LXXXIV.—*The Determination of the Dissociation Pressures of Hydrated Salts by a Dynamical Method. Part III.*

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A FULL account of previous work on the subject of dissociation pressures of salt hydrates is given in Parts I and II of this series (Partington, J., 1911, **99**, 467; Partington and Huntingford, J., 1923, **123**, 160) and by Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 978, 1952).

Since the publication of Part II, two papers have appeared in which a method similar to that described has been employed (Schumb, *J. Amer. Chem. Soc.*, 1923, **45**, 342; Baxter and Cooper, *ibid.*, 1924, **46**, 923. These workers used a method almost identical with that used by Baxter and Lansing, *ibid.*, 1920, **42**, 419, entailing the measurement of the volume of air aspirated over the salt).

In this research the original method of Parts I and II has been employed, which is essentially as follows. Air, dried over calcium chloride and phosphoric oxide, is passed successively over the salt, through phosphoric oxide tubes, through a water bubbler, and finally through a further apparatus for absorbing water vapour. Since the salt and the water are both maintained at the same temperature, the weights of water absorbed in the respective series of tubes are, apart from small corrections applied, directly proportional to the vapour pressures of the salt and of the water.

Apparatus.—The **U**-tube containing the salt was 2 cm. in internal diameter and the total length of the column of salt was 50 cm. It was connected with a trap to condense part of the water vapour before the moist air reached the absorption tubes (see Part I). The water bubbler had a similar trap fitted. This part of the apparatus was immersed in an electrically controlled thermostat, steady to within ± 0·01°.

The absorption apparatus consisted of two **U**-tubes fitted with glass stoppers and filled with phosphoric oxide and glass wool. Only the first tube was weighed, the other acting as a guard tube between the absorption tube proper and the water bubbler or the aspirator. The traps and corresponding absorption tubes were weighed together.

Air was drawn through this apparatus by an aspirator bottle of 10 litres capacity, out of which water was siphoned. This bottle was fitted with a mercury manometer to indicate the difference in pressure between the atmosphere and the inside of the bottle.

Before passing through the apparatus, the air was dried and freed from carbon dioxide by passage through (i) a sulphuric acid bubbler which also served to indicate the rate of flow, (ii) a series of caustic soda tubes, (iii) a calcium chloride tube, and finally (iv) a phosphoric oxide tube, since this reagent was used in the absorption tubes.

When in use the ground joints were cemented outside with Faraday wax, with the exception of the joints in the traps, which were lubricated with petroleum jelly. Both the wax and the jelly were removed by cotton wool and benzene before the respective parts were weighed. The traps and tubes were weighed against counterpoises of similar structure.

Materials.—(1) *Disodium hydrogen phosphate dodecahydrate*, $Na_2HPO_4,12H_2O$. A.R. Salt from B.D.H. was used after one recrystallisation. A small amount of the heptahydrate was prepared by crystallising the salt above 36°, the transition point between these two hydrates being at 35·4° (D'Ans and Schreiner, *Z. physikal. Chem.*, 1911, **75**, 99). An intimate mixture of the two powdered hydrates was used. This overcame the necessity of passing air through the salt for a considerable time before the actual determinations were commenced, as had been done previously, since the two phases were present from the start.

(2) *Disodium hydrogen arsenate hydrates.* In Part II, dissociation pressures of sodium arsenate dodecahydrate were determined at 25°, 30°, and 35°. It was pointed out that the result at 25°, *viz.*, 11·10 mm., did not agree with that obtained by Lescœur (*Compt. rend.* 1887, **164**, 1171; *Ann. Chim. Phys.*, 1890, **21**, 556), *viz.*, 9·8 mm. at that temperature. At 30° the difference was only 0·25 mm. Lescoeur had, however, indicated a transition point at 23° between two hydrates to which he assigned the formulæ "$2NaO,AsO^5,25HO$" and "$2NaO,AsO^5,15HO$," which correspond with the dodeca- and hepta-hydrates $Na_2HAsO_4,12H_2O$ and $Na_2HAsO_4,7H_2O$. Confirmation of this transition was obtained by Rosenheim and Thon (*Z. anorg. Chem.*, 1927, **167**, 7), who found that the solubility curve for sodium arsenate in water shows a marked transition at 22° between these two hydrates. It was clear, therefore, that the determinations above 20° were in need of revision.

Tilden (J., 1884, **45**, 269) gives the m. p. of sodium arsenate dodecahydrate as 28°, but if this were correct the results in Part II could not have been obtained, since the apparatus employed would have become choked with the fused salt. Lescœur says that the salt partially melts at 23°. Actually, at 22°, we found that the salt becomes only damp, and this increases with temperature until the salt finally becomes completely liquid; this liquid becomes clear at

56·2°, and is then a true solution of the heptahydrate. The liquid, when supercooled to, say, 40° and seeded with a crystal of salt, deposits crystals of the heptahydrate and the temperature rises to 56·2°. There is a similar evolution of heat at 22°, but this is not so well marked. The original tube used in Part II was available and it showed that the salt used had not undergone fusion.

It was hoped that the dissociation-pressure curves would also show the transition point at 22° with some accuracy, but it became clear that the solubility curve (Rosenheim and Thon, *loc. cit.*) provided a more accurate result, as the angle between the dissociation-pressure curves is small. We have therefore, in calculating the heats of hydration and plotting the curves, assumed that the latter actually cut at 22°, an assumption which was made very probable by the actual results.

The dodecahydrate was prepared by crystallising the salt below 22°; it is efflorescent at room temperature in air. The heptahydrate was similarly prepared by crystallisation above 22°, *viz.*, at about 30°; this hydrate does not effloresce appreciably at room temperature in air. The anhydrous salt was obtained by heating the crystalline salt at 120° until it lost its water of crystallisation. The appropriate pairs of phases were then intimately mixed and used in the **U**-tubes as indicated above.

Results.

The method of working out the results is the same as that used in Part II of this series. The equation derived,* with which the results are calculated, is

$$p = \frac{p'KB}{B + p'K} = \frac{\frac{w_1}{w_2}\pi \cdot \left(\frac{B - b}{B - b - \pi}\right)B}{B + \frac{w_1}{w_2}\pi \cdot \left(\frac{B - b}{B - b - \pi}\right)} \quad . \quad . \quad . \quad (1)$$

where p is the dissociation pressure of the salt at $t°$; w_1 and w_2 are the weights (in grams) of water vapour absorbed from the salt and the water, respectively; π is the vapour pressure of water at $t°$; B is the barometric height; and b is the difference of levels in the gauge fitted to the aspirator. All pressures are given in mm. of mercury.

This method corrects for: (*a*) the pressure difference between the air in the bottle and the atmosphere; (*b*) the head of water in the bubbler; (*c*) the larger volume of the moist air in equilibrium with the water as compared with that in equilibrium with the salt.

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* The formula given on p. 167 of Part II was incorrectly reproduced, but all the results given in that paper were in fact calculated by the correct formula as now given.

Sodium arsenate dodecahydrate in presence of heptahydrate.

Temp. 14·90°; π = 12·706 mm.

w_1.	w_2.	B.	b.	p.
0·0162	0·0403	762·5	22	5·16
0·0202	0·0491	757·0	22·5	5·27
0·0172	0·0430	756·9	22	5·13
0·0186	0·0442	753·8	22·5	5·38
0·0193	0·0468	761·5	20	5·29
0·0174	0·0431	766·2	19·5	5·17
0·0178	0·0439	753·6	22	5·20
0·0178	0·0439	757·3	22	5·29

Mean result : $p_{14\cdot 90^\circ}$ = 5·24 mm.

Temp. 20°; π = 17·535 mm.

w_1.	w_2.	B.	b.	p.
0·0236	0·0562	761·2	21	7·47
0·0197	0·0482	769·06	20·5	7·27
0·0179	0·0417	774·3	19·5	7·42
0·0228	0·0544	759·5	20	7·25
0·0198	0·0478	756·2	20	7·23
0·0179	0·0430	772·7	18·5	7·41
0·0209	0·0488	760·05	18·5	7·50

Mean result : p_{20° = 7·36 mm.

Sodium arsenate heptahydrate in presence of anhydrous salt.

Temp. 24·92°; π = 23·658 mm.

0·0499	0·1197	762·87	18·5	9·95
0·0454	0·1019	769·6	19	10·11
0·0430	0·1029	765·6	19·5	10·11
0·0408	0·0972	763·4	19	10·16
0·0423	0·1047	770·3	19	9·80
0·0468	0·1057	772·7	20	10·17
0·0423	0·1043	775·0	21	9·82
0·0444	0·1088	773·4	21·5	9·86
0·0417	0·1002	762·9	19·7	10·07
0·0433	0·1013	766·9	20	10·20
0·0435	0·1039	780·9	19	10·12
0·0463	0·1054	781·7	20	10·14
0·0430	0·1013	764·6	19·4	10·28
0·0464	0·1131	766·5	19·7	9·93
0·0501	0·1193	764·15	18·5	9·73

Mean result : $p_{24\cdot 92^\circ}$ = 9·98 mm.

Temp. 30°; π = 31·824 mm.

0·0417	0·0939	766·9	28	14·48
0·0443	0·0993	763·0	25	14·55
0·0486	0·1109	762·0	26·5	14·30
0·0439	0·1010	758·3	25·6	14·20
0·0489	0·1112	768·7	25	14·34
0·0389	0·0870	761·2	25	14·60
0·0428	0·0958	759·0	24·2	14·60

Mean result : p_{30° = 14·39 mm.

Temp. 35°; π = 42·175 mm.

0·0684	0·1434	767·1	22	20·75
0·0639	0·1341	763·0	22	20·73
0·0603	0·1275	757·2	22	20·56
0·0723	0·1515	758·0	21	20·75
0·0717	0·1509	749·3	22·5	20·67
0·0619	0·1296	760·0	19	20·78
0·0601	0·1254	757·7	22	20·84
0·0597	0·1250	753·2	23	20·77

Mean result : p_{35° = 20·73 mm.

Sodium phosphate dodecahydrate in presence of heptahydrate.

Temp. 14·90°; π = 12·706 mm.

0·0358	0·0513	751·0	22	8·91
0·0328	0·0468	757·7	20	8·95
0·0354	0·0507	758·1	19·5	8·92
0·0368	0·0529	759·0	22	8·87
0·0401	0·0569	762·5	21	9·01
0·0372	0·0534	768·2	22·5	8·90
0·0385	0·0549	760·0	22·5	8·96

Mean result : $p_{14\cdot 90^\circ}$ = 8·93 mm.

Temp. 20°; π = 17·535 mm.

0·0472	0·0661	748·3	22	12·91
0·0503	0·0703	752·4	22	12·94
0·0487	0·0681	757·3	21	12·91
0·0453	0·0637	755·7	20·5	12·90
0·0496	0·0691	762·0	22	12·95
0·0521	0·0727	763·1	22·5	12·95
0·0453	0·0633	764·3	22	12·94

Mean result : p_{20° = 12·93 mm.

Temp. 24·92°; π = 23·658 mm.

0·0755	0·0933	768·3	16	19·27
0·0678	0·0838	773·6	15·5	19·14
0·0710	0·0884	764·6	16	19·01
0·0650	0·0818	764·5	16	18·97
0·0696	0·0855	762·05	18	19·14
0·0707	0·0874	761·9	17	19·27
0·0602	0·0745	760·6	17	19·27
0·0571	0·0710	759·3	16	19·18
0·0698	0·0864	756·9	16	19·27
0·0605	0·0759	748·06	19·5	19·01
0·0714	0·0890	755·12	19·1	19·14

Mean result : $p_{24\cdot 92^\circ}$ = 19·10 mm.

Temp. 30°; π = 31·824 mm.

0·0905	0·1064	767·06	23	27·29
0·0815	0·0974	769·6	22	26·86
0·0786	0·0915	768·8	21	27·47
0·0695	0·0836	769·3	21	26·66
0·0695	0·0828	768·6	21	26·92
0·0801	0·0934	755·4	20·5	27·48
0·0724	0·0870	753·1	21	26·71

Mean result : p_{30° = 27·05 mm.

Discussion.

The foregoing results are collected in Table I, and Fig. 1 shows the curves obtained by plotting p against t and also log p against $1/T$ (where $T = t + 273°$). The logarithmic plots are straight

FIG. 1.

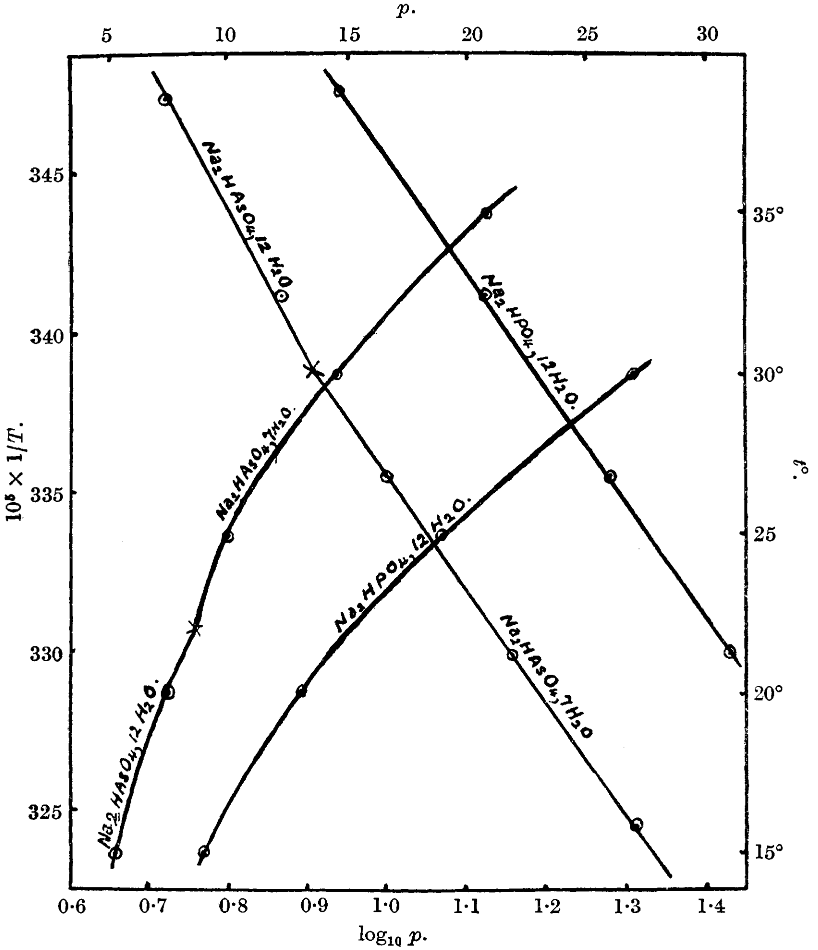

TABLE I.

Hydrates.	$p_{14\cdot90°}$, mm.	$p_{20°}$, mm.	$p_{24\cdot92°}$, mm.	$p_{30°}$, mm.	$p_{35°}$, mm.
$Na_2HAsO_4,12H_2O \longrightarrow 7H_2O$	5·24	7·36	—	—	—
$Na_2HAsO_4,7H_2O \longrightarrow 0H_2O$	—	—	9·98	14·39	20·73
$Na_2HPO_4,12H_2O \longrightarrow 7H_2O$	8·93	12·93	19·10	27·05	—

lines, and in the case of sodium arsenate there is a definite intersection of the lines for the two hydrates. It has been pointed out, however, that this is not a very accurate method of finding the transition point.

For comparison with those of other authors, the present results were plotted and the values for 15° and 20° interpolated. Where possible, results for 15°, 20°, 25°, and 30° were found by a similar process from results of previous workers. In the case of Lescœur's results for sodium arsenate this was not possible, as the points did not lie on a regular curve. The same was found to be the case with the results of Müller Erzbach (*Ber.*, 1887, **20**, 137; *Z. physikal. Chem.*, 1896, **19**, 134) above 20°.

Sodium arsenate. Lescœur gives, for this salt, three series of vapour pressures, one for each of the two hydrates, and one for the saturated solution. His results for the dodecahydrate and the solution led to comparatively smooth curves and the vapour pressure is given for both as 16 mm. at 20°; but those for the dodeca- and the hepta-hydrate do not agree with ours, being: at 15°, 11·5 mm. and 3·4 mm. respectively, and at 20°, 16 mm. and 4·6 mm. respectively. The only comparable results are:

At 25° : This research 10 mm.; Lescœur 9·8 mm.
At 30° : This research 14·39 mm.; Lescœur 15 mm.

Sodium phosphate. The results given by Lescœur (*Ann. Chim. Phys.*, 1890, **21**, 548) for this salt are identical in every way with those given by Debray (*Compt. rend.*, 1868, **66**, 194). Table II compares the results of several previous workers with the present results.

TABLE II.

Author.	p_{15°, mm.	p_{20°, mm.	p_{25°, mm.	p_{30°, mm.
Debray * (interpolated)	9·0	13·0	18·2	27·1
Müller Erzbach † (interpolated)	9·0	13·5		
Frowein ‡ (interpolated)	8·84	12·6	18·5	28
Foote and Scholes §			18	
Wilson ‖			19·13	
Baxter and Cooper ¶	8·93		19·05	
This research	8·95	12·93	19·18	27·05

* *Loc. cit.*

† *Loc. cit.*

‡ *Z. physikal. Chem.*, 1887, **1**, 362; "Revue de Chimie physique d'Ostwald et van 't Hoff," t. ii, p. 362.

§ *J. Amer. Chem. Soc.*, 1911, **33**, 1309.

‖ *Ibid.*, 1921, **43**, 704.

¶ *Ibid.*, 1924, **46**, 923.

Heats of Hydration.—The heats of hydration were calculated from the dissociation pressures by the Clapeyron–Clausius equation in the form

$$Q(\text{g.-cals.}) = 4{\cdot}576\,\frac{T_2T_1}{T_2 - T_1}\log\left(\frac{p_2/\pi_2}{p_1/\pi_1}\right) \quad . \quad . \quad (2)$$

The values obtained are given in Table III. Those for sodium phosphate may be compared with those of Baxter and Cooper (*loc. cit.*), Q being given in g.-cals. :

TABLE III.

Reaction.	Temperature range.	Q per mol. H_2O.	Q for whole reaction.
$Na_2HAsO_4,12H_2O \longrightarrow Na_2HAsO_4,7H_2O + 5H_2O$(liq.)	14·90—20°	579	2,895
	20 —22	589	2,949
$Na_2HAsO_4,7H_2O \longrightarrow Na_2HAsO_4 + 7H_2O$(liq.)	22 —24·92	2,847	19,929
	24·92—30	3,065	21,455
	30 —35	3,092	21,644
$Na_2HPO_4,12H_2O \longrightarrow Na_2HPO_4,7H_2O + 5H_2O$(liq.)	14·90—20	2,339	11,697
	20 —24·92	2,359	11,795
	24·92—30	2,396	11,978

	$Q_{15-20°}$.	$Q_{20-25°}$.	$Q_{25-30°}$.
Baxter and Cooper	11,340	12,180	—
Present work	11,697	11,795	11,978

The three series of heats of hydration show an increase with rise of temperature, as Baxter and Cooper also found for sodium phosphate, acetate, and carbonate. For the last two salts, however, directly determined values show the opposite effect.

In the case of sodium phosphate hydrates, data are available for the heats of solution at 18° and a dilution of 400 mols. of water per mol. of salt. For the dodecahydrate, Thomsen (*J. pr. Chem.*, 1878, **17**, 174) gives − 22,820 g.-cals., and Pfaundler (*Ber.*, 1871, **4**, 775) − 22,500 g.-cals. For the heptahydrate at the same dilution and temperature, Pfaundler (*loc. cit.*) gives − 11,300 g.-cals. Pfaundler's values give the heat of the reaction

$$Na_2HPO_4,12H_2O \longrightarrow Na_2HPO_4,7H_2O + 5H_2O(\text{liq.})$$

as 11,200 g.-cals. (*i.e.*, 2240 g.-cals. per mol. of water) at 18°, which is in satisfactory agreement with the results obtained from the dissociation pressures.

Another method available for the calculation of the heats of hydration of the salts is based on Nernst's heat theorem. This gives for the intrinsic energy change (here the quantity of heat liberated as found thermochemically) :

$$Q = Q_0 + \alpha T^2 + \beta T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and for the free-energy change :

$$A_{T°} = Q_0 - \alpha T^2 - \frac{\beta}{2}T^3 . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

α and β being the same constants in both equations. The values of A_{T° (in g.-cals.) may be found from the dissociation pressures by the equation

$$A_{T^\circ} = RT \log_e \pi/p \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where p and π have the values assigned in equation (1) and $R = 1{\cdot}9875$.

The most satisfactory method for calculating Q_0 and α (β being negligibly small) from the equations obtained by applying (4) to each experimental temperature is that of least squares. By substituting the values of Q_0 and α so obtained in equation (3) we obtain the values of Q for various temperatures. Table IV compares the results thus derived with those calculated by the Clapeyron–Clausius equation (2) as in Table IV : the former are somewhat lower than the latter.

TABLE IV.

Reaction.	Temp.	Q_0 per mol. H_2O.	$\alpha \times 10^5$.	A_{T°,	Q,	Q for whole reaction,	
				per mol. of H_2O.		eq. (3).	eq. (2).
$Na_2HAsO_4,12H_2O \longrightarrow Na_2HAsO_4,7H_2O + 5H_2O$(liq.)	14·90°	542·43	43·71	506·20	578·8	2,894	2,895
	20			504·90	579·9	2,899	
$Na_2HAsO_4,7H_2O \longrightarrow Na_2HAsO_4 + 7H_2O$(liq.)	24·92	1646·9	1278	510·40	2781·2	19,468	21,455
	30			477·36	2820·3	19,742	21,644
	35			434·21	2858·3	20,008	
$Na_2HPO_4,12H_2O \longrightarrow Na_2HPO_4,7H_2O + 5H_2O$(liq.)	14·90	1186·8	1180	196·95	2175·8	10,879	11,697
	20			177·17	2209·6	11,048	11,795
	24·92			153·77	2241·8	11,209	11,978
	30			97·76	2280·1	11,400	

For sodium phosphate dodecahydrate, by the method just employed, Müller (*J. Chim. physique*, 1909, **7**, 534) found from Frowein's results (*loc. cit.*) that $Q = 2215{\cdot}3$ g.-cals. per mol. of water at 18° ($Q_0 = 1200{\cdot}58$; $\alpha = 1198{\cdot}27 \times 10^{-5}$).

To values of the specific heats of the dodeca- and hepta-hydrates of sodium phosphate as found by Nernst, Koref, and Lindemann (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1910, **12**, 247), *viz.*, between 34·4° and 1·9°, 0·3723 for the dodecahydrate, and 0·3230 for the heptahydrate, an equation of the type

$$dQ/dT = C_A + C_B - C_C = \alpha t \quad . \quad . \quad . \quad . \quad (6)$$

has been applied, in which C_A, C_B, and C_C are the molecular heats of the heptahydrate, of $5H_2O$(liq.), and of the dodecahydrate, respectively. Since the specific heats were determined over a wide range, t is not accurately defined but it was taken as 18°, this being approximately the mean of 34·4° and 1·9°; α then becomes 0·1501, which is about ten times the value calculated previously.

There being no data concerning the specific heats of the hydrates of sodium arsenate, these were determined approximately over the range + 16° to − 12°, the method of mixtures being used with carbon tetrachloride as the calorimetric liquid. The value 0·206 was taken as the specific heat of carbon tetrachloride at − 12° by interpolation from the results of Latimer (*J. Amer. Chem. Soc.*, 1922, **44**, 90), Mills and MacRae (*J. Physical Chem.*, 1911, **15**, 54), and Timofejew (*Iszw. Kiew polyt. Inst.*, 1905, 1).

The results so obtained were: Dodecahydrate, 0·414 g.-cal./g.; heptahydrate, 0·350 g.-cal./g., whence the respective molecular heats are 166·3 and 109·3 g.-cals. Then, from equation (6), for the reaction $Na_2HAsO_4,12H_2O \longrightarrow Na_2HAsO_4,7H_2O + 5H_2O$(liq.), $\alpha = 0{\cdot}1178$, again about ten times that previously calculated.

Summary.

The dissociation pressures of sodium arsenate hydrates have been redetermined, and some values for sodium phosphate hydrates are also given. The results obtained are:

For the reaction $Na_2HAsO_4,12H_2O \longrightarrow Na_2HAsO_4,7H_2O + 5H_2O$, at 14·90°, 5·24 mm.; and at 20°, 7·36 mm.

For the reaction $Na_2HAsO_4,7H_2O \longrightarrow Na_2HAsO_4 + 7H_2O$, at 24·92°, 9·98 mm.; at 30°, 14·39 mm.; and at 35°, 20·73 mm.

For the reaction $Na_2HPO_4,12H_2O \longrightarrow Na_2HPO_4,7H_2O + 5H_2O$, at 14·90°, 8·93 mm.; at 20°, 12·93 mm.; at 24·92°, 19·10 mm.; and at 30°, 27·05 mm.

The dissociation pressure–temperature curves for sodium arsenate show a transition at about 22° between the hepta- and the dodecahydrate.

The heats of hydration of the same reactions have been calculated at several temperatures by the aid of the Clapeyron–Clausius and the Nernst equation.

The specific heats of the two hydrates of sodium arsenate have been approximately determined.

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