

'Acceleration' of Chemical Reactions

In a recent monograph on the thermodynamics of irreversible processes, Prigogine¹ has investigated in some detail the time variation of the entropy production (d_i^3S/dt^2). An examination of the implications of the general theory for the case of a chemical reaction leads to some interesting new concepts.

The entropy production at any particular time is given by

$$\frac{d_i S}{dt} = \frac{1}{T} A v \quad (1)$$

where T is the absolute temperature, v the reaction velocity at that moment and A the instantaneous affinity defined as $-\sum_i \nu_i \mu_i$ (ν_i is here the stoichiometric coefficient and μ_i the instantaneous chemical potential of the i^{th} component involved in the reaction). The coefficients ν_i are positive for products and negative for reactants.

On differentiation of equation (1)

$$\frac{d_i^3 S}{dt^2} = \frac{1}{T} (A \dot{v} + \dot{A} v) \quad (2)$$

where, in general, \dot{v} and \dot{A} represent differential coefficients with respect to time. We now propose to term the quantity \dot{v} the 'acceleration' of a chemical reaction. This conception is valid only when the reaction velocity is not constant; otherwise, of course, $\dot{v} = 0$.

Utilizing Prigogine's theorem that the contribution to the rate of change of the entropy production per unit time by the rate of change of the generalized 'force' is equal to the contribution due to the 'acceleration', we obtain from equation (2)

$$A \dot{v} = \dot{A} v \quad (3)$$

The reaction velocity v may be expressed as the rate of change of the 'degree of advancement' of the chemical reaction, ξ . Thus,

$$v = \frac{d\xi}{dt} \quad \text{and} \quad \dot{v} = \frac{d^2\xi}{dt^2}$$

$d\xi = dn_i/\nu_i$, where n_i is the mole number of the i^{th} component.

The affinity A is a function of the variables of state p (pressure), T (temperature) and ξ . At constant pressure and temperature,

$$\dot{A} = \left(\frac{\partial A}{\partial \xi} \right)_{p,T} \frac{d\xi}{dt}$$

and equation (3) becomes

$$A \dot{v} = \left(\frac{\partial A}{\partial \xi} \right)_{p,T} v^2$$

Hence,

$$\dot{v} = \left(\frac{\partial \ln A}{\partial \xi} \right)_{p,T} v^2 \quad (4)$$

It is this equation (4) that provides us with an explicit relation for the 'acceleration' of a chemical reaction.

In addition, Prigogine has established a general theorem which, for our purposes, may be expressed as

$$v \dot{A} \leq 0 \quad (5)$$

or by

$$v^2 \left(\frac{\partial A}{\partial \xi} \right) \leq 0$$

However, since v^2 is always a positive quantity, the above relation implies that

$$\left(\frac{\partial A}{\partial \xi} \right)_{p,T} \leq 0$$

that is, the affinity decreases during the course of a chemical reaction and, at equilibrium, $A = 0$ —a result well known to workers in chemical thermodynamics.

Moreover, extending the foregoing theory, we find, from equations (3) and (5),

$$A \dot{v} \leq 0 \quad (6)$$

and the 'acceleration' of a chemical reaction has, in general, the opposite sign to the affinity.

These results may easily be generalized to several simultaneous, accelerated reactions by following the usual methods as outlined by Prigogine.

To sum up: some of the basic properties of the newly defined 'acceleration' of a chemical reaction—equation (4)—have here been developed for those cases where Prigogine's theorems are applicable, that is, under certain restrictive conditions indicated in his work.

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¹ Prigogine, I., "Introduction to Thermodynamics of Irreversible Processes" (Charles C. Thomas, Springfield, Illinois, 1955).

'Macrocrystalline' Carbon

FROM a mathematical analysis of the X-ray diffraction patterns of products obtained at various stages during the graphitization of carbon, Franklin¹, and later Houska and Warren², have shown that only two carbon interlayer spacings are possible: 3.35 Å. for the orientated stacking in graphite, and 3.44 Å. for the random orientation of the planes in carbon. Precise measurement of the interlayer spacing of cokes and carbons is not possible because of the very diffuse nature of the diffraction maxima, and it is therefore of interest to report that 'macrocrystalline' carbon with an interlayer spacing of 3.45 Å. has been prepared by sublimation of artificial graphite under high vacuum. The material, as deposited, has a nodular surface with a grey metallic sheen. It has a low porosity, a hardness of between 1 and 2 on the Moh scale (compared with a value of less than 1 for graphite) and a true density of 2.22. The carbon content is greater than 99 per cent and the ash less than 0.4 per cent. The carbon planes of the individual crystallites are found to lie very approximately