NOTES

A Convenient Thermostat Heater.—A dependable thermostat heater that does not emit any light, that is perfectly insulated from the bath and that does not corrode and render the water turbid, became necessary in the work of the author. The usual lamps and metallic heating coils failed to meet one or more of these requirements. A capillary thread of mercury worked very successfully on an A. C. line stepped down by a toy transformer, but it was found impractical to make a mercury resistance high enough to go across a 110-volt D. C. line directly. Accordingly, a new heater had to be developed.

The following device met all these needs very satisfactorily. A Pyrex tube about 40 cm. long and 3 mm. bore was bent into a U and filled with fine flake graphite packed tightly by tapping. Contact was made by means of pieces of copper rod, the ends of which were turned down to conical points to increase the area of contact with the graphite and which were held in place by means of spring leads from the binding posts as indicated (see Fig. 1). A heater of these approximate dimensions, now in use, was found to have a resistance of 270 ohms and accordingly has a heating capacity of 45 watts when put on the 110-volt line. On testing the regulation with a Beckmann thermometer, the heater was found to go on and off regularly in an interval of 0.012°. It would be difficult to distribute this lag between the lag of the heater, the stirring, or the sensitivity of the mercury regulator used. In any case, as this degree of regulation was quite ample for the work in hand, no attempt was made to improve it.

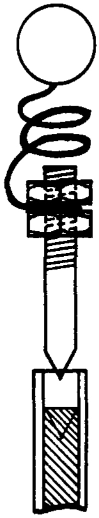

Fig. 1.

This graphite heater is easily made, has given excellent service under the conditions indicated above, and should find application wherever a heater fulfilling these requirements is desirable.

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The Computation of Partial Molal Quantities of Binary Solutions.—The method here developed will be particularly useful in those cases in which great accuracy is desired. For a general discussion of partial molal quantities and methods of their calculation the reader is referred to the work of Lewis and Randall.[1]

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

Let G be any extensive property of a system consisting of n_1 moles of A and n_2 moles of B. The mole fraction, N_1, of constituent A is $n_1/(n_1 + n_2)$, and similarly for N_2. The molal value, G, of an extensive property of the system is by definition

$$\mathrm{G} = G/(n_1 + n_2) \tag{1}$$

The corresponding molal quantities of the pure constituents are obtained by equating n_2 or n_1 to zero, respectively. Let us note that

$$n_1 = \mathrm{N}_1 n_2/\mathrm{N}_2 \tag{2}$$

The variation of the molal values may be considered as due solely to the change in the number of moles of one of the constituents, the amount of the second constituent being considered constant. Differentiating Equations 1 and 2, respectively, we obtain

$$(\mathrm{d}G)_{n_2} = \mathrm{G}\mathrm{d}n_1 + (n_1 + n_2)\mathrm{dG} \tag{3}$$

$$\mathrm{d}n_1 = n_2\mathrm{dN}_1/\mathrm{N}_2^2 \tag{4}$$

By definition

$$\bar{\mathrm{G}}_1 = \mathrm{d}G/\mathrm{d}n_1 \tag{5}$$

$$= \mathrm{G} + (n_1 + n_2)\mathrm{dG}/\mathrm{d}n_1 \tag{6}$$

We will now define a new function,

$$\Delta = \mathrm{G} - (\mathrm{N}_1\mathrm{G}_1 + \mathrm{N}_2\mathrm{G}_2) \tag{7}$$[2]

from which

$$\mathrm{dG} = \mathrm{d}\Delta + \mathrm{G}_1\mathrm{dN}_1 + \mathrm{G}_2\mathrm{dN}_2 \tag{8}$$

Substituting the values of G and dG from Equations 7 and 8 into Equation 6 and simplifying,

$$\bar{\mathrm{G}}_1 = \mathrm{G}_1 + \Delta + \mathrm{N}_2\frac{\mathrm{d}\Delta}{\mathrm{dN}_1} \tag{9}$$

By means of Equation 9 we may obtain the partial molal quantities from the directly measured molal quantities and a correction term that is small for all solutions that are approximately perfect. The graph of Δ, calculated from the directly measured molal quantities against mole fraction, will in general have one of the following three forms (Fig. 1). (From its definition Δ will be zero for $\mathrm{N} = 0$ or 1.) The intercept of the tangent to the curve on the axis of the pure constituent is the difference between the partial molal value and the molal value for the constituent chosen at the

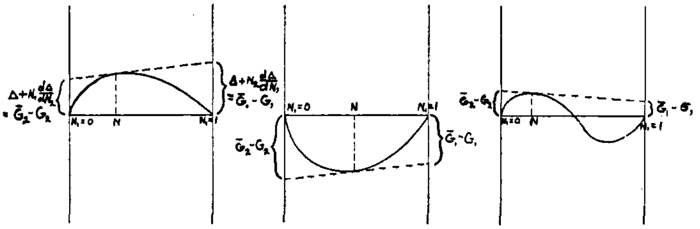

Fig. 1.

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[2] In certain cases it may be desirable to take an arbitrary constant in place of G_2.

mole fraction of the point of tangency. This is indicated in the above diagrams.

An accuracy greater than the practicable limit of the previous method may be obtained by the following continuation, if the accuracy of the original data is sufficient to warrant it. Let $y = f(\mathrm{N})$ be an analytical curve which fits that of $\Delta = f(\mathrm{N})$ fairly closely. Treating the deviation $\Delta' = \Delta - y$, in the same way as before, we obtain the equation

$$\overline{\mathrm{G}}_1 = \mathrm{G}_1 + (y + \mathrm{N}_2\, dy/d\mathrm{N}_1) + (\Delta' + \mathrm{N}_2\, d\Delta'/d\mathrm{N}_1) \qquad (10)$$

Equation 10 gives the partial molal value as the sum of the directly measured molal value, a readily computed term, and a quantity which as before can be obtained graphically.

Contribution from the Chemical
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The Saponification of Ethyl Acetate.—It was found that F. Thomas[1] had reported that the velocity of saponification of ethyl acetate by barium hydroxide in aqueous solution is influenced by light. Although the data reported seemed too inaccurate for acceptance, it was desired to ascertain if such variation of intensity of light as may be expected in a laboratory illuminated by diffuse daylight has any effect on the rate of hydrolysis of ethyl acetate in aqueous sodium hydroxide solution. Accordingly, measurements were carried out by me as follows. The technique and apparatus described in a previous paper[2] were used except that in the first experiment and in each alternate experiment thereafter, the container of the reaction mixture was wrapped in tin foil and the operations of mixing the reagents and of removing the samples of the mixture for analysis were carried out with a dim ruby lamp as the only source of illumination. The respective concentrations of ester and sodium hydroxide were 0.008 and 0.01. The average coefficient found for the reaction in darkness (ten experiments) was 6.77 at 25.00°. The average (eight experiments) for the reaction in diffuse daylight was also 6.77 at 25.00°. It was, therefore, established that variations of intensity of diffuse daylight such as may occur under varying laboratory conditions have no effect on the rate of the reaction in question.

Contribution from the
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[1] Thomas, *Diss.*, Freiburg i/Br., Speyer and Kraener, **1908**.

[2] Terry and Stieglitz, This Journal, **49**, 2216 (1927).