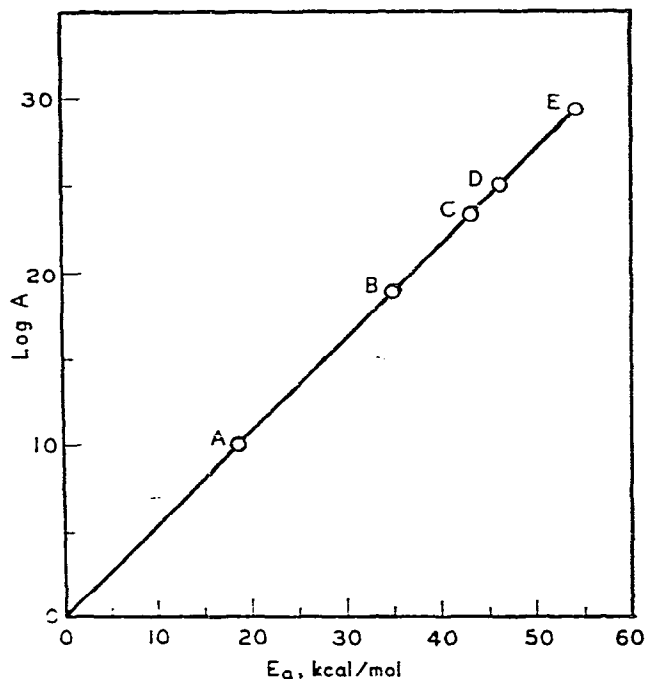
Fig. 1. Log A versus E_a as brought on by the variation in the water vapor pressure. Values calculated from the publication of Dollimore et al.[8]. Vapor pressure are in kNm^{-2}: A = 10^{-5}; B = 0.067; C = 0.133; D = 0.440; E = 1.310.

maximum as a function of the environmental vapor pressure. The effect has been ascribed, in part at least, to the difference in end products. These investigators showed by means of gas adsorption and X-ray diffraction techniques that dehydration at low relative vapor pressures was associated with the production of an amorphous dehydrated product while at the higher vapor pressure the dehydrated product was crystalline.

More recently, the Smith–Topley effect has been reinvestigated by Bertrand and co-workers[10]. Their findings point to the Smith–Topley effect as an artifact caused by the thermal conductivity of the gases and the endothermic nature of the dehydration reaction, the crystallitivity of the end products apparently being of secondary significance. Clearly, chemical causation for the Smith–Topley effect is doubtful. In view of this development, we thought it would be of interest to see whether the data of Dollimore et al.[8] could yield the Arrhenius factor versus the activation energy as a function of the vapor pressure, particularly in the range where the two extrema are present. We have been able to abstract this information using their Fig. 4 which displays the isothermal rate constants versus the environmental vapor pressures. The results are shown in Fig. 1. A least squares solution yields the equation*

$$\log A = 0.542 \, E_a - 0.043$$

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* Figures 2 and 3 of Dollimore et al.[8], result in the equation, $\log A = 0.542 \, E_a - 0.107$, which is well within the experimental error of the above calculated value.
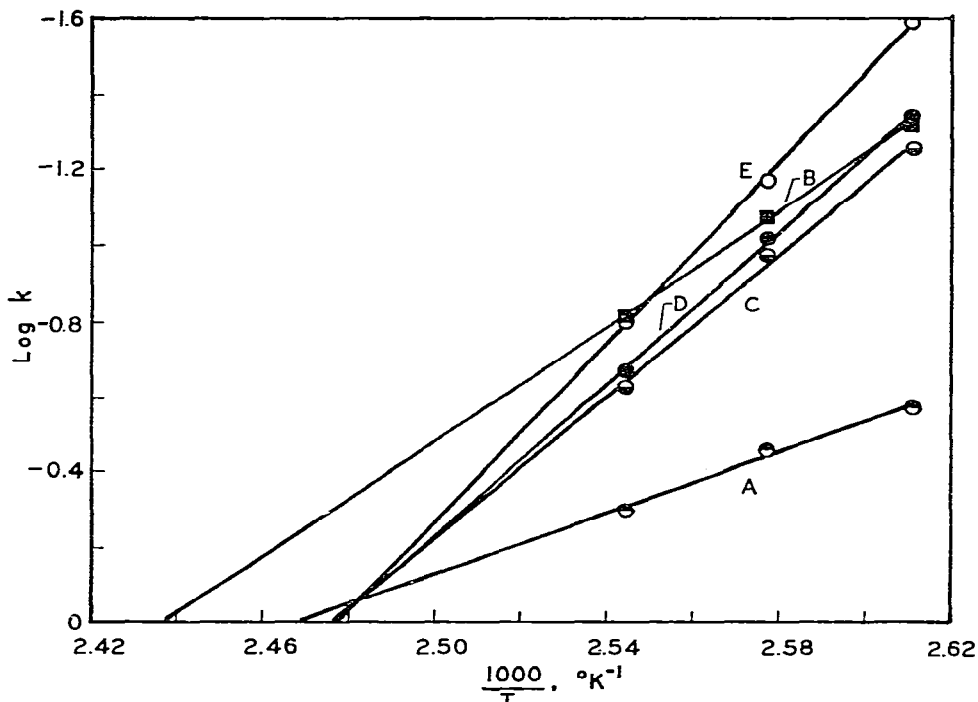
Fig. 2. Plot of log k versus $1/T$. Lines A–E correspond to the water vapor pressure indicated in Fig. 1.

with E_a given in kcal mole^{-1}. Points B and C, in Fig. 1, correspond to the two extrema that constitute the Smith–Topley effect.

The slope of the linear plot leads to an isokinetic temperature of 130 °C. However, a plot of the log of the rate constants versus the reciprocal of the absolute temperature, as shown in Fig. 2, clearly shows that the rate constant for the vapor pressure of 0.067 kNm^{-2} (see point B in Fig. 1) is off by seven degrees[*]. Apparently, in the compensation plot (Fig. 1) this disparity is masked.

The linear relationship between log A and E_a may be considered as a linear relationship between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ in terms of activated complex theory. The latter symbols are the entropy and enthalpy of activation, respectively.

Not only heterogeneous, but also many homogeneous reactions have been shown to exhibit the compensation pattern[7]. In all cases, the $\Delta S^{\ddagger}$ is not determined independently but calculated via the Arrhenius equation as is the case for $\Delta H^{\ddagger}$. As for equilibrium measurements, the literature for the linear correlation of ΔS and ΔH has been well established for many reactions in solutions[11]. However, in these cases as in reaction kinetics, the entropy change is not evaluated independently but is calculated via the Gibbs or van 't Hoff equation. Neither kinetic nor equilibrium data has shown a correlation between entropy and enthalpy when the entropy change has been determined independently as is possible for gaseous systems. Though it has been suggested that a large negative change in the enthalpy (exothermic reaction) indicates a strong resulting bond which may lead to a decrease in the entropy, there

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[*] This disparity also appears to be indicated in Fig. 2 of Dollimore et al.[8].

seems to be no reason for a linear relationship between the pair of thermodynamic functions.

The kinetic compensation effect for solid state reactions has been discussed at length by Garn[5] and Gallagher and Johnson[6]. Their basic reasons that high correlation between log A and E_a does not necessarily indicate chemical causation have been further developed for both kinetic and equilibrium data by Krug and co-workers[7]. The latter investigators have given a detailed mathematical treatment of the compensation problem. They have shown that a true functional dependence, if any should exist, is usually masked by a dominant statistical compensation pattern that arises solely from experimental errors. Thus, estimated correlation coefficients >0.95 do not imply an extrathermodynamic enthalpy–entropy effect. Apparently, enthalpy and entropy data are distributed by experimental errors in elliptical probability regions that are very elongated and appear as lines, the slope of the lines being close to the experimental harmonic mean temperature. In the present case of calcium oxalate monohydrate the experimental temperature range, which was $10\,^{\circ}\text{C}$, yields a harmonic mean of $2.58 \times 10^{-3}\ \text{K}^{-1}$. The slope of the log A versus E_a line in Fig. 1, yields a value of $2.48 \times 10^{-3}\ \text{K}^{-1}$. Again, though run B in Fig. 2 does not go through the isokinetic temperature, this run yields a point on the log A–E_a linear plot in Fig. 1. Evidently the spread of the experimental isokinetic temperature is masked in compensatory plots. In view of this, many of the linear relationships obtained in the thermal decomposition of solids, which have been ascribed to possible chemical factors, are open to question.

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