not in accord with the best data, the following values based on results of the present investigation and on the most dependable results given in the literature are suggested for adoption: melting point, 166.05°; specific rotation $[\alpha]_{E}^{25°} = -0.244° \pm 0.002$ and $[\alpha]_{D}^{25°} = -0.208 \pm 0.002$ (calculated); density 1.48_7 (room temperature), specific heat $C_{(28-100°)} = 0.327_7$ cal./deg. and $C_{(14-26°)} = 0.31_5$ cal./deg.; heat of combustion, 4.00° cal./gram.

The writer wishes to acknowledge his indebtedness to Dr. E. W. Washburn under whose direction this investigation was made.

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THE CALCULATION OF THE TEMPERATURE COEFFICIENT OF THE DISTRIBUTION RATIO.

BY F. H. MACDOUGALL.

Received July 10, 1919.

The present communication owes its origin to a recent paper[1] by Forbes and Coolidge dealing with the system water, ether and succinic acid and contains some new relations between various functions of the variables of ternary systems not contained in their article and, in particular, new additional relationships between the various partial derivatives to be defined later. The authors determined the composition of a large number of solutions both unsaturated and saturated with respect to various components. They use the following system of symbols:

s = mole fraction of succinic acid in water layer.
e = mole fraction of ether acid in water layer.
w = mole fraction of water acid in water layer.
σ = mole fraction of succinic acid in ether layer.
ω = mole fraction of water acid in ether layer.
ϵ = mole fraction of ether acid in ether layer.

The distribution ratio is $R = s/\sigma$ and the temperature coefficient is $\frac{dR}{dt} = \frac{1}{\sigma}\frac{ds}{dt} - \frac{s}{\sigma^2}\frac{d\sigma}{dt} = \frac{1}{\sigma}\left(\frac{ds}{dt} - R\frac{d\sigma}{dt}\right)$.

The authors put $\left(\frac{ds}{de}\right)_t = a$, $\left(\frac{ds}{dt}\right)_e = b$, $\left(\frac{de}{ds}\right)_t = m$, and $\left(\frac{de}{dt}\right)_s = n$. Then since $\frac{ds}{dt} = \left(\frac{ds}{dt}\right)_e + \left(\frac{ds}{de}\right)_t\frac{de}{dt} = b + a\frac{de}{dt}$ and $\frac{de}{dt} = \left(\frac{de}{dt}\right)_s + \left(\frac{de}{ds}\right)_t\frac{ds}{dt} = n + m\frac{ds}{dt}$ they obtain $\frac{ds}{dt} = \frac{b + an}{1 - am}$. Similarly they obtain $\frac{d\sigma}{dt} = \frac{\beta + \alpha\nu}{1 - \alpha\mu}$, where $\alpha = \left(\frac{d\sigma}{d\omega}\right)_t$, $\beta = \left(\frac{d\sigma}{dt}\right)_\omega$, $\mu = \left(\frac{d\omega}{d\sigma}\right)_t$ and $\nu = \left(\frac{d\omega}{dt}\right)_\sigma$.

[1] THIS JOURNAL, 41, 150 (1919).

They thus arrive at the following relationship for the temperature coefficient: $\frac{dR}{dt} = \frac{b + an}{\sigma(1 - am)} - \frac{s}{\sigma^1}\left(\frac{\beta + \alpha v}{1 - \alpha\mu}\right)$

Now, at first glance, the reader is surprised to see $\left(\frac{ds}{de}\right)_t$ put equal to a and $\left(\frac{de}{ds}\right)_t$ put equal to m and not equal to $\frac{1}{a}$. The reason of course is that the two derivatives in question refer to different curves representing different series of solutions. Otherwise $1 - am$ would equal zero and so would $(b + an)$ equal zero and the ratios would be indeterminate. It seemed to the present writer worth while to put the mathematical relations on a clearer and more definite basis, so that the student might see at once the particular set of solutions or the particular curve to which each partial derivative refers. With that end in view let us adopt the following scheme of symbols for the ternary system water, ether and succinic acid:

Water Layer.

s_1 = mole fraction of acid in water layer, saturated with acid but not with ether.

e_1 = mole fraction of ether in water layer, saturated with acid but not with ether.

s_2 = differs from s_1 in that the solution is saturated with ether but not with acid.

e_2 = differs from e_1 as s_2 differs from s_1.

s_s and e_s refer to acid and ether in solutions saturated with both.

Ether Layer.

σ_1 and ω_1 = mole fractions of acid and water, respectively, in ether layer saturated with acid but not with water.

σ_2, ω_2, σ_s, ω_s have meanings which are almost self-evident.

We have the following functional equations: $s_1 = f_1(t,e_1)$ and $s_2 = f_2(t,e_2)$, represented at a fixed temperature, t, by two curves which intersect at a point where s_1 and s_2 become s_s and e_1 and e_2 become e_s. We can express these results as follows: $s_s = \lim\limits_{e_1 = e_s} f_1(t,e_1) = \lim\limits_{e_2 = e_s} f_2(t,e_2) = f_3(t) = f_4(e_s)$. Similarly we could write $\sigma_1 = \varphi_1(t,\omega_1)$; $\sigma_2 = \varphi_2(t,\omega_2)$ and $\sigma_s = \lim\limits_{\omega_1 = \omega_s} \varphi_1(t,\omega_1) = \lim\limits_{\omega_2 = \omega_s} \varphi_2(t,\omega_2) = \varphi_3(t) = \varphi_4(\omega_s)$. And finally, $\frac{ds_s}{dt} = \lim\limits_{\substack{s_1 = s_s \\ e_1 = e_s}}\left(\frac{ds_1}{dt}\right) = \lim\limits_{\substack{s_2 = s_s \\ e_2 = e_s}}\left(\frac{ds_2}{dt}\right)$.

Now from the 4 equations (only two of which are independent)

$$\frac{ds_1}{dt} = \left(\frac{ds_1}{dt}\right)_{e_1} + \left(\frac{ds_1}{de_1}\right)_t \cdot \frac{de_1}{dt}$$

$$\frac{ds_2}{dt} = \left(\frac{ds_2}{dt}\right)_{e_2} + \left(\frac{ds_2}{de_2}\right)_t \cdot \frac{de_2}{dt}$$

$$\frac{de_1}{dt} = \left(\frac{de_1}{dt}\right)_{s_1} + \left(\frac{de_1}{ds_1}\right)_t \cdot \frac{ds_1}{dt}$$

$$\frac{de_2}{dt} = \left(\frac{de_2}{dt}\right)_{s_2} + \left(\frac{de_2}{ds_2}\right) \cdot \frac{ds_2}{dt}$$

we obtain for the point at which the aqueous solution is saturated with both acid and ether,

$$\frac{ds_s}{dt} = \lim_{e_1 = e_s}\left(\frac{ds_1}{dt}\right)_{e_1} + \lim_{e_1 = e_s}\left(\frac{ds_1}{de_1}\right)_t \cdot \frac{de_s}{dt} =$$

$$\lim_{e_2 = e_s} = \left(\frac{ds_2}{dt}\right)_{e_2} + \lim_{e_2 = e_s}\left(\frac{ds_2}{de_2}\right)_t \cdot \frac{de_s}{dt}$$

$$\frac{de_s}{dt} = \lim_{s_1 = s_s}\left(\frac{de_1}{dt}\right)_{s_1} + \lim_{s_1 = s_s}\left(\frac{de_1}{ds_1}\right)_t \cdot \frac{ds_s}{dt}$$

$$= \lim_{s_2 = s_s}\left(\frac{de_2}{dt}\right)_{s_2} + \lim_{s_2 = s_s}\left(\frac{de_2}{ds_2}\right)_t \cdot \frac{ds_s}{dt}.$$ [1]

If we write the last 4 equations as follows:

$$\frac{ds_s}{dt} = b_1 + a_1 \frac{de_s}{dt} = b_2 + a_2 \frac{de_s}{dt}$$

$$\frac{de_s}{dt} = n_1 + m_1 \frac{ds_s}{dt} = n_2 + m_2 \frac{ds_s}{dt}$$

the meaning of the symbols a_1, b_1, n_1, m_1, etc., will be evident. For example $a_1 = \lim_{e_1 = e_s}\left(\frac{ds_1}{de_1}\right)_t$ and $a_2 = \lim_{e_2 = e_s}\left(\frac{ds_2}{de_2}\right)_t$, etc. Note that $a_1 = \frac{1}{m_1}$, $a_2 = \frac{1}{m_2}$, $n_1 = \frac{-b_1}{a_1}$, $n_2 = \frac{-b_2}{a_2}$.

From the equations we can get the following relations:

$$\frac{ds_s}{dt} = \frac{b_1 + a_1 n_2}{1 - a_1 m_2} = \frac{b_2 + a_2 n_1}{1 - a_2 m_1} = \frac{a_2 b_1 - a_1 b_2}{a_2 - a_1}$$

$$\frac{de_s}{dt} = \frac{n_1 + m_1 b_2}{1 - a_2 m_1} = \frac{n_2 + m_2 b_1}{1 - a_1 m_2} = \frac{b_1 - b_2}{a_2 - a_1}$$

An additional result such as $\frac{ds_s}{dt} = \frac{b_1 + a_1 n_1}{1 - a_1 m_1}$ is meaningless since the fraction is of the form $\frac{0}{0}$. In the same way we can obtain for the ether layer,

$$\frac{d\sigma_s}{dt} = \frac{\beta_1 + \alpha_1 \nu_2}{1 - \alpha_1 \mu_2} = \frac{\beta_2 + \alpha_2 \nu_1}{1 - \alpha_2 \mu_1} = \frac{\alpha_2 \beta_1 - \alpha_1 \beta_2}{\alpha_2 - \alpha_1}$$

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[1] Only the first two of these 4 equations are independent. The four are written down to show the relationship to the results obtained by Forbes and Coolidge.

$$\frac{d\omega_s}{dt} = \frac{\nu_1 + \mu_1\beta_2}{1 - \alpha_2\mu_1} = \frac{\nu_2 + \mu_2\beta_1}{1 - \alpha_1\mu_2} = \frac{\beta_1 - \beta_2}{\alpha_2 - \alpha_1}$$

where the Greek letters have meanings for the ether phase, analogous to the Roman letters for the aqueous phase. Written in the above manner, there is no chance of mistaking the curve to which the partial derivatives refer. We readily see that in our notation,

$$\frac{dR}{dt} = \frac{1}{\sigma_s}\left(\frac{a_2b_1 - a_1b_2}{a_2 - a_1} - R.\ \frac{\alpha_2\beta_1 - \alpha_1\beta_2}{\alpha_2 - \alpha_1}\right)$$

or if we retain some of the letters, n_1, n_2, m_1, m_2, etc., we obtain the expression

$$\frac{dR}{dt} = \frac{1}{\sigma_s}\left(\frac{b_1 + a_1n_2}{1 - a_1m_2} - R.\ \frac{\beta_1 + \alpha_1\nu_2}{1 - \alpha_1\mu_2}\right)$$

identical, of course, with the one given by Forbes and Coolidge when the proper interpretation is given to the letters used by them.

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RELATIONS BETWEEN DISTRIBUTION RATIO, TEMPERATURE AND CONCENTRATION IN SYSTEM: WATER, ETHER, SUCCINIC ACID.

BY G. S. FORBES AND A. S. COOLIDGE.

Received July 23, 1919.

F. H. MacDougall, in the preceding article, points out the possibility of misunderstanding the physical significance of certain partial derivatives in our paper as published in THIS JOURNAL.[1] He shows how confusion may be rendered impossible by use of a more elaborate set of symbols. On page 161 of our article directions are given for finding the derivatives by drawing tangents to the intersecting curves in Fig. 3 and reading the slopes. The values given for the slopes will identify the derivatives beyond question even if doubt previously existed concerning them. We are glad to note that Professor MacDougall agrees with our final conclusion.

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[1] 41, 150 (1919).