CCCXIV.—*Comments on the Paper by Fenton and Garner entitled "The Heats of Association of Acetic and Heptoic Acids in the Vapour State."*

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FENTON and GARNER, from the effect of temperature upon the equilibrium, calculate the heat of dissociation of the double molecule of acetic acid as being 13,790 cals., and they compare this value with the heat of vaporisation determined calorimetrically (this vol., p. 694). If such a comparison is to be made, it would be preferable to make use of the heat of vaporisation as determined from the variation of vapour tension with temperature, wherein the alteration in energy of the two phases with the temperature is eliminated in a manner similar to that employed by Fenton and Garner in their paper. By this method, a value of 9,700 cals. is obtained for acetic acid (Dunkel, *Z. physikal. Chem.*, 1928, **138**, 42). Moreover, the heat of vaporisation is the energy required for $6{\cdot}06 \times 10^{23}$ single molecules, whereas the value calculated by Fenton and Garner relates to $2 \times 6{\cdot}06 \times 10^{23}$ single molecules, and accordingly must be halved, giving 6,900 cals.

A value for the heat of association of benzoic acid can be similarly determined. For this acid in benzene, Beckmann found considerable association. Since he carried out measurements at the freezing point and at the boiling point of the solvent, his data can be used for approximately determining the heat of association of benzoic acid. In the accompanying table, his values (*Z. physikal. Chem.*, 1888, **2**, 729; 1890, **6**, 440) are given in cols. 1 and 2, the former showing

	M (cryoscopic),			
a, g.	old constant.	new constant.	*b*, g.	*K*.
0·268	219	228	0·019	$0{\cdot}69 \times 10^3$
0·567	223	231	0·021	$1{\cdot}25 \times 10^3$
1·444	228	237	0·038	$0{\cdot}97 \times 10^3$
2·603	232	242	0·023	$4{\cdot}8 \times 10^3$
4·725	236	246	—	—
	M (ebullioscopic),			
	old constant.	new constant.		
1·71	210	202	0·36	$1{\cdot}04 \times 10^1$
3·59	228	219	0·41	$1{\cdot}28 \times 10^1$
6·81	243	234	0·29	$7{\cdot}8 \times 10^1$
10·75	250	241	0·14	$4{\cdot}8 \times 10^2$

a, the weight of acid in 100 g. of benzene, and the latter showing his value for the molecular weight, *M*. Beckmann, in calculating the molecular weights, used the value 4,900 for the molecular lowering of freezing point and 2,670 for the molecular elevation of boiling point, which differ slightly from the more exact values 5,100 and 2,570, respectively, now used. We have, therefore, recalculated his results with these constants, and the corrected data are given in col. 3. Col. 4 indicates the unassociated portion b, calculated from the values given in col. 3, and col. 5 gives the association constant, $K = (a - b)/b^2$, based on the assumption that the equilibrium is represented by $2C_6H_5{\cdot}CO_2H \rightleftharpoons (C_6H_5{\cdot}CO_2H)_2$. The increase of this constant with increasing concentration of the benzoic acid is due to the solvation of the dissolved acid, and probably also to association of more than 2 molecules of benzoic acid in concentrated solutions. For calculating the heat of association of benzoic acid it will therefore be best to use only the lowest values. From the values $K_1 = 0{\cdot}69 \times 10^3$ and $K_2 = 1{\cdot}04 \times 10$, the heat of association of 2 g.-mols. of benzoic acid is found by means of the van 't Hoff isochore, $- W = R \,.\, d \log K/d(1/T)$, to be $1{\cdot}12 \times 10^4$ cals., *i.e.*, 5,600 cals. per mol.

This value is of the same order as the 6,900 cals. calculated for acetic acid from the measurements of Fenton and Garner. The two values are both of the same order as that of other forces between several molecules caused by the mutual electrostatic influence of two dipoles. Accordingly, Fenton and Garner's conclusion that the association of acetic acid is concerned with " chemical " combination can no longer be maintained. Unless the more exact terms " linkage by ions " and " homopolar combination " are used, or reference is made to the forces of dispersion, induction, and orientation constituting the forces of van der Waals, instead of a difference being made between " chemical " and " physical " combination, the former term should be used only when dealing with a combination of ions or with the action of principal valencies in a homopolar combination.

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