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AN EXAMINATION OF THE KINETIC COMPENSATION EFFECT

PAUL D. GARN*

Mineralogisch-Petrographisches Institut der Universität zu Köln,
Federal Republic of Germany

* Permanent Address: The University of Akron, Akron, Ohio, USA, 44325

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The "kinetic compensation effect" arises from deficiencies in the Arrhenius equation. Determination of the pre-exponential factor generally comprises only the reconciliation of the expression of the temperature dependence of the rate (the exponential term) with the observed rate. The applicability of the Arrhenius equation to a particular reaction could be tested by finding constancy or a predictable variation in the "frequency factor" with changes in experimental conditions or sample treatment or history.

The Arrhenius equation is widely used in heterogeneous kinetics for two reasons. First, the relationship is well established in homogeneous kinetics; second, the form of the equation assures the user that numbers for the constants in the equation can be calculated. It is only necessary to adjust the form of $f(d\alpha/dt)$ or, for non-isothermal reactions, $f(d\alpha/dt)$ until, subjectively, a straight-line relationship is found when the logarithm of that function is plotted against $1/T$.

When this plot has been prepared and the "best straight line" drawn, the slope is ascribed to an activation energy, divided, of course, by R ln 10. The difference is ascribed to a frequency factor according to the equation

$$\log\left[f(\alpha)\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right] = \log A - \frac{E}{2.3\,RT}\,. \tag{1}$$

The value of this "frequency factor" can vary by several orders of magnitude for a given reaction by different observers and sometimes by the same observer with small changes in conditions. The variation suggests immediately that the equation

$$k_T = Ae^{-E/RT} \tag{2}$$

is not complete, but this has been pointed out before [1], as has the doubtful applicability to heterogeneous reactions [2, 3]. The important point is that any experimental values which vary in a systematic way and show increasing rate with increasing temperature can be adjusted to approximate a straight line.

This intercept, integration constant, frequency factor or, more cautiously, pre-exponential factor, A, should have a physical significance, as it does in homogeneous kinetics. The absence of a discernible meaning should warn the experimenter that an interpretation based upon values calculated from the equation is of doubtful validity. (The suggestion that A is related to the frequency of some vibration of the molecule or ion has certainly not been shown to be true in the general case.)

The variations in A, along with the lack of a physical meaning, has led to use of a phenomenon referred to as the "kinetic compensation effect", expressed as

$$\log A = aE + b\,, \tag{3}$$

where a and b are constants. Originally in catalysis studies, the concept was developed [4, 5] to explain the failure of an apparent change in the activation energy to reflect an appropriate change in the reaction velocity. That is, different treatments of a catalyst led to differing *temperature dependences* of the reaction velocity but did not substantially change the magnitude of the velocity. The differing temperature dependence led to different calculated activation energies. As stated above, the value of A is simply an adjustment having whatever magnitude required to fit the data.

Equation 2 can be restated as

$$A = \frac{k_T}{e^{-\frac{E}{RT}}} = e^{\frac{E}{RT}} \cdot k_T\,, \tag{4}$$

so

$$\log A = \frac{E}{2.3\,RT} + \log k_T\,. \tag{5}$$

From the similarities of *Equation 3* and *Equation 5*, it is clear that they are equivalent over any small temperature range. That is, over a small range $a = 1/2.3RT$ and $b = \log k_T$.

The similarity can be tested easily enough from published data, and this is done below. But it should be noted that complete generality of the expression is not suggested because k_T is in many cases a function of pressure, etc., rather than only of A, E, T, and α.

The first three sets of data at hand are those of Zsakó and Lungu [6], Zsakó et al. [7], and Hulbert and Popowich [8]. In the absence of published rate constants, the value of $1/a$ can be compared with the value of $2.3RT$.

In the first case [6], the values describing the decomposition of several complexes of bisdioximatocobalt (III) yielded values of a of 0.44 – 0.52 moles/kcal, so $1/a$ is ca. 1.8 – 2.2 kcal/mole. But these reactions occur in the 160 – 200° range, or ca. 450 K, so the agreement is very good.

Similar agreement is found using the data of Zsakó et al. [7] on [$CoBr_2$(*m*-toluidine)$_2$]. The value given for a is 0.47 – 0.48 for temperatures in the 200 – 230° range.

Since this agreement may arise from some special characteristic of the cobalt complex, proper criticism requires comparison of another type of reaction. Most sets of values of E and A obtained in dynamic experiments cannot be compared, because the temperature interval of the process has shifted significantly with heating rate, sample size, etc. Where the changes in conditions are not great, but the changes in apparent activation energies are significant, the comparison is simple. For pairs of data, $1/a$ is calculated from $\Delta E/\Delta \log A$ and compared with $RT \ln 10$ or $4.58T$, remembering that E is in *kilo*calories per mole. The data of Hulbert and Popowich [8] are particularly illustrative because rather subtle changes in a reactant caused marked changes in the apparent activation energy.

Hulbert and Popowich reported that for the reactions of partially reduced rutile with strontium carbonate, the calculated activation energy varied with the stoichiometry of the rutile. The values for the activation energy in kcal/mole and the frequency factor in min^{-1} for pure rutile and the samples reduced under vacuum were, for TiO_2, 97.8 and 3.2×10^{15}; $TiO_{1.995}$, 86.1 and 2.1×10^{13}; $TiO_{1.983}$, 72.1 and 5.8×10^{10}; $TiO_{1.975}$, 67.2 and 7.3×10^{9}; $TiO_{1.970}$, 61.4 and 6.8×10^{8}. Calculations of $1/a$ for adjacent pairs of data yielded, 5.4, 5.5, 5.4 and 5.6 kcal/mole, respectively. Calculating $1/a$ for 900°, the temperature singled out by Hulbert and Popowich for intensive reporting, yielded a value of 5.4 kcal/mole. The values given for anatase and for rutile reduced to $TiO_{1.975}$ in carbon monoxide, were also in good agreement.

From examination of the general nature of the "kinetic compensation effect", it appears that the reactions involved in these examples have a feature in common – a principal reaction in which some parameter changes the temperature variation without changing the general nature of the reaction. In the complexes, the breaking of particular bonds may determine the temperature of initiation and the specific nature of the ligand has a secondary effect upon the temperature dependence. For the inorganic reaction, the diffusion of strontium oxide, presumably enabled by carbonate decomposition, can begin. The secondary effect which helps to determine the temperature dependence is the defect nature of the non-stoichiometric titanium oxide. In either case, the apparent activation energy is calculated from this secondary effect and the "frequency factor" is calculated to satisfy the Arrhenius equation.

The same phenomena are probably operative in catalysis, a lower limit of temperature determined by the principal process, but the variation with temperature then influenced by surface effects, etc. In catalysis, thermal reactions or decompositions, examples of apparent agreement with the "kinetic compensation effect" should be common. This agreement should not be anticipated in all cases, because there is no basis from physical principles. Agreement, however, may be instructive in deducing the nature of the temperature dependence.

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