

The Absolute Rate of Reactions in Condensed Phases. A Criticism

E. A. MoelwynHughes

Citation: [The Journal of Chemical Physics](#) **4**, 292 (1936); doi: 10.1063/1.1749837

View online: <http://dx.doi.org/10.1063/1.1749837>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/4/4?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Semiclassical calculation of nonadiabatic thermal rate constants: Application to condensed phase reactions](#)

J. Chem. Phys. **124**, 114508 (2006); 10.1063/1.2178323

[On a Theory of Absolute Reaction Rates](#)

J. Chem. Phys. **47**, 1235 (1967); 10.1063/1.1712074

[Errata: The Absolute Rate of Reactions in Condensed Phases](#)

J. Chem. Phys. **4**, 740 (1936); 10.1063/1.1749779

[The Absolute Rate of Reactions in Condensed Phases](#)

J. Chem. Phys. **3**, 492 (1935); 10.1063/1.1749713

[The Absolute Rate of a Chemical Reaction](#)

J. Chem. Phys. **3**, 242 (1935); 10.1063/1.1749644



LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor

not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

The Absolute Rate of Reactions in Condensed Phases.¹ A Criticism

In the treatment of bimolecular reactions in solution, which forms the bulk of a recent publication by Wynne-Jones and Eyring¹ there appear two errors. It is the object of this letter to disclose them, and to show how their accidental cancelation has led to "entropy" values which, while possessing no physical significance, have escaped the fantastic magnitudes which they would have had if only one of the errors had been committed.

Omitting the transmission coefficient, κ , which is always assumed to be unity, the expression for the specific reaction rate is written

$$k' = e^{-\Delta H^\ddagger/RT} \cdot e^{\Delta S/RT} kT/h. \quad (1)$$

Combining this equation with the experimental relation

$$k' = Z \cdot e^{-E/RT} \quad (2)$$

enables Wynne-Jones and Eyring to calculate the "entropy of activation." We have repeated the calculations, and find values in substantial agreement, as shown by the results in Table I. Where small differences appear, they are due to the fact that we have calculated the results for specified temperatures at which the experiments were performed. The agreement, however, has been made possible only by following their steps closely, and thereby ignoring the facts that Eq. (1) is dimensionally incorrect, and that Eq. (2) gives results in the experimental units of liters per mole-second, rather than in the theoretical units of cc per molecule-second.

Eq. (1) is based on the following expression given by Wynne-Jones and Eyring for the equilibrium constant governing the formation of the complex;—

$$K^\ddagger = e^{-\Delta H^\ddagger/RT} \cdot e^{\Delta S/R}, \quad (3)$$

TABLE I.

REACTION	SOLVENT	T	Z	$-\Delta S^\ddagger$ (W.-J. & E.) (recalc.)
$\text{NH}_4^+ + \text{CNO}^-$	H_2O	326	4.27×10^{12}	0.9 0.9
$(\text{CH}_3)_2\text{CO} + \text{C}_2\text{H}_5\text{COOH}$	H_2O	298	1.12×10^7	26.7 26.3
$\text{CH}_3\text{I} + \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{NO}_2$	303	2.47×10^4	37.5 38.5
$\text{C}_2\text{H}_5\text{Br} + (\text{C}_2\text{H}_5)_3\text{N}$	C_6H_6	331	1.47×10^2	48.1 48.8

This expression is dimensionless, and is inconsistent with the other expressions

$$K^\ddagger = \frac{c^\ddagger}{c_1 c_2 \cdots c_i} \cdot \frac{\alpha^\ddagger}{\alpha_1 \alpha_2 \cdots \alpha_i} \quad (4)$$

and

$$K^\ddagger = (F_a'/F_n) \cdot e^{-E_0/kT} \quad (5)$$

which are also quoted in the paper, and which give (correctly) the equilibrium constant in terms of activities and of partition functions respectively. The satisfactory adjustment of Eq. (3) requires that we multiply the expression on the right-hand side by a volume term. A little consideration will show that, if we multiply it by the volume occupied by the complex (which we shall call $(4/3)\pi r^3$), the equation becomes dimensionally correct, and gives numerically the equilibrium constant in cc per molecule:

$$K^\ddagger = (4/3)\pi r^3 \cdot e^{-\Delta H^\ddagger/RT} \cdot e^{\Delta S/R}, \quad (3a)$$

Hence, to express the bimolecular velocity constant in cc per molecule-second, we must multiply Eq. (1) also by $(4/3)\pi r^3$;

$$k' = (4/3)\pi r^3 \cdot e^{-\Delta H^\ddagger/RT} \cdot e^{\Delta S/R} kT/h. \quad (1a)$$

To convert the experimental Eq. (2) into the same units, we must introduce the factor $1000/N_0$, where N_0 is the Avogadro number;

$$k' = (1000/N_0) \cdot Z \cdot e^{-E/RT}. \quad (2a)$$

The apparent success attending the theory of Wynne-Jones and Eyring is thus due to the circumstance that the ratio $(4/3)\pi r^3/1000/N_0$ is of the order of magnitude 1 for rational values of r . To make the ratio exactly 1, r would have to be 7.33Å. While this circumstance explains the order of magnitude of the "entropy" values calculated by Wynne-Jones and Eyring, it can confer no validity on their theory, which is fundamentally spurious.

E. A. MOELWYN-HUGHES

University Chemical Laboratory,
Cambridge, England,
October 5, 1935.

¹ W. F. K. Wynne-Jones and Henry Eyring, J. Chem. Phys. 3, 492 (1935).