Applications of ebullioscopic methods have, until recently, been limited to the determination of molecular weights [1-3] and other physical constants [6], the control of solvent purities [4], and the study of liquid—vapor equilibria [5]. The lack of sensitivity in the experimental methods left something to be desired in the accuracy of the results obtained in this earlier work. The refinement of experimental techniques and the elimination of background effects [7] has led to the development of apparatus permitting rapid, and highly precise, measurements on processes occurring in extremely dilute solutions. By combining ebullioscopic methods with ebulliographic recording, it is possible to obtain time curves reflecting the course of such processes.

In general, the ebulliogram is an integral curve (Fig. 1) obtained by plotting the increase in solution boiling point resulting from successive introduction of g\textsubscript{i} charges of molecular weight M into the ebulliometer. Each recorded ordinate in such plot is given by

\[ Y_i = \frac{Q_i}{M} = QA_i \]  

(1)*

where \( A_i \) is the number of moles of the dissolved substance; the movement of the recorder pen is proportional to the number of dissolved particles in solution, regardless of their structure and composition.

\[ Y = Q[(A_1 + A_2 + \ldots + A_n) + (B_1 + B_2 + \ldots + B_m)] = Q(\Sigma A_i + \Sigma B_j) \]  

(2)

It is customary to fix attention on that portion of the ebulliogram over which the boiling point of the solution is constant under stationary values of the concentrations and number of dissolved particles in the system. A change in the concentration resulting from solute dissolution is followed by the recording of a nonstationary process which is due, in part, to the increase in the number of dissolved particles in the solution and, in part, to transient processes in the measuring system. Assuming that the transient section of the curve can furnish information concerning the state of the solution, the attempt has been made to interpret the ebulliogram describing the processes initiated by alteration in the total number of dissolved particles in the system. Since the modern ebulliograph has a time constant of something less than 0.5 min, recording lag should have no effect on the study of reactions with half-life periods in excess of 3 min.

Many physical processes (sorption from solution by solids or insoluble liquids, distribution between liquid and vapor phases, dissolution, etc.) and chemical processes (addition and polymerization reaction, depolarization, acylation of cyclic systems) proceed with alteration in the number of dissolved particles.† No difficulty attends the interpretation of ebulliograms for physical processes since these record the change in concentration of a single dissolved solute.

It is not so obvious as to how one is to interpret ebulliograms for chemical reaction systems which contain both reactants and reaction products.

Let us analyze the general case in which two compounds A and B enter into reaction through a scheme such as \( aA + bB \rightarrow pP \), which entails an alteration, \( p/(a+b) \neq 1 \), of the total number of particles; \( a \), \( b \), and \( p \) being

* \( Q \) is the instrument factor, determined experimentally and defined as \( RT_0^2S/L_0\rho_0\nu_0 \), (mass/mole), where \( T_0 \) is the boiling point of the solvent, in °K; \( \nu_0 \) is the volume of the solvent, in ml; \( \rho_0 \) is the solvent density in g/ml; \( L_0 \) is the latent heat of vaporization, in cal/g; \( R \) is the molar gas constant, in cal/mole·deg; and \( S \) is the absolute sensitivity, in mm/deg.

† Condensation processes which proceed stoichiometrically, without change in the number of particles but with the formation of a product which is volatile and escapes or precipitates, or is removed from solution in some other way, should also be included here.


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Fig. 1. Integral ebulliogram. The arrows indicate the points of introduction of masses $g_{al}$-$g_{a2}$ and $g_{b1}$-$g_{b5}$ of A and B into the system. $\tau_0$ marks the time at which reaction was initiated by introducing $g_q$ grams of the catalyst into the system. $Y_A = f(\tau)$ is the equation for the resulting reaction curve.

stoichiometric coefficients, $P$ the reaction products, and $[A_1]$ and $[B_1]$ the initial concentrations of A and B, respectively. The introduction of a small amount of a catalyst into the system at time $\tau_0$ will give rise to a process resulting in an alteration in the total number of particles, the ebulliogram assuming the form shown in Fig. 1. Let us assume that amount $[P]$ of reaction products has been formed at time $\tau$, the concentrations of A and B falling by $(a/p)[P]$ and $(b/p)[P]$, respectively. The change in the overall solution concentration ($\Delta C$), the factor determining the shift in the boiling point on the curve section following initiation of reaction, is given by

$$\Delta C = [P] - (a/p)[P] - (b/p)[P] = -\{(a + b)/p - 1\}[P] \quad (3)$$

Multiplying each side of this equation by $Qv_0$, one has

$$Y_A = -Qv_0\left(\frac{a + b}{p} - 1\right)[P] \quad (4)$$

a formula relating the alteration in the ordinate on the ebulliogram with the concentration of the reaction products. This change in ordinate will be negative for processes in which $(a+b)/p < 1$, and the total number of particles diminishes, and positive for processes for which $(a+b)/p > 1$. Reactant concentrations at any point can be calculated from the equations

$$Y_A = \left(\frac{p - b}{a} - 1\right)(Y_A - Qv_0[A]) \quad [A] = \frac{Y_A - Y^A\left(\frac{p - b}{a} - 1\right)}{Qv_0} \quad (5)$$

$$Y_B = \left(\frac{p - a}{b} - 1\right)(Y_B - Qv_0[B]) \quad [B] = \frac{Y_B - Y^B\left(\frac{p - a}{b} - 1\right)}{Qv_0} \quad (6)$$

Fig. 2. Ebulliogram for a polymerization reaction.

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