347. *The Vapour Pressure and Lattice Energy of Hydrogen-bonded Crystals. Part II.* α- and β-Anhydrous Oxalic Acid and Tetragonal Pentaerythritol.*

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The vapour pressures and lattice energies of α- and β-anhydrous oxalic acid have been determined over the respective ranges 37·62—51·91° and 37·62—50·06°. The α-form is stable at room temperature. The transition temperature lies above the decomposition point. Pressures of water vapour in the system β-anhydrous acid–dihydrate–water vapour have been measured at 32·75—46·9°, but no equilibrium was reached with the α-anhydrous acid in the presence of dihydrate and water vapour, because the dihydrate gives the β-acid on dehydration. The vapour pressure and lattice energy of tetragonal pentaerythritol have been determined at 106·4—135·1°. Some preliminary discussion is given of the contribution of hydrogen bonding to the lattice energies of these compounds.

ALTHOUGH the dimorphism of anhydrous oxalic acid has been reported, and *X*-ray studies have been made by Hoffmann and Mark (*Z. physikal. Chem.*, 1924, **3**, 321) and by Hendricks (*Z. Krist.*, 1935, **91**, 48), no reliable indication was found as to which is the more stable form at room temperature, and it was not known whether there was a transition point. It was therefore decided to obtain values of the vapour pressure and thermodynamic data for the two forms, and if possible to relate these data to the structures, which are being studied by other workers in this Department (Cox and Dougill). It was hoped, in addition, to study the vapour pressure of water in equilibrium, metastable or otherwise, with the dihydrate in the presence of either of the two forms. This work is reported in Section (*a*).

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* Part I, preceding paper.

With pentaerythritol, Section (*b*), it was convenient to study only the one form, that for which the structure has been determined (Cox, Goodwin, and Llewellyn, *J.*, 1937, 883; Nitta and Watenabe, *Nature*, 1937, **140**, 365), since the transition to the cubic form occurs at 180°.

EXPERIMENTAL

Section (*a*).—The α (orthorhombic) form of anhydrous oxalic acid was prepared by dehydrating " AnalaR " dihydrate *in vacuo* at 100°, admitting dry air, and adding acetone (dried over Na_2SO_4). The solution was placed in a vacuum desiccator [over $Mg(ClO_4)_2$, which absorbed acetone vapour], and deposited crystals overnight.

The β (monoclinic) form was prepared by dehydrating the dihydrate *in vacuo* at 100°, needle-shaped crystals subliming on the cold neck of the flask. This method was more convenient than that of Partington and Johnson (*J.*, 1930, 1510), which involves distillation with toluene; these authors did not specify which form was prepared.

The samples were shown to be pure by titration with potassium permanganate. Both forms had d_4^{18} 1·89, as determined by the flotation method, by the use of mixtures of carbon tetrachloride and ethylene dibromide.

Vapour pressures were determined by an application of Knudsen's effusion method, the apparatus being similar to that described in the preceding paper; the balance case was immersed in a thermostat at 37—52°. Consistent results for the vapour pressure were obtained under a variety of conditions in which the hole size was varied and the cooling medium was changed from solid carbon dioxide and acetone to liquid nitrogen. It was necessary to hang the effusion vessel about 10 cm. from the cold finger and further to protect it by means of a radiation shield of aluminium foil if the vessel was surrounded by tubing 2·5 cm. in radius. It was shown that the errors described in the preceding paper were absent. Benzophenone was used as the calibrating substance, together with Neumann and Volker's data (*Z. physikal. Chem.*, 1931, *A*, **161**, 33), but in addition, an absolute determination was made by measuring the area and thickness of the effusion hole photomicrographically. When allowance had been made by Clausing's method (*Ann. Physik*, 1932, **12**, 961) for the tube resistance of the hole, agreement between the relative and absolute determinations was secured to within 1%. Recalibration at the end of the experiments gave a consistent result.

During the transfer of the samples to the effusion vessel, some hydration necessarily occurred, and this water was lost during the early stages of the evacuation. When the β-acid was studied, the rate of effusion at a particular temperature became constant and reproducible when all this water had been evolved, but with the α-form the apparent vapour pressure decreased in successive runs, becoming constant only after several days. It appears, therefore, that the dihydrate gives the β-acid on dehydration, and that a mixture of the α- and the β-form slowly reverts to the pure α-form. The β is thus the unstable form at room temperatures, in agreement with the higher vapour pressure which we have found for this form. Special precautions had to be taken owing to the ease of hydration of the anhydrous form. When the balance had moved over its range, it was necessary to replace the weight lost by silica; the joint of the balance case was lowered only a few cm., the requisite amount of silica was added to the hook supporting the effusion vessel, and the joint was quickly re-sealed.

TABLE 1. *Vapour pressures* (*cm.* Hg) *of* α- *and* β-*anhydrous oxalic acid.*

Data for α-form						Data for β-form			
Effusion vessel 1		Effusion vessel 2				Effusion vessel 1		Effusion vessel 2	
T	V. p. × 10^4	T	V. p. × 10^4	T	V. p. × 10^4	T	V. p. × 10^4	T	V. p. × 10^4
37·62°	0·445	37·81°	0·452	47·37°	1·47	38·60°	0·847	37·62°	0·755
39·12	0·559	41·00	0·669	50·00	1·98	41·96	1·27	40·45	1·03
42·37	0·836	41·71	0·734	51·91	2·45	45·18	1·79	43·40	1·49
45·58	1·21	43·80	0·990	—	—	48·48	2·60	47·02	2·22
48·63	1·74	46·83	1·39	—	—	51·83	3·61	50·06	3·15

The vapour pressures of the α- and the β-form of oxalic acid are given in Table 1. They are given respectively by the equations

$$\log_{10} p = 12{\cdot}17 - 5130/T \qquad (1)$$

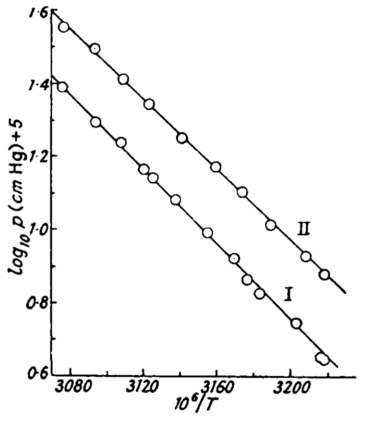
and

$$\log_{10} p = 11{\cdot}57 - 4875/T \qquad (2)$$

The two lines are shown in the Figure. The lattice energies of the α- and the β-form are 23,450 and 22,280 cal. mole^{-1}, and the entropies of sublimation 47·0 and 44·3 cal. degree^{-1} mole^{-1}, respectively; owing to the low vapour pressures the lattice energy may be equated to the latent heat of vaporisation. The heat content and entropy change for the transition $\beta \rightarrow \alpha$ are $\Delta H = -1170$ cal. mole^{-1}, $\Delta S = -2{\cdot}7$ cal. degree^{-1} mole^{-1}. The transition temperature, at which the vapour pressures become equal, is 152° according to equations (1) and (2), but this assumes that these equations can be extrapolated to higher temperatures without allowing for the change of heat of vaporisation with temperature. Since oxalic acid decomposes on sufficient heating, the transition point cannot be realised in practice. Noyes and Wobbe (*J. Amer. Chem. Soc.*, 1926, **48**, 1882), who prepared their anhydrous acid by dehydrating the hydrate *in vacuo*, and who must therefore have studied the β-form, give $\log_{10} p_{\text{cm. Hg}} = 11{\cdot}22 - 4727/T$, which gives values of the vapour pressures up to 30% higher than ours.

A determination of the molecular weight of the vapour was made, in order to detect decomposition or association, by the use of the apparatus described in Part I (*loc. cit.*). A value of 91·1 was obtained, showing that no decomposition occurs, and that association is negligible—as would be expected from the low values of the vapour pressures studied.

The pressures of water vapour for the system anhydrous acid–dihydrate–water vapour were measured by means of an accurate wide-bore mercury manometer. With the β-anhydrous acid no difficulty was experienced, and the system came rapidly to an apparent equilibrium (although the β is the unstable form). The vapour pressures of water are given in Table 2 and are well represented by the equation



Vapour pressures of anhydrous oxalic acid.
I. α-Orthorhombic. II. β-Monoclinic.

$$\log_{10} p_{\text{cm. Hg}} = 9{\cdot}427 - 2995/T \quad \ldots\ldots\ldots \quad (3)$$

giving a heat of dehydration of 13,700 cal. per mole of water removed. This result agrees well with that of Bell (*J.*, 1940, 72), *viz.*, 13,600 cal., although the values of the vapour pressures obtained by us are about 15% lower than those given by his equation, $\log_{10} p_{\text{cm. Hg}} = 9{\cdot}45 - 2983/T$; Bell's results show, however, considerably greater scatter than ours. Becker and Roth (*Z. Elecktrochem.*, 1935, **40**, 836) have calculated the heat of hydration from thermochemical data to be 3300 cal. per mole of water, giving ΔH for the dehydration 13,300—13,440 cal. per mole of water, the variation allowing for the temperature change of the heat of vaporisation of water.

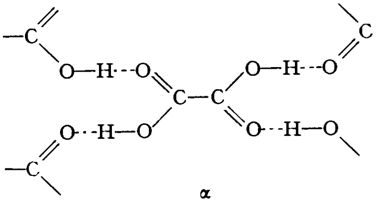
TABLE 2. *Pressure of water vapour (cm.* Hg) *for the system β-oxalic acid–dihydrate–water vapour.*

T	32·75°	35·30°	39·95°	42·00°	44·50°	46·90°
Pressure	0·444	0·518	0·739	0·847	1·004	1·180

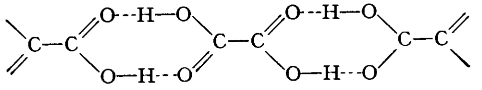
All attempts to measure the equilibrium pressure of water vapour in the system α-anhydrous acid–dihydrate–water vapour failed, apparently because the dihydrate gives the β-form on dehydration. The situation is similar to that in the system sodium sulphate hydrate–anhydrous sodium sulphate (which exists in a number of forms)–water vapour, for which we have not seen any statement of the form which is produced on dehydration of the hydrate.

The β-form has the lower lattice energy and might be expected to have the lower surface energy and be the form which would appear from the vapour according to nucleation theory. This is in fact the case; in the dehydration of the dihydrate interfacial energies must be considered, but a similar argument may apply. The appearance of the α-form from solution may be related to solvation effects or to the effects of adventitious particulate impurities.

Discussion on Lattice Energy of the Two Forms of Oxalic Acid.—The α-form of anhydrous oxalic acid contains molecular sheets, whereas in the β-form the molecules are arranged in chains, represented diagrammatically thus :



α



β

In both forms there are two hydrogen bonds per molecule (apart from end effects), so there is a considerable " background " contribution to the lattice energy in addition to the hydrogen-bonding energy; the latter may be assumed to be *ca.* 8 kcal. per bond (cf. Part I, *loc. cit.*). The differences in energy between the two structures are small; the entropy difference is rather larger than might be expected from the packing in the two forms, and may be associated with the restricted rotation about the C–C axis of the eight-membered ring of the β-form, which has the higher entropy (lower entropy of sublimation), whereas in the α-form this rotation is suppressed. At sufficiently high temperatures it is possible that the rotation becomes free, as might be revealed by specific-heat studies.

Section (*b*). *Tetragonal Pentaerythritol.*—*Experimental.* The pentaerythritol used had been purified by hydrolysis of the dibenzylidene compound. It was recrystallised from water and had m. p. 256°. The thermostat used in Section (*a*) was replaced by a double-walled vapour jacket, and temperatures were read on an Anschütz thermometer hanging near the effusion vessel. It was shown that the error in the thermometer due to expansion of the glass *in vacuo* was negligible. The rate of effusion was studied over the range 106·4—135·1° by the use of toluene, *n*-butyl alcohol, *iso*butyl alcohol, and chlorobenzene as boiling liquids. The same precautions were taken as in Section (*a*) to reduce errors. The results (Table 3) are well represented by the equation $\log_{10} p_{\text{cm. Hg}} = 15{\cdot}17 - 7528/T$. The lattice energy is 34,400 cal. mole^{-1}, and the entropy of sublimation 60·8 cal. degree^{-1} mole^{-1}. These values differ considerably from those of Nitta, Seki, and Suzuki (*Bull. Chem. Soc. Japan*, 1951, **24**, 63), who carried out measurements at 124—137° and give $\log_{10} p_{\text{cm. Hg}} = 13{,}525 - 6861/T$, lattice energy 31,400 cal. mole^{-1}.

TABLE 3. *Vapour pressures* (*cm.* Hg) *of tetragonal pentaerythritol.*

	Euffsion vessel 3					Effusion vessel 4				
T	106·40°	109·90°	110·15°	116·25°	119·20°	114·90°	119·15°	121·15°	128·50°	135·10°
V. p. × 10^5	2·12	3·34	3·48	6·97	9·84	5·84	9·45	12·40	28·1	52·4

Discussion on Lattice Energy of Tetragonal Pentaerythritol.—In this form of pentaerythritol the molecules are linked by hydrogen bonds in sheets (Cox *et al.*, *loc. cit.*), with four hydrogen bonds per molecule. If we accept approximately 6 kcal. for the hydrogen-bond energy in alcohols, with the reservations mentioned in Part I (*loc. cit.*) (see Searcy, *J. Chem. Phys.*, 1949, **17**, 210), approximately 10 kcal. remain in the lattice energy owing to " background " interactions.

Nitta *et al.* (*loc. cit.*) attempted an analysis of the lattice energy of pentaerythritol, using the Slater–Kirkwood approximation for the dispersion energy, and splitting up the molecular interactions into those between groups (OH and CH_2). The electrostatic energy is calculated by the point charge method, but considerable difficulty arises in the assignment of residual charges to the atoms, and the values for the calculated lattice energy range from 28·59 to 32·12 kcal. mole^{-1} according to the assignment of 36—42% ionic character to the hydrogen bond. The contribution to the electrostatic energy of next nearest neighbours is considerable. The calculation is provisional and may be criticised on the grounds that the energy of repulsion, higher (quadrupole) terms in the dispersion energy, and any small " resonance " contribution to the O–H–O bond energy are neglected. The dangers of neglecting the repulsion energy are revealed by Searcy's calculation for ice (see Part I, preceding paper). The calculation of Nitta *et al.*, with its summation of electrostatic interactions and dispersive interactions over the whole crystal, brings out the difficulty of defining the hydrogen-bond energy, a quantity which may in fact be dispensed with in the calculation of lattice energies, although the hydrogen bond provides a useful description of the shortening of O–O distances.

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