

184. *Fortuitous Empirical Relationships in Chemical Kinetics.*

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THE equation of Arrhenius for the variation of the velocity constant of a reaction with temperature is $k = Be^{-E/RT}$, which may be written

$$\log_e k = \log_e B - E/RT \quad . \quad . \quad . \quad . \quad (1)$$

Many investigators have attempted to find an empirical relationship between E and $\log B$, but it is not generally recognised how far the data are automatically selected to meet the needs of convenience. For example, Holzschmidt (*Z. anorg. Chem.*, 1931, **200**, 82), for bimolecular reactions in solution, proposed the formula $\log B = \log K + E/C$, where C and K are constants, the latter perhaps being specific to the solvent. In support of this suggestion, he quotes 48 cases and shows that the plot of $\log B$ against E is, very roughly, linear, the points all lying on a broad, straight band.

From the nature of the solvents employed, it is clear that all the measurements were made somewhere in the neighbourhood of 300° K. All but six of the velocity constants at this temperature lie within the range $\log_e k = -3.0$ to -8.0 . It is incredible that all bimolecular reactions in solution should inherently have constants lying within this range, but readily understandable that only those which have proceed at such a rate as to be measurable at, or near, this temperature. The equation is, in fact, nothing but a rearrangement of (1), with the condition that T and $\log k$ are approximately constant unconsciously imposed upon it by experimental convenience. The constancy of T is the more important, since in the majority of cases $E/600$ is above 20, thus making this far the more decisive term of the expression.

TABLE I.

Reaction.	E .	$\log_e B$.	T_m .	$\log_e k_m$.	$E/T_m \log_e B$.
<i>Gaseous reactions.</i>					
Acetone ¹	68,500	34.95	800°	-7.87	2.45
Propaldehyde ²	54,000	27.93	773	-7.00	2.50
Diethyl ether ³	53,000	26.47	773	-7.82	2.59
Dimethyl ether ⁴	58,500	30.36	773	-7.48	2.50
Phosphine ⁵	75,000	34.24	900	-7.43	2.43
Propylamine ⁶	44,000	21.97	773	-6.49	2.58
Pinene ⁷	43,700	33.21	491	-11.29	2.68
Azomethane ⁸	51,200	36.73	573	-7.95	2.43
Azoisopropane ⁸	40,900	31.36	573	-4.33	2.28
Nitric anhydride ⁹	24,700	31.45	318	-7.39	2.47
Carbonyl chloride ¹⁰	52,540	34.83	655	-5.78	2.31
<i>Reactions in solution.</i>					
Fluosilicate ¹¹	19,120	29.8	298°	-2.27	2.15
Chloroamylamine ¹²	20,800	30.09	298	-4.81	2.32
Acetonedicarboxylic acid ¹³	23,100	32.00	313	-4.90	2.31
[Co(NH ₃) ₅ Cl] ⁺⁺ ¹⁴	22,134	31.33	298	-5.81	2.37
[Cr(NH ₃) ₅ Cl] ⁺⁺ ¹⁵	21,780	29.09	298	-7.47	2.51
[Cr en ₂ Cl ₂] ⁺ ¹⁶	20,850	29.26	298	-5.73	2.39
Bromoethylamine ¹⁵	25.158	38.77	289	-4.76	2.25

References.—¹ Hinshelwood and Hutchinson, *Proc. Roy. Soc.*, 1926, **111**, A, 245. ² Hinshelwood and Thompson, *ibid.*, 1926, **113**, A, 221. ³ Hinshelwood, *ibid.*, 1927, **114**, A, 84. ⁴ Hinshelwood and Askey, *ibid.*, 1927, **115**, A, 215. ⁵ Trautz and Bandharker, *Z. anorg. Chem.*, 1919, **106**, 45. ⁶ Taylor and Achilles, *J. Physical Chem.*, 1931, **35**, 2660. ⁷ D. F. Smith, *J. Amer. Chem. Soc.*, 1927, **49**, 43. ⁸ Ramsperger, *ibid.*, pp. 849, 912, 1495. ⁹ Daniels and Johnson, *ibid.*, 1921, **43**, 53. ¹⁰ Christiansen, *Z. physikal. Chem.*, 1923, **103**, 99. ¹¹ Hudleston and Bassett, *J.*, 1921, **119**, 405. ¹² "International Critical Tables," Vol. III, p. 126. ¹³ Wiig, *J. Physical Chem.*, 1930, **34**, 597. ¹⁴ Lamb and Marden, *J. Amer. Chem. Soc.*, 1911, **33**, 1873. ¹⁵ Freundlich and Bartels, *Z. physikal. Chem.*, 1922, **101**, 177. ¹⁶ Freundlich and Pape, *ibid.*, 1914, **86**, 458.

Even when we consider data measured at widely different temperatures (so that at any one temperature $\log k$ varies greatly), we are still subject to the influence that $\log k$ at the temperature of

measurement must lie within a comparatively narrow range. This is well borne out by Table I. By again re-arranging the Arrhenius equation we obtain

$$E/T \log_e B = R(1 - \log k/\log B) \quad . \quad . \quad . \quad (2)$$

In the table we have taken for T , T_m the mean temperature at which the measurements were made in each case, k_m being the corresponding velocity constant, and it will be seen that the quotient does not vary more than 10% about the mean value. Such an equation, containing as it does the purely arbitrary term T_m , cannot possibly have any real theoretical significance, though "empirically" its success is striking. This, of course, is only because data are "selected" by experimental convenience to give nearly constant values of $\log k_m$, together with the fact that these values are small compared with $\log B$, so that the factor $(1 - \log k/\log B)$ is never far from unity.

This arbitrary relation bears a suspiciously close resemblance to the formula put forward for unimolecular reactions by Syrkin (*Z. anorg. Chem.*, 1931, **199**, 28), viz., $\log B = E/C$, where C varies according to the type of reaction concerned, and, in fact, on the figures put forward, in a manner such that C is roughly proportional to T_m . It is true that in the earlier part of his paper Syrkin suggests an independent method of calculating C , but it is not shown whether this method was employed to determine the values given or whether they were simply chosen to suit the velocity measurements.

We conclude that the artificial selection imposed by experimental convenience entirely vitiates any attempt to make theoretical deductions from any "empirical" regularities of this nature which may be observed.

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