Full details are being published elsewhere. Some of the formulæ for the case of a binary mixture in which the molecules of one type occupy single sites have already been given by Orr[3].

E. A. GUGGENHEIM.
Imperial College of Science and Technology,
London, S.W.7.   March 7.

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A Modification to the Cryoscopic Equation

IT is known that the molecular weights of pure solutes as calculated by the cryoscopic method are not found to be constant for varying dilutions, and it has been reported[1] that K_f also varies, the tendency being for the cryoscopic constant to decrease in value as the concentration increases. Meldrum, Saxer and Jones[2] studied this anomaly in the case of camphor and found that for various solutes of known molecular weights, the constant for one gram-molecule per 1,000 grams of solvent fell from 50 at low concentrations to 39·7 in solutions of molality greater than 0·2.

These observations were confirmed by us not only for camphor but also for benzene, where K_f decreased from 7·20 to 5·35 between molalities 0·075 and 1·0.

The difficulty which arises from variations in both K_f and molecular weights at different concentrations has been overcome by using a modified equation of the form :
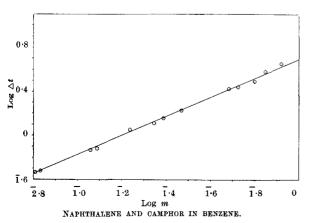
$$\Delta t = K_f . m^b \qquad (1)$$
$$\text{or } \log \Delta t = \log K_f + b \log m \qquad (2)$$

The validity of this equation was checked by plotting $\log \Delta t$ versus $\log m$ for different solutes of known molecular weights in the cryoscopic solvents benzene and camphor respectively. For all cases studied, straight lines were obtained similar to the accompanying diagram showing the plot for naphthalene and camphor in benzene.

Applying a summation method to equation 2 :
$$\Sigma \log K_f + b \Sigma \log m - \Sigma \log \Delta t = 0$$
$$\log K_f \Sigma \log m + b \Sigma \log^2 m - \Sigma \log \Delta t . \log m = 0,$$
we obtained $K_f = 5 \cdot 14$ and $b = 0 \cdot 8961$.

Hence the modified equation for pure solutes in this sample of benzene was : $\Delta t = 5 \cdot 14 \ m^{0 \cdot 8961}$. For the results quoted by Meldrum et al. on camphor : $\Delta t = 38 \cdot 73 \ m^{0 \cdot 9580}$.

K_f is found by this method to vary for different samples of the cryoscopic solvent. Thus for a different stock of benzene, $K_f = 5 \cdot 229$, whereas b, although constant for all pure solutes in a given sample of solvent, is extremely sensitive to impurities. It should be pointed out that cases may be found in which the value of b is unity and the modified equation consequently becomes identical with the classical.

The accompanying table gives the molecular weights of tetralin in benzene (a) using the classical equation, $\Delta t = K_f m$; (b) using the modified equation $\Delta t = K_f m^b$.

Concentration (per cent by weight)	Depression ($\Delta t °$ C.)	Molecular weight calculated on $\Delta t = 5 \cdot 229 \ m$ (classical)	Molecular weight calculated on $\Delta t = 5 \cdot 229 \ m^{0 \cdot 9394}$ (modified)
0·68	0·321	111·6	133·2
1·98	0·876	118·0	132·4
3·98	1·636	127·1	137·0
7·94	3·165	131·2	135·5
11·13	4·316	134·9	136·6

It is seen that by applying the classical equation the calculated molecular weight increases and approaches a value in the region of 132–136. Application of the modified equation, however, produces a set of reasonably consistent values, the mean of which is 136·1.

No attempt is made here to explain the anomaly of K_f at different concentrations, but it is suspected that a more rigid application of thermodynamic theory, on which the classical equation is based, is necessary. For the present, the above equation is proposed as one which gives consistent results at all concentrations below 1·0 molality.

A. V. BRANCKER.
S. J. LEACH.
V. A. DANIELS.

Research Department,
Manchester Oil Refinery, Ltd.,
Twining Road, Barton,
Manchester.
Feb. 25.

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NAPHTHALENE AND CAMPHOR IN BENZENE.

Dissociation Energy of Nitrogen

VAN DER ZIEL[1] has observed weak predissociation in the First Positive system of N_2 for bands with v' greater than 11. The predissociation was reported to be of the type which increases in strength with the rotational quantum number J, and both Λ doubling components of the $B^3\Pi_g$ state are affected. Van der Ziel therefore concluded, apparently with good reason, that the state causing the predissociation was of type Δ. This led to the conclusion that a dissociation limit, the products of which were capable of producing a Δ state, must lie below the energy of the predissociation. Combining this information with the known predissociation limit for the $C^3\Pi_u$ state at 12·145 e.v., this gave a value of 7·383 e.v. for the dissociation energy of nitrogen, a value which has been generally accepted.

Gaydon and Penney[2] have pointed out that if this value is correct, then the rule that potential energy curves of molecular states of the same species may not cross must be violated. They suggested that the dissociation energy was probably about 9 e.v. This is now supported by the discovery that Van der Ziel's interpretation of his predissociation is not a unique solution.