

that is being investigated. The mass-flowmeter has yet to be examined as has the constancy of the humidity.

The control of air temperature and the generation of the sinusoidal temperatures are achieved by magnetic amplifiers, controlled, via DC amplifiers, by the error signals from resistance thermometers. The reference signal for the sine-wave generator comes from a sine-cosine potentiometer. The resistance thermometers give average values of temperature across the tube: the radial distributions of temperature and velocity have not yet been investigated. The control of the air temperature is expected to be improved, both as regards the temperature limits and the span of time, when the apparatus is reassembled in its vacuum-jacketed tube.

It is hoped to present the mathematics more fully and to give results exemplifying the accuracy of the method after it has been applied to materials of known thermal properties.

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The fundamental arbitrariness in stoichiometry

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IN A RECENT communication (this journal, 17 573 1962) PINGS has called attention to the value of some convention for the stoichiometric coefficients in a reaction and suggested that the sum of their moduli should be one. Such a convention would indeed be valuable though the prospects of its commanding the allegiance of chemists and engineers of all types are remote. Perhaps it is more important to notice the essential ambiguity which must be present in the description of any system of chemical reactions. Thus a reaction

$\sum_{i=1}^S \alpha_i A_i = 0$ is only defined up to a constant factor and this may be chosen to make the α_i (a) mutually prime integers, (b) rationals with $\sum_{i=1}^S |\alpha_i| = 1$, (c) reals with $\sum_{i=1}^S \alpha_i^2 = 1$, or what you will.

The set of R simultaneous independent reactions $\sum_{i=1}^S \alpha_{ji} A_i = 0$ is arbitrary up to any non-singular transformation $\bar{\alpha}_{ki} = \sum_{j=1}^R \beta_{kj} \alpha_{ji}$, $k = 1, \dots, R$ and $\det \beta_{kj} \neq 0$.

All formulae for concentration changes, equilibrium, etc., can be converted from the reaction system $\sum \alpha_{ji} A_i = 0$ to $\sum \bar{\alpha}_{ki} A_i = 0$ without difficulty. For example, if the equilibrium constant of the j^{th} reaction of the first set is K_j

$$\prod_{i=1}^S c_i^{\alpha_{ji}} = K_j$$

the equilibrium constants of the transformed reactions are

$$K_k = \prod_{i=1}^S c_i^{\bar{\alpha}_{ki}} = \prod_{j=1}^R K_j^{\beta_{kj}}$$

Far-fetched though it may seem, there are some conceptual and practical advantages to making the sum of the squares of the stoichiometric coefficient equal to one and making independent reactions orthogonal. This is done by the

Schmidt orthogonalization process. Take the first reaction and normalize the coefficients α_{1i} by dividing by the square root of the sum of their squares, $\bar{\alpha}_{1i} = \alpha_{1i}/(\sum \alpha_{1i}^2)^{1/2}$. Let

$$\gamma = \sum_{i=1}^S \alpha_{2i} \bar{\alpha}_{1i}$$

and put

$$\alpha'_{2i} = \alpha_{2i} - \gamma \alpha_{1i}.$$

Then

$$\sum_{i=1}^S \alpha'_{2i} \alpha_{1i} = 0$$

and we can put

$$\bar{\alpha}_{2i} = \alpha'_{2i}/(\sum \alpha'_{2i}^2)^{1/2}.$$

Similarly if

$$\sum_{i=1}^S \alpha_{3i} \bar{\alpha}_{1i} = \gamma_1$$

and

$$\sum_{i=1}^S \alpha_{3i} \bar{\alpha}_{2i} = \gamma_2$$

then

$$\alpha'_{3i} = \alpha_{3i} - \gamma_1 \bar{\alpha}_{1i} - \gamma_2 \bar{\alpha}_{2i}$$

is orthogonal to both $\bar{\alpha}_{1i}$ and $\bar{\alpha}_{2i}$ may be normalized to give $\bar{\alpha}_{3i}$. In this way an orthonormal set of reactions is obtained. In the same way a set of $(S-R)$ orthonormal vectors which are orthogonal to all the reactions may be obtained by starting with an arbitrary vector which is not dependent on any of the preceding ones and continuing the Schmidt process. For example take $\alpha_{R+1,1} = 1$, $\alpha_{R+1,i} = 0$,

$i = 2, \dots, S$ and form $\alpha'_{R+1,i} = \alpha_{R+1,i} - \sum_{j=1}^R \alpha_{ji} \bar{\alpha}_{ji}$. This is orthogonal to all the preceding R vectors $\bar{\alpha}_{ji}$, $j = 1, \dots, R$ and may be normalized to $\bar{\alpha}_{R+1,i}$. This process may be continued until a set of S^2 coefficients $\bar{\alpha}_{ji}$ is obtained; $\bar{\alpha}_{ji}$ is the stoichiometric coefficient of A_i in the j^{th} reaction,

$j = 1, \dots, R$ and $\bar{\alpha}_{ki}$, $k = R+1, \dots, S$ is the coefficient of A_i in the k^{th} invariant of the reaction. An invariant of the reaction, as will be seen below, is a linear combination of the reacting species whose composition does not change during reaction.

Having demonstrated the process by which a set of reactions may be orthonormalized let us drop the bar and assume from now on that the reactions are $\sum_{i=1}^S \alpha_{ji} A_i = 0$, $j = 1, \dots, R$ and that $\sum_{i=1}^S \alpha_{ji} \alpha_{li} = \delta_{jl}$ ($\delta_{jl} = 0$, $j \neq l$; $\delta_{jl} = 1$, $j = l$). Further let α_{ki} , $k = R+1, \dots, S$ be the orthonormal extension of the reactions $\sum_{i=1}^S \alpha_{ki} \alpha_{mi} = \delta_{km}$, $k = R+1, \dots, S$, $m = 1, \dots, S$. If n_i denote the number of moles of A_i present at any instant and n_{i0} the number present at some reference time t_0 . Then

$$n_i = n_{i0} + \sum_{j=1}^R \alpha_{ji} \xi_j$$

where the ξ_j are the extents or degrees of advancement of the several reactions. The quantity

$$\eta_k = \sum_{i=1}^S \alpha_{ki} n_i, \quad k = R+1, \dots, S,$$

is constant during reaction, for

$$\eta_k = \sum_{i=1}^S \alpha_{ki} (n_{i0} + \alpha_{ji} \xi_j) = \sum_{i=1}^S \alpha_{ki} n_{i0} = \eta_{k0}$$

It remains to show that values ξ_{j0} of the extents at time t_0 can be chosen to give

$$c_i = \sum_{j=1}^R \alpha_{ji} \xi_{j0} + \sum_{k=R+1}^S \alpha_{ki} \eta_{k0}.$$

But this is possible for if $l = 1, \dots, R$

$$\sum_{i=1}^S \alpha_{li} c_i = \sum_{i=1}^S \alpha_{li} \sum_{j=1}^R \alpha_{ji} \xi_{j0} = \sum_{j=1}^R \delta_{jl} \xi_{j0} = \xi_{l0}.$$

Hence the initial values of the extents and invariants are

$$\xi_{j0} = \sum_{i=1}^S \alpha_{ji} c_{i0} \quad \text{and} \quad \eta_{k0} = \sum_{i=1}^S \alpha_{ki} c_{i0}.$$

The practical advantage of orthonormal reactions is that the book-keeping of conversions between concentrations and extents and invariants is very simple. The conceptual advantage is that it gives normal basis in each subspace and clearly shows the division between them. It is still an arbitrary convention even within itself for any rotation that leaves the two subspaces separate is of the same type. It would be possible to dispense with the orthonormalization but then the conversion between concentration and extent would be rather messy.

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Mass transfer in a stirred vessel extractor

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RECENTLY, OLANDER [1] has calculated the rate of liquid-liquid extraction in a model stirred vessel. The model was a vertical cylindrical vessel containing approximately equal volumes of the two liquid phases, each stirred by means of a rotating stirrer bar. The rates of stirring of the two phases were considered to be within the limits set by the necessity to maintain uniform bulk concentration and a quiescent interface.

Olander defined two parts of the interface, viz.: the core, which is within the vertically projected sweep of the stirrer bars, and the annulus, which is outside the projected sweep. Briefly, his conclusions—based on a simplified theoretical model—were that no steady state mass transfer can occur across the interface in the core region and that the apparent mass transfer coefficient per unit area, k , was given by

$$k/\nu = f \cdot a \cdot (\omega/\nu)^{1/2} \cdot \text{Sc}^{-2/3} \quad (1)$$

The apparent mass transfer coefficient can be related to experimental data or to the true mass transfer coefficient (i.e. mass transfer per unit effective area) only if it is assumed that the area over which transition from annulus conditions to core conditions occurs is negligible. Before such an assumption can be accepted it is clearly essential either to refine the theory to include the transition region or to provide experimental justification for the theory as it stands.

In a research into the kinetics of liquid-liquid extraction of metals we have used a cell which is similar to the model

cell of Olander. The cell was a vertical glass cylinder of height 8.0 cm and i.d. 8.9 cm. The two phases used were aqueous and kerosene solutions of equal volume and they were stirred by means of contra-rotating disks in order to minimize surface oscillations. The disks were 6.3 cm dia., 0.12 cm thick and were situated 1.5 cm from the interface. The hydrodynamics of this cell differ from those of the model cell in that there are two regions of flow in each phase—above and below the disk. Uniformity of concentration was maintained throughout the bulk of each phase, presumably by diffusion and turbulence at the boundary between the two flow regions. Various regions of the interface were investigated by blanking off the remaining area with a stationary disk or ring of 0.12 cm thickness. The disk was 3.8 cm dia. and the ring was 5.1 cm i.d. and the same external diameter as the cylinder.

The process investigated was the extraction of 8-hydroxyquinoline (oxine) from aqueous solutions buffered at pH = 7.5 into kerosene. The initial concentration of oxine was 0.0032 M and the rate of extraction was followed by spectrophotometric analysis of samples of the kerosene phase. The rate was directly proportional to the concentration of oxine in the aqueous phase as expected since the distribution coefficient (kerosene/water) was found to be greater than 100. At a stirring speed (both disks) of 79 rev/min the influence of the area and position of the interface with respect to the rotating disks was investigated. The interfacial areas