ditions. Other implications are involved, namely, the variation of the fluid content of the circulating blood. This may be due to the action of the liver on water metabolism, and reference may be made to Lichtman's work[2], who describes this effect.

It is possible that a study of the control of water metabolism, suggested by this work, may be of importance to an understanding of the physiology of cattle in hot climates or in times of drought.

R. N. T.-W.-FIENNES

East African Veterinary Research Organization,
Veterinary Research Laboratory,
P.O. Kabete, Kenya.
July 15.

[1] Wintrobe, P. Maxwell, "Clinical Hematology", 218 (London : Henry Kimpton, 1946).
[2] Lichtman, S. S., "Diseases of the Liver, Gall Bladder and Bile Ducts", 106 (London : Henry Kimpton, 1949).

Vapour-Liquid Equilibrium Relationships in Extractive Distillation

THE advantages of using binary data to calculate the effect of a high-boiling solvent on the volatility of a pair of liquids have frequently been emphasized. Recently, a thermodynamic method of calculating the average value of the logarithm of the volatility ratio of the low-boiling pair (components 1 and 2) at a constant mole fraction of the high-boiling solvent (component 3) under isothermal conditions from binary data has been advanced[1]. A treatment of this type has now been developed for single liquid-phase systems under a pressure of one atmosphere and the following approximate expression obtained

$$[\log \bar{\alpha}_{12x_3}]\ _{x_3'.\text{isobaric}} \approx 4\cdot559\ [\Delta T_{21} + (\Delta T_{23} - \Delta T_{13})/x_3']/T \qquad (1)$$

These terms have the following significance: $[\log \bar{\alpha}_{12x_3}]_{x_3'.\text{isobaric}}$ is the average value of the logarithm of the volatility ratio of component 1 with respect to component 2 at a constant mole fraction, x_3', of the high-boiling solvent taken from the composition $x_1 \to 0$ to $x_2 \to 0$ under isobaric conditions. Thus this quantity is defined by equation (2), where the integral on the right-hand side is to be taken for a pressure of one atmosphere and for a constant mole fraction, x_3', of component 3.

$$[\log \bar{\alpha}_{12x_3}]_{x_3'.\text{isobaric}} = \left[\int_0^{1-x_3} \log \alpha_{12x_3} dx_1\right]/(1-x_3') \quad (2)$$

ΔT_{21} is the normal boiling point of pure component 2 minus the normal boiling point of pure component 1, in degrees Celsius ; ΔT_{23} is the normal boiling point of the mixture of components 2 and 3 containing a mole fraction x_3' of the extractive solvent 3, minus the normal boiling point of pure component 2, in degrees Celsius ; ΔT_{13} is the normal boiling point of the mixture of components 1 and 3 containing a mole fraction x_3' of the extractive solvent 3, minus the normal boiling point of pure component 1, in degrees Celsius ; T is the mean of the normal boiling points in degrees absolute of the mixtures (1,3) and (2,3) containing a mole fraction x_3' of component 3.

For many systems the value of $[\log \bar{\alpha}_{12x_3}]_{x_3'.\text{isobaric}}$ will be found to be nearly equal to that of the logarithm of the volatility ratio of component 1 with

respect to component 2 in the mixture containing equal mole fractions of components 1 and 2 and a mole fraction x_3' of component 3.

Previously, it was shown[1] that for isothermal data the most satisfactory third component will, in general, be that material which yields the largest numerical value of the function $[\log \bar{\alpha}_{12x_3}' - \log \bar{\alpha}_{12}]$, where the pure substance 1 is the component with the highest vapour pressure and where $\log \bar{\alpha}_{12}$ is the average value of $\log \alpha_{12}$ for the binary (1,2). From expression (1) it follows that, subject to the approximations used, the most satisfactory third component at a given mole fraction x_3' is that material which gives the largest numerical value for the expression $(\Delta T_{23} - \Delta T_{13})/T$.

The derivation of expression (1) is based on a rigorous thermodynamic treatment, but it involves many additional assumptions, of which the following are some of the more important. The vapours have been assumed to behave as ideal gases and the molar volume of the liquids has been assumed to be negligible compared with that of the vapour. The vapour pressure of the extractive solvent has been assumed to be negligible at the normal boiling temperatures of the mixtures (1,3) and (2,3) containing a mole fraction x_3' of component 3. The activity coefficients in the binary (1,3) have been assumed to obey the relationships $\log \gamma_1 = C_1(x_3')^2$; $\log \gamma_3 = C_1(1 - x_3')^2$, where C_1 is a constant. Equations of a similar type involving a constant C_2 have been assumed to be applicable to $\log \gamma_2$ and $\log \gamma_3$ in the mixture (2,3). A term on the right-hand side equal to $\left[\int_{T_{23}}^{T_{13}} (\Delta H/T^2)dT\right]/2\cdot303R(1 - x_3')$ has been neglected in the derivation of expression (1), where ΔH is the molar heat of mixing of the mixture containing x_1, x_2 and x_3' mole fractions of components 1, 2 and 3, and T_{13}, T_{23} are the normal boiling points on the absolute scale of mixtures (1,3) and (2,3) containing a mole fraction x_3' of component 3. The latent heats of vaporization of the pure components 1 and 2 and of these materials from the binary mixtures (1,3) and (2,3) have been assumed to satisfy Trouton's rule.

Application of expression (1) to the experimental results for seven systems and a total of nineteen concentrations of third component where the experimental values of $[\log \bar{\alpha}_{12x_3}]_{x_3'.\text{isobaric}}$ varied from 0·05 to 0·44 showed a standard deviation of 0·043 units between the calculated and observed figures. This value is equivalent to a deviation of approximately 10 per cent in the anti-logarithm of $[\log \bar{\alpha}_{12x_3}]_{x_3'.\text{isobaric}}$.

Although a considerable number of assumptions is made in the derivation of expression (1), and although this expression is only approximate, nevertheless it is thought that this relationship is sufficiently accurate for use in the preliminary selection of the most suitable solvent for the separation of a given binary (1,2). The small amount of experimental measurement required for use in expression (1) is an attractive feature of this treatment.

This work has been carried out as part of the programme of the Chemistry Research Board, and is published by permission of the Director, Chemical Research Laboratory.

E. F. G. HERINGTON
Chemical Research Laboratory,
Teddington,
Middlesex.
April 25.

Herington, *Research*, 3, 41 (1950).