Time Variation of Chemical Affinity

IN two previous communications[1,2] we have shown that an accelerated chemical reaction is always characterized by the variation of the chemical affinity of the system with time. For a reaction with constant velocity this time derivative would, of course, be zero. In this communication we shall consider further the properties of the function $\dot{A} \equiv (dA/dt)$. A is the instantaneous chemical affinity defined by

$$A = -\sum_i \nu_i \mu_i \qquad (1)$$

In this equation, ν_i is the stoichiometric coefficient, and μ_i is the instantaneous chemical potential of the ith component. Since this potential is a function of the activity of the particular substance, it will vary with concentration, and hence with time. Bearing this in mind, we can now differentiate equation (1) with respect to time :

$$\dot{A} = -\sum_i \nu_i \dot{\mu}_i \qquad (2)$$

Throughout this discussion the pressure and temperature will be assumed constant.

Utilizing the definition of μ_i in terms of the activity coefficient[3]

$$\mu_i = \mu_i^0 + RT \ln a_i$$

where a_i is the activity of the component i and μ_i^0 is the chemical potential of this substance in the arbitrary standard state, we obtain

$$\dot{\mu}_i = RT \, d/dt(\ln a_i)$$

By substitution in equation (2) we have

$$\dot{A} = -RT \sum_i \nu_i \, d/dt(\ln a_i) \qquad (3)$$

This equation can alternatively be established from the relation[3] between the affinity and the equilibrium constant K :

$$A = RT \ln K - RT \ln \prod_i a_i^{\nu_i}$$

Differentiating this relation with respect to time, we get

$$\dot{A} = -RT \, d/dt \, (\ln \prod_i a_i^{\nu_i})$$
$$= -RT \, d/dt(\sum_i \nu_i \ln a_i)$$
$$= -RT \sum_i \nu_i \, d/dt(\ln a_i) \qquad (3a)$$

If the behaviour of the substances participating in the reaction tends to ideality, we may replace activities by concentrations (that is, the activity coefficient can be regarded as unity for our purposes). Thus,

$$\dot{A} = -RT \sum_i \nu_i \, d/dt(\ln c_i)$$

where c_i is the concentration of the ith component at any instant. As an approximation, therefore, we arrive at $\dot{A}$ from the experimental observation of the change of $(\ln c_i)$ with time. We should note, of course, that the rate of change of concentration with time is related to the reaction velocity, but in the case of the accelerated reaction under consideration the velocity has different values with successive instants of time.

For the sake of completeness we can show how the acceleration of a chemical reaction may be related to the time variation of the chemical affinity.

We can define the acceleration and velocity of a chemical reaction by

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

where $d\xi = dn_i/\nu_i$ (n_i is the mole number of the ith component). Previously[1] we formulated the relation

$$\dot{v} = (\dot{A}/A)v$$

which, in terms of equation (3), becomes

$$\dot{v} = \frac{-RT \sum_i \nu_i \, d/dt(\ln a_i)}{RT \ln K - RT \ln (\prod_i a_i^{\nu_i})} v$$
$$= \frac{-\sum_i \nu_i \, d/dt(\ln a_i)}{\ln K - \ln(\prod_i a_i^{\nu_i})} v$$

or approximately,

$$\dot{v} = \frac{-\sum_i \nu_i \, d/dt(\ln c_i)}{\ln K - \ln(\prod_i c_i^{\nu_i})} v \qquad (4)$$

However, from the experimental point of view it is much simpler to obtain the acceleration directly from the definition

$$\dot{v} = \frac{d^2\xi}{dt^2} = \frac{1}{\nu_i} \frac{d^2 n_i}{dt^2} = \frac{1}{\nu_i} \frac{d^2(Vc_i)}{dt^2} \qquad (5)$$

where V is the volume. Equation (5) implies that data for only one reactant are required to compute the acceleration. Equation (4) can thus claim no heuristic value, but is relevant to our discussion as a merely theoretical deduction.

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[2] Yourgrau, W., and Raw, C. J. G., *Nuovo Cimento*, 5, Supp. 3, 472 (1957).
[3] Prigogine, I., and Defay, R., "Chemical Thermodynamics" (Longmans, Green and Co., London, 1954).

Complex Formation between Groundnut Skin Pigments and Conarachin II

WHEN defatted groundnut meal containing a portion of the red skins of the nut was extracted with 10 per cent (w/v) sodium chloride solution and the extract dialysed against phosphate–sodium chloride buffer, ionic strength I 0·5, pH 8, the sedimentation-velocity diagram (Fig. 1a) revealed the presence of three components : arachin, the major component (sedimentation constant, $s^\circ_{20} = 13\cdot3$ S., conarachin II ($s^\circ_{20} = 8\cdot4$ S.) and conarachin I ($s^\circ_{20} \approx 2$ S.)[1]. When the extraction was carried out at pH 8–9 with sodium hydroxide, the solution was considerably more red in colour, the conarachin II component was less apparent, and the presence of a fourth, very fast sedimenting component ($s^\circ_{20} = 32$ S.) was observed (Fig. 1b). This fast component was absent, however, in extracts of blanched nuts or white skinned nuts. It would therefore appear to be connected with the presence of the red skin pigments in the meal.

The addition of calcium chloride (4 gm./l.) was found to precipitate most of the protein from a pH 8–9 extraction liquor leaving the colour in the supernatant liquor. When the latter was saturated with ammonium sulphate, the remaining protein precipitated along with the red pigment leaving an