

the packing of molecules, in some directions at least, is of the type in which separate molecules cannot be distinguished, that is, in which there is continuous bonding throughout the crystal.

Summary

Measurements of the planar spacings in crystalline benzene are described, and the results compared with those of Broomé.

Comment is made upon the interesting coincidence of some of the diffraction maxima found for liquid benzene with those of the crystals.

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THE AQUEOUS PRESSURE OF HYDRATED CRYSTALS. II. OXALIC ACID, SODIUM SULFATE, SODIUM ACETATE, SODIUM CARBONATE, DISODIUM PHOSPHATE, BARIUM CHLORIDE

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In a recent paper by Wilson¹ the critical discussion of methods for determining vapor pressures of salt hydrates contains the implication that in the gas-current method of determining vapor pressures, equilibrium may be established only from the side of under-saturation. That such an implication is unwarranted is shown by experiments described in this paper, in which equilibrium in the gas phase is approached from the side of over-saturation. The results of these experiments agree within the limit of error with those obtained in the usual way.

The apparatus used for our work corresponded very closely with that used by Baxter and Lansing² and for details their paper should be consulted.³ Furthermore, two of the substances examined by them, oxalic acid and sodium sulfate, were re-investigated, as well as four others.

Two sets of experiments were made with each substance at each temperature. In one set, dry air was passed over the carefully prepared mixture of hydrated crystals containing at least one-tenth of the first product of efflorescence. In the other set the air was first drawn over sulfuric acid solution of considerably higher aqueous pressure than that of the crystals, and then over a mixture of dehydrated crystals with a liberal proportion of hydrated material. The aqueous pressure of the sulfuric acid could in no case have fallen below that of the crystals

¹ R. E. Wilson, *THIS JOURNAL*, **43**, 709 (1921).

² Baxter and Lansing, *ibid.*, **42**, 419 (1920).

³ Schumb has recently suggested improvements on this method, *ibid.*, **45**, 342 (1923).

because the air drawn in, possessed initially the aqueous pressure existing in the room, which in many cases was higher than that of the sulfuric acid.

Calculation of the aqueous pressure of the crystals was made from the weight of water collected in the weighed phosphorus pentoxide tube and the volume of air drawn over the salt after correction to standard conditions. The volume of a mole of water vapor is assumed to be 22.41 liters under standard conditions.

While no particular difficulties were encountered with five of the substances examined, barium chloride was found to be extremely troublesome because of the slowness with which equilibrium is established from either direction, a fact which has already been noted by many other investigators.^{1,3,4} By suitable choice of conditions false equilibria may be set up almost at will. Using very slow currents of air with salt columns of extreme length (1.2×280 cm.) we finally succeeded in eliminating a large part of the uncertainty. Schumb reached the same end by using a salt column of large diameter and considerable length (5×50 cm. at a maximum). In our experiments, and also in Schumb's, the results with barium chloride lack the consistency obtained with the other salts. Furthermore, our results with barium chloride are perceptibly higher than Schumb's at 25° , and since ours agree better with those of Wilson at this temperature obtained by another method, the possibility exists that equilibrium was not quite reached with this substance in Schumb's experiments. It is to be noted that in Wilson's experiments as well as in ours equilibrium was approached from both sides.

TABLE I
AQUEOUS PRESSURES
 $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} - \text{H}_2\text{C}_2\text{O}_4$

Temp. $^\circ\text{C}$.	No. of tubes	Initial state of air current	Weight of water G.	Volume of dry air at 0° and 760 mm. Liters	Rate per hour Liters	Average interior pressure Mm.	Aqueous pressure Mm.
0	1	dry	0.0029	7.5	2.1	759	0.37
			.0057	16.5	3.1	758	.33
			.0055	17.7	2.8	771	.30
			.0055	15.7	2.8	764	.33
						Av.	.33
	2	wet	.0028	7.4	2.1	755	.35
			.0058	16.3	3.1	752	.34
			.0060	17.6	2.7	765	.32
			.0061	16.8	3.0	759	.34
						Av.	.34
					Av. of all	.34	
25	2	dry	.0221	7.57	1.5	765	2.77
			.0214	7.58	1.5	764	2.67
			.0220	7.43	1.5	754	2.77

⁴ Partington, *J. Chem. Soc.*, 99, 471 (1911).

TABLE I (Continued)

Temp. °C.	No. of tubes	Initial state of air current	Weight of water G.	Volume of dry air at 0° and 760 mm. Liters	Rate per hour Liters	Average interior pressure Mm.	Aqueous pressure Mm.
			.0213	7.45	1.5	753	2.67
						Av.	2.72
	2	wet	.0211	7.59	1.6	758	2.61
			.0104	3.73	1.0	763	2.64
			.0213	7.55	1.6	764	2.67
			.0191	6.71	1.5	764	2.70
						Av.	2.66
						Av. of all	2.69
50	2	dry	.1249	7.130	1.6	747.2	(15.94)
			.1242	7.260	1.4	746.2	15.55
			.1235	7.255	1.6	752.3	15.60
			.0883	5.198	1.4	750.6	15.53
						Av.	15.56
	2	wet	.1232	7.131	1.6	745.4	15.69
			.1253	7.291	1.4	744.8	15.59
			.1251	7.359	1.6	751.4	15.56
			.1012	5.865	1.6	748.6	15.73
						Av.	15.64
						Av. of all	15.60
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{SO}_4$							
0	1	dry	0.0226	7.43	2.0	757	2.85
			.0226	7.58	1.5	762	2.82
			.0218	7.68	2.7	764	2.69
			.0229	7.50	2.5	746	2.82
			.0222	7.50	2.1	751	2.75
						Av.	2.79
	1	wet	.0230	7.43	2.0	757	2.90
			.0224	7.56	1.4	762	2.80
			.0215	7.65	2.7	763	2.78
			.0222	7.47	2.5	745	2.74
			.0226	7.46	2.1	750	2.81
						Av.	2.81
						Av. of all	2.80
20	3	dry	.1055	7.564	1.5	764.1	(13.03)
	3		.1055	7.330	1.6	752.6	13.22
	1		.1051	7.348	1.6	753.4	13.17
	1		.1073	7.444	1.4	755.9	13.31
	1		.1069	7.488	1.3	761.4	13.28
	1		.1075	7.630	1.4	769.0	13.25
	1		.1067	7.422	1.6	754.1	13.25
	1		.1066	7.423	1.4	756.2	13.27
						Av.	13.25
	3	wet	.1071	7.411	1.4	754.9	13.33
	3		.1062	7.456	1.3	760.5	13.24
	1		.1068	7.622	1.5	770.6	13.20

TABLE I (Continued)

Temp. °C.	No of tubes	Initial state of air current	Weight of water G.	Volume of dry air at 0° and 760 mm. Liters	Rate per hour Liters	Average interior pressure Mm.	Aqueous pressure Mm.
	1		.1069	7.418	1.6	755.2	13.30
	1		.1063	7.411	1.5	757.2	13.27
						Av.	13.27
						Av. of all	13.26
			$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O} - \text{NaC}_2\text{H}_3\text{O}_2$				
0	1	dry	.0066	7.18	1.7	763	0.87
			.0071	7.19	1.6	756	.93
			.0071	7.13	1.8	750	.93
			.0066	7.15	1.5	762	.87
						Av.	.90
0	2	wet	0.0068	7.37	1.6	763	0.87
			.0070	7.37	1.6	755	.89
			.0075	7.30	1.8	749	.96
			.0066	7.34	1.5	762	.85
						Av.	.89
						Av. of all	.90
15	1	dry	.0227	7.14	1.1	764	3.01
			.0226	7.20	1.3	767	2.98
			.0229	7.16	1.4	762	3.02
						Av.	3.00
	2	wet	.0234	7.30	1.2	764	3.03
			.0234	7.37	1.4	767	3.02
			.0239	7.33	1.6	762	3.08
						Av.	3.04
						Av. of all	3.02
25	2	dry	.0504	7.35	1.6	754	6.38
	1		.0488	7.16	1.6	755	6.35
	2		.0409	6.01	1.7	761	6.38
	1		.0249	3.67	1.0	762	6.37
	1		.0484	7.10	1.6	755	6.35
	1		.0482	6.97	2.0	750	6.40
						Av.	6.37
	2	wet	.0504	7.37	1.7	755	6.37
			.0498	7.16	2.1	749	6.43
						Av.	6.40
						Av. of all	6.39
40	1	dry	.1436	7.050	1.6	752.7	18.60
			.1447	7.072	2.0	754.1	18.72
			.1440	7.075	1.5	753.6	18.61
			.1440	7.141	1.8	761.6	18.64
						Av.	18.64
	2	wet	.1489	7.230	1.6	751.2	18.76
			.1490	7.265	1.5	752.9	18.73
			.1492	7.324	1.8	760.8	18.80
						Av.	18.77
						Av. of all	18.70

TABLE I (Continued)
 $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} - \text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$

Temp. °C.	No. of tubes	Initial state of air current	Weight of water G.	Volume of dry air at 0° and 760 mm. Liters	Rate per hour Liters	Average interior pressure Mm.	Aqueous pressure Mm.
0	1	dry	.0203	7.26	1.9	757	2.62
			.0198	6.89	2.2	768	2.74
			.0212	7.39	2.1	761	2.71
						Av.	2.69
	2	wet	.0199	7.08	1.8	755	2.63
			.0197	6.79	2.1	766	2.75
			.0212	7.38	2.1	758	2.70
						Av.	2.69
				Av. of all	2.69		
	15	1	dry	.0665	7.16	2.0	757
.0691				7.42	1.8	763	8.72
.0672				7.23	1.8	762	8.71
				Av.	8.69		
2		wet	.0693	7.38	2.1	756	8.72
			.0716	7.64	1.8	761	8.77
			.0703	7.56	1.8	760	8.70
						Av.	8.73
				Av. of all	8.71		
25		1	dry	.1404	7.277	1.8	764.2
	.1400			7.225	2.1	763.7	17.97
	.1370			6.979	1.6	755.0	18.00
	.1218			6.167	1.9	755.9	18.12
				Av.	18.00		
	2	wet	.1412	7.274	1.8	762.6	17.98
			.1410	7.222	2.1	762.3	18.07
			.1376	6.997	1.6	753.7	18.00
			.1356	6.794	2.1	754.3	(18.27)
				Av.	18.02		
			Av. of all	18.01			
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} - \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$							
0	2	dry	.0209	7.58	1.5	760	2.60
			.0214	7.63	1.3	768	2.67
			.0209	7.48	1.2	762	2.63
			.0211	7.35	1.5	755	2.69
			.0212	7.32	2.0	751	2.70
				Av.	2.66		
	2	wet	.0212	7.53	1.5	759	2.65
			.0204	7.34	1.3	768	2.65
			.0211	7.46	1.2	762	2.67
			.0209	7.32	1.5	755	2.67
			.0206	7.31	2.0	752	2.68
				Av.	2.65		
				Av. of all	2.66		

TABLE I (Continued)

Temp. °C.	No. of tubes	Initial state of air current	Weight of water G.	Volume of dry air at 0° and 760 mm. Liters	Rate per hour Liters	Average interior pressure Mm.	Aqueous pressure Mm.
15	2	dry	.0717	7.48	1.8	757	8.92
			.0657	6.84	1.8	759	8.96
			.0709	7.60	1.8	768	8.80
			.0716	7.44	1.8	760	8.99
						Av.	8.92
	2	wet	.0717	7.47	1.8	757	8.93
			.0643	6.71	1.8	759	8.95
			.0710	7.61	1.8	768	8.82
			.0716	7.43	1.8	761	9.02
						Av.	8.93
					Av. of all	8.93	
25	2	dry	.1510	7.320	1.8	759.0	18.99
			.1522	7.370	1.8	760.7	19.05
			.1538	7.367	2.1	753.1	19.06
							Av.
	2	wet	.1508	7.323	1.8	759.8	18.98
			.1524	7.372	1.8	761.1	19.08
			.1538	7.365	2.1	753.5	19.08
							Av.
						Av. of all	19.04

BaCl₂·2H₂O—BaCl₂·H₂O

In the experiments at 15° six of the saturating tubes contained a mixture averaging BaCl₂·1.3H₂O while the seventh contained BaCl₂·1.9H₂O. In all the other experiments four of the tubes contained BaCl₂·1.9H₂O.

15	7	dry	0.0081	2.55	0.5	756	2.98
			.0071	2.57	.5	767	2.63
			.0074	2.40	.6	760	2.90
			.0071	2.39	.4	753	2.77
					Av.	2.82	
	7	wet	.0109	3.67	.6	760	2.80
			.0111	3.59	.6	756	2.90
			.0130	4.29	.6	758	2.85
							Av.
						Av. of all	2.83
25	7	dry	.0226	3.60	.6	754	5.84
			.0219	3.60	.7	754	5.66
			.0226	3.60	.5	748	5.79
			.0219	3.61	.6	760	5.69
					Av.	5.75	
	7	wet	.0154	2.46	.6	742	5.73
			.0216	3.58	.6	754	5.63
			.0213	3.44	.6	756	5.78
							Av.
						Av. of all	5.73
40	7	dry	0.0402	2.361	0.4	752	15.59

TABLE I (Concluded)

Temp. °C.	No. of tubes	Initial state of air current	Weight of water G.	Volume of dry air at 0° and 760 mm. Liters	Rate per hour Liters	Average interior pressure Mm.	Aqueous pressure Mm.
			.0430	2.558	.4	758	15.52
			.0388	2.328	.3	766	15.56
			.0425	2.527	.3	759	15.57
			.0437	2.442	.5	748	16.29
			.0631	3.534	.6	737	16.00
			.0428	2.477	.6	748	15.74
			.0449	2.590	.4	756	15.96
			.0319	1.828	.4	755	16.03
			.0434	2.509	.4	751	15.83
			.0430	2.500	.4	751	15.74
			.0271	1.566	.6	755	15.90
			.0418	2.411	.4	757	15.98
						Av.	15.75
	7	wet	.0438	2.478	.4	746	16.04
			.0429	2.525	.4	752	15.57
			.0628	3.733	.6	762	15.62
			.0627	3.649	.6	749	15.67
			.0610	3.587	.6	749	15.52
			.0455	2.475	.4	753	(16.82)
			.0425	2.345	.4	746	(16.45)
			.0423	2.476	.5	755	15.70
			.0421	2.447	.4	751	15.74
			.0423	2.422	.5	748	15.90
			.0427	2.421	.4	751	16.13
			.0429	2.389	.5	746	16.30
						Av.	15.82
						Av. of all	15.78

Although in the greater proportion of cases the average result with dry air is a trifle lower than that with wet air, it is by no means universally the case and in no instance is the difference so pronounced as to be beyond the experimental error.

The results with oxalic acid and sodium sulfate when compared with those obtained by Baxter and Lansing show satisfactory agreement.

$H_2C_2O_4 \cdot 2H_2O$			
	0°	25°	50°
Baxter and Lansing.....	0.38	2.65	15.55
Baxter and Cooper.....	.34	2.69	15.60
$Na_2SO_4 \cdot 10H_2O$			
	0°	20°	
Baxter and Lansing.....	2.77	13.33	(interpolated)
Baxter and Cooper.....	2.80	13.26	

The curves represent aqueous pressure plotted against the temperature, and the logarithm of the aqueous pressure plotted against the reciprocal

of the absolute temperature. In the latter case the points lie very nearly upon straight lines, which may be represented by the following equations.⁵

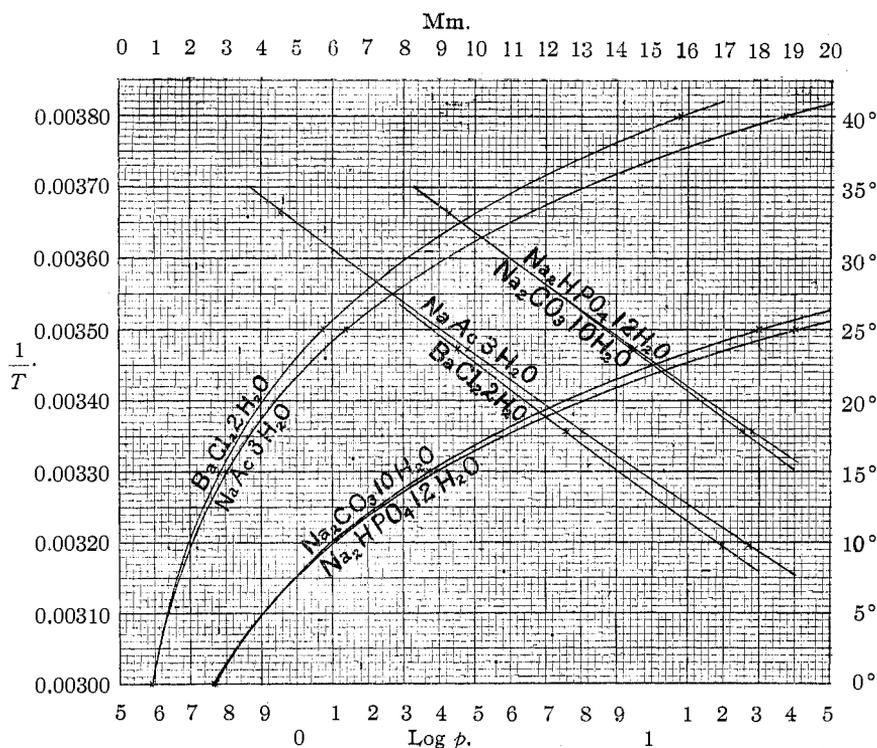
$$\text{NaAc} \cdot 3\text{H}_2\text{O} \log p = 19.5821 - \frac{11042.9}{T + 290.1}$$

$$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \log p = 11.8071 - \frac{3634.51}{T + 46.45}$$

$$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \log p = 14.1572 - \frac{5172}{T + 103.63}$$

$$\text{BaCl}_2 \cdot 2\text{H}_2\text{O} \log p = 17.9678 - \frac{9839.58}{T + 273.75}$$

In Table II the observed values are compared with those calculated from the equations, and the calculated values are extrapolated beyond the range



of the experiments. Similar equations and tables have already been prepared for oxalic acid, strontium chloride and sodium sulfate.²

Using the Clausius-Clapeyron equation, [Heat of efflorescence = $T \frac{dp}{dt} (V_{\text{vapor}} - V_{\text{solid}})$], and values for the vapor pressure found from

⁵ Antoine, *Compt. rend.*, 110, 632 (1890); $\log p = A + \frac{B}{T + C}$.

TABLE II
AQUEOUS PRESSURES, MM.

Na ₂ C ₂ H ₃ O ₂ ·3H ₂ O ⁶									
Temp., °C.	-25	-15	0	5	10	15
Obs.....	0.90	3.02
Calc.....	0.11	0.27	0.94	1.39	2.06	3.02
Na ₂ CO ₃ ·10H ₂ O									
Temp., °C.	-25	-15	0	5	10	15	20	25	32.02 ⁷
Obs.....	2.69	8.71	...	18.01	...
Calc.....	0.29	0.74	2.69	4.03	5.96	8.71	12.59	18.01	29.26
Na ₂ HPO ₄ ·12H ₂ O ⁸									
Temp., °C.	-25	-15	0	5	10	15	20	25	35
Obs.....	2.66	8.93	...	19.04	...
Calc.....	0.28	0.72	2.66	4.03	6.03	8.93	13.10	19.04	39.13
BaCl ₂ ·2H ₂ O ⁹									
Temp., °C.	0	10	15	20	25	30	35	40	50
Obs.....	2.83	...	5.73	15.78	...
Calc.....	0.94	1.97	2.83	4.04	5.73	8.08	11.32	15.78	30.15

the logarithmic vapor-pressure equations¹⁰ for 2° intervals, the heats of efflorescence per gram of water have been calculated. Table III contains also the heat of evaporation of water at the same temperatures.¹¹

Since the heat absorbed in efflorescence is the heat evolved in the combination of water vapor with the less hydrated phase, it may be considered¹²

⁶ Lescoeur gives the following values [*Compt. rend.*, 104, 60 (1887); *Z. physik. Chem.*, 2, 761 (1888)].

15°	20°	30°	40°	50°
2.4	4.4	10.5	20.6	35.3

⁷ Transition temperature, Richards and Fiske, *THIS JOURNAL*, 36, 485 (1914).

⁸ The following values were found by Frowein, *Z. physik. Chem.*, 1, 362 (1887).

0°	15°	25°
2.63 (interpolated)	8.84	18.71 (interpolated)

Dickenson found 19.13 mm. at 25°, *THIS JOURNAL*, 43, 723 (1921).

⁹ Frowein, *Z. physik. Chem.*, 1, 5, 362 (1887), interpolated

15°	25°	40°
2.19 mm.	5.13 mm.	16.60 mm.

Partington, *J. Chem. Soc.*, 99, 466 (1911); 25.01°, 5.26 mm. Foote and Scholes, *THIS JOURNAL*, 33, 1309 (1911); 25°, 4.8 mm. Wilson, Ref. 1, p. 704; 25°, 5.8 mm. Schumb, Ref. 3, p. 351; 25°, 5.50 mm.

¹⁰ Baxter and Lansing's equations are used for oxalic acid, strontium chloride and sodium sulfate. Ref. 2.

¹¹ Smithsonian Physical Tables, 1920, 7th ed., p. 234.

¹² van't Hoff, "Lectures," 1898, I, 59.

TABLE III
HEATS OF EFFLORESCENCE PER GRAM OF WATER IN 15° CALORIES

°C.	H ₂ O	H ₂ C ₂ O ₄ · 2H ₂ O	Na ₂ C ₂ H ₃ O ₂ · 3H ₂ O	SrCl ₂ · 6H ₂ O	Na ₂ SO ₄ · 10H ₂ O	Na ₂ CO ₃ · 10H ₂ O	Na ₂ HPO ₄ · 12H ₂ O	BaCl ₂ · 2H ₂ O
0	595	672	660	670	705	676	693	...
15	588	709	698	695	697	686	713	661
25	582	725	720	712	698	693	732	681
40	574	762	757	713
50	568	786

to be made up of (1) the heat evolved in the condensation of the water to the liquid state and (2) that evolved in the combination of liquid water with the less hydrated phase. The latter quantity, therefore, is obtained as the difference between the heat of efflorescence and the heat of evaporation of water at the same temperature.

In Table IV these values are given in kilogram calories per mole of salt, and in Table V per mole of water.

TABLE IV
HEATS OF REACTION I KG. CAL.

Temp. °C.	H ₂ C ₂ O ₄ +2H ₂ O	Na ₂ C ₂ H ₃ O ₂ +3H ₂ O	SrCl ₂ · 2H ₂ O +4H ₂ O	Na ₂ SO ₄ +10H ₂ O	Na ₂ CO ₃ · 7H ₂ O +3H ₂ O	Na ₂ HPO ₄ · 7H ₂ O +5H ₂ O	BaCl ₂ ·H ₂ O +H ₂ O
0	2.76	3.49	5.38	19.8	4.36	8.79	..
15	4.37	5.97	7.74	19.7	5.32	11.30	1.32
25	5.14	7.44	9.35	20.8	5.98	13.49	1.78
40	6.77	9.88	2.51
50	7.84

TABLE V
HEATS OF REACTION PER MOLE OF WATER KG. CAL.

Temp. °C.	H ₂ C ₂ O ₄ +2H ₂ O	Na ₂ C ₂ H ₃ O ₂ +3H ₂ O	SrCl ₂ · 2H ₂ O +4H ₂ O	Na ₂ SO ₄ +10H ₂ O	Na ₂ CO ₃ · 7H ₂ O +3H ₂ O	Na ₂ HPO ₄ · 7H ₂ O +5H ₂ O	BaCl ₂ ·H ₂ O +H ₂ O
0	1.38	1.16	1.35	1.98	1.45	1.76	..
15	2.19	1.99	1.94	1.97	1.77	2.26	1.32
25	2.57	2.48	2.34	2.08	1.99	2.70	1.78
40	3.39	3.29	2.51
50	3.92

If the heat of reaction is calculated according to the method suggested by van't Hoff,¹³ $\text{heat} = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{F_2}{F_1}$, where F is the quotient of the aqueous pressure of the salt divided by that of water at the same temperature, values not very different from those in Table IV are obtained. It is to be noted that this method uses the experimental values for the vapor pressure of water instead of the experimental heats of evaporation of water. Aqueous pressures for the salts are found from the logarithmic equations in computing Table VI.

¹³ Frowein, Ref. 8, Ref. 12.

TABLE VI
 HEATS OF REACTION II KG. CAL.

Temp. °C.	H ₂ C ₂ O ₄ +2H ₂ O	NaC ₂ H ₃ O ₂ +3H ₂ O	SrCl ₂ · 2H ₂ O +4H ₂ O	Na ₂ SO ₄ +10H ₂ O	Na ₂ CO ₃ · 7H ₂ O +3H ₂ O	Na ₂ HPO ₄ · 7H ₂ O +5H ₂ O	BaCl ₂ ·H ₂ O +H ₂ O
0-5	2.82	3.73	5.44	17.69	4.27	8.74	..
10-15	3.86	5.37	7.09	18.85	5.28	10.51	1.10
20-25	4.85	6.70	8.69	19.88	5.65	12.18	1.59
35-40	6.31	9.28	2.32
45-50	7.33

Direct determination of the heat of reaction has been made by Thomsen by finding the heats of solution of the more and less hydrated phases. His experiments were carried out at 18° and are expressed in 18° calories. Table VII gives a comparison of results calculated at 18° in the above fashion and the values found directly.

 TABLE VII
 HEATS OF REACTION KG. CAL.

	Calc. I 18°	Calc. II 17.5°	Found ¹⁴ 18°
H ₂ C ₂ O ₄ + 2H ₂ O.....	4.50	4.30	6.33
NaC ₂ H ₃ O ₂ + 3H ₂ O.....	6.43	6.11	8.68
SrCl ₂ ·2H ₂ O + 4H ₂ O.....	8.14	7.81	9.60
Na ₂ SO ₄ + 10H ₂ O.....	20.18	19.14	19.2
Na ₂ CO ₃ ·7H ₂ O + 3H ₂ O.....	5.51	5.23	5.49
Na ₂ HPO ₄ ·7H ₂ O + 5H ₂ O.....	11.71	11.19	11.22
BaCl ₂ ·H ₂ O + H ₂ O.....	1.41	1.32	3.83

The agreement between the two sets of calculated results is on the whole better than that between the calculated and experimental quantities. Furthermore, although both sets of calculated results show a marked increase with rise in temperature, Pickering⁴ found experimentally the heat of hydration of anhydrous sodium acetate, sodium carbonate and strontium chloride to *decrease* somewhat with rising temperature.

Summary

1. The air-current method for determining the aqueous pressures of salt hydrates has been further tested by establishing equilibrium from the side of over-saturation of the air current as well as from the side of under-saturation and identical results have been obtained by both methods.

2. Aqueous pressures of several salts at different temperatures have been determined.

3. Heats of reaction of the wholly or partially dehydrated salts with water have been calculated at different temperatures and compared with experimentally determined values of these quantities as found by Thomsen.

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¹⁴ Thomsen, "Thermochem. Untersuch.," II, p. 293; III, pp. 119, 123, 125, 157, 161, 191, Leipzig, 1882, 1883.