

A Fallacy in Some Interpretations of the Quasi-Thermodynamics of Reaction Kinetics

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Abstract

The fact that experimentally determined 'volumes of activation' and 'entropies of activation' obey a relationship that is formally similar to one of Maxwell's thermodynamic relations is a mathematical consequence of the definitions of those quantities. Contrary to suggestions in the literature, it provides no evidence in support of the quasi-thermodynamic and equilibrium assumptions of the transition-state theory.

In the transition-state theory of reaction rates,¹ a 'volume of activation', ΔV^\ddagger , and an 'entropy of activation', ΔS^\ddagger , are defined as

$$-\Delta V^\ddagger = (\partial RT \ln k / \partial P)_T \quad (1)$$

$$\Delta S^\ddagger = (\partial RT \ln k / \partial T)_P - R[1 + \ln(k_B T / h)] \quad (2)$$

where P , T and R denote the pressure, absolute temperature and gas constant, respectively; k_B and h are Boltzmann's constant and Planck's constant, and k is the rate constant expressed in concentration units that are independent of P and T .²⁻⁴ In these relationships, it is assumed that the transmission coefficient¹ is unity. Equation (1) corresponds to equation (148), page 470, of Glasstone *et al.*,¹ and (2) is given by combining their formulae (166) and (178), pages 198 and 199.

A number of workers⁵⁻⁸ have measured reaction rate constants as functions of both pressure and temperature, and derived values of ΔV^\ddagger and ΔS^\ddagger and of their derivatives with respect to temperature and pressure, respectively. They have observed

¹ Glasstone, S., Laidler, K. J., and Eyring, H., 'Theory of Rate Processes' (McGraw-Hill: New York 1941).

² Guggenheim, E. A., *Trans. Faraday Soc.*, 1937, **33**, 607.

³ Hamann, S. D., in 'High Pressure Physics and Chemistry' (Ed. R. S. Bradley) Vol. 2, p. 163 (Academic Press: New York 1963).

⁴ Hamann, S. D., and le Noble, W. J., *J. Chem. Educ.*, 1984, **61**, in press.

⁵ Dickson, S. J., and Hyne, J. B., *Can. J. Chem.*, 1971, **49**, 2394.

⁶ Brauer, H.-D., and Kelm, H., *Z. Phys. Chem. (N.F.)*, 1972, **79**, 96.

⁷ Caldin, E. F., and Hasinoff, B. B., *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 515.

⁸ Tiltscher, H., and Wang, Y. K., *Z. Phys. Chem. (N.F.)*, 1976, **99**, 299; *High Temp.—High Pressures*, 1977, **9**, 529.

that the experimental values of the derivatives are approximately equal and opposite, that is, they conform quite well to the relationship

$$(\partial \Delta V^\ddagger / \partial T)_P = -(\partial \Delta S^\ddagger / \partial P)_T \quad (3)$$

which has a similar form to Maxwell's thermodynamic equality⁹

$$(\partial V / \partial T)_P = -(\partial S / \partial P)_T \quad (4)$$

where V and S denote the volume and entropy of a closed phase of constant composition. The authors^{5-7,10,11} have taken that resemblance, and the experimental near-agreement of the two derivatives of (3), to mean that the assumption made in the transition-state theory that thermodynamic equilibrium exists between the reactants and the transition-state species is probably correct. It has been said, for example, that the agreement 'supports the application of real state thermodynamics to kinetic systems';⁵ that it shows that 'the transition-state equations in their thermodynamic form are applicable... [and that] there is no indication of departure from the quasi-equilibrium assumptions of the transition-state theory';⁷ and that it is 'evidence for the existence of an equilibrium system and that no change of mechanism occurs over the investigated pressure and temperature ranges'.¹¹

If it were true that experimental conformity to (3) provided some thermodynamic justification of the transition-state theory, that would indeed be important. But it is not true. The equality (3) is simply a mathematical consequence of the definitions (1) and (2), and it *must* be obeyed unless the authors make arithmetical mistakes.

It is a property of partial differentials that the order of successive differentiations of a continuous function $z(x,y)$ is immaterial, so that

$$\left\{ \frac{\partial}{\partial x} \left(\frac{\partial z}{\partial y} \right) \right\}_y = \left\{ \frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x} \right) \right\}_x \quad (5)$$

In the present instance, we are concerned with relationships in which $x = T$ and $y = P$. If z is then the Gibbs function, G , of a system, and if we substitute in (5) the thermodynamic identities⁹

$$(\partial G / \partial P)_T = V \quad \text{and} \quad (\partial G / \partial T)_P = -S \quad (6)$$

we obtain Maxwell's relationship (4). If z denotes $RT \ln k$ and we insert the definitions (1) and (2) in (5), we obtain (3). But that result does not mean that $RT \ln k$ or ΔV^\ddagger or ΔS^\ddagger are thermodynamic quantities or even 'quasi-thermodynamic' ones. The quantity z could represent any property that depends upon P and T : it could, for instance, be the refractive index or the viscosity or the electrical conductivity of the system, which are neither thermodynamic nor equilibrium properties. They would all yield relationships analogous to (3) and (4), and these would all apply exactly.

⁹ Guggenheim, E. A., 'Thermodynamics' (North-Holland: Amsterdam 1967).

¹⁰ Kelm, H., and Palmer, D. A., in 'High Pressure Chemistry' (Ed. H. Kelm) p. 282 (D. Reidel: London 1978).

¹¹ Eldik, R. van, and Kelm, H., *Rev. Phys. Chem. Jpn.*, 1980, **50**, 185.

In short, equation (3) follows automatically from the definitions (1) and (2), so that it is hardly surprising that it is obeyed experimentally by quantities derived from (1) and (2). The fact that it applies proves nothing about thermodynamics or reaction mechanisms.*

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* This is equally true of a 'Maxwell relationship' involving the pressure derivative of the 'enthalpy of activation', ΔH^\ddagger :

$$(\partial \Delta H^\ddagger / \partial P)_T = \Delta V^\ddagger - T(\partial \Delta V^\ddagger / \partial T)_P$$

Some authors^{5,7} have found that their experimental results fit that expression and have taken this to be evidence supporting the quasi-thermodynamic assumptions of the transition-state theory, which it is not.