rium, to give long swings, in place of its natural short ones, in order to do a vast amount of useless work. The suspicion is unavoidable that the simple pendulum principle of the balance has been lost sight of in the entirely false expectation that the absolute variation of a swing would be increased by lengthening it. Possibly it has been supposed that short swings would be more likely to stop or to be erratic than long ones, but this is contrary to the very great amount of experience of those who use short swings, and it is contrary also to the precepts of high authorities, such as Fresenius and Carnot, already alluded to in this article. There is little doubt that many have merely followed the example of others in adopting this astonishing practice, without due consideration of the matter, and perhaps the mathematical and physical aspects of the method, or possibly its spectacular features, have had some influence in leading to its adoption.

It is to be hoped that all recommendations of long-swing weighing will soon disappear from our text-books of quantitative analysis, so that our future workers in chemistry may not be in danger of being burdened with a preposterously laborious method.

The writer is indebted to his colleague, Dr. John Zeleny, Professor of Physics, who has kindly examined the arguments presented in this article and has approved of its main conclusions in regard to long and short swings of the balance.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE AQUEOUS PRESSURE OF SOME HYDRATED CRYSTALS. OXALIC ACID, STRONTIUM CHLORIDE AND SODIUM SULFATE.

BY GREGORY PAUL BAXTER AND JOHN ERNEST LANSING.

Received January 17, 1920.

Information concerning the aqueous pressure of hydrated crystals is in an unsatisfactory state, partly because the different methods used have not yielded concordant results, and partly because no systematic attempt has been made to cover the ground thoroughly, so that data in this field are meagre. Yet, a knowledge of aqueous pressure of crystals is often desirable, for either theoretical or practical purposes, such as the determination of conditions under which hydrated crystals are stable. The present investigation was undertaken chiefly for the purpose of perfecting a reliable method of measuring aqueous pressures of crystals, although the data obtained may possess some intrinsic value.

The "air current" or "transference" method which was chosen, has frequently been employed for the purpose in the past, but as the results obtained have been on the whole unsatisfactory, this method has acquired an undeservedly bad reputation. We have found, however, that with suitable precautions very uniform and satisfactory results may be obtained.

One of the chief difficulties has been due to the fact that the transition from a more to a less hydrated phase frequently does not take place unless the original substance is scratched or crushed or, best, inoculated with the less hydrated phase. An important precaution is, therefore, to mix intimately by grinding the more hydrated and a considerable proportion of the less hydrated phase. The presence of the latter substance is of further advantage in absorbing any excess of water coming possibly from pockets of mother liquor in the crystals or other sources. Beyond this precaution those involved in the accurate determination of moisture are necessary.

The experiments described in this paper were carried out with the 3 systems following: oxalic acid ($H_2C_2O_4.2H_2O \longrightarrow H_2C_2O_4$), strontium chloride ($SrCl_2.6H_2O \longrightarrow SrCl_2.2H_2O$), and sodium sulfate ($Na_2SO_4.10H_2O \longrightarrow Na_2SO_4$). These substances were purified by one crystallization and then were air dried. Some of the oxalic acid was heated to 100° for some time to expel the crystal water and then was intimately mixed with 10 times its weight of hydrated crystals by comparatively fine grinding. Considerable portions of the strontium chloride and sodium sulfate were exposed for some time in a vacuum desiccator over sulfuric acid and were then intimately mixed with from 10 to 20 times the amount of hydrated salt. The mixtures, interspersed with glass beads, were packed in large U-tubes which could be closed with ground joints and stopcocks, and were allowed to stand for some time before use, so that equilibrium might be established. The column of beads and substance was about 1.5 cm. in diameter and 30 to 40 cm. long, and was immersed to a considerable depth in the thermostat.

The method of experimentation was to pass a measured volume of dry air over the substance at constant temperature into a weighed tube containing phosphorus pentoxide, and finally into an aspirator bottle, in which the volume of air was determined. In order to purify and dry the air it was passed over silver nitrate solution, fused potassium hydroxide and conc. sulfuric acid, all contained in a system of large, glass-drying towers. The phosphorus pentoxide had been freshly sublimed in a current of oxygen, and was mixed with a considerable proportion of beads in the absorbing tube to prevent clogging. The absorbing tube was provided with glass stopcocks for the protection of the pentoxide when the tube was not in use. Great pains were taken that the moist air should always enter the pentoxide tube from the same side, so as to avoid the evaporation of the moisture from the end of the tube nearest the outlet.

The pentoxide tube was always weighed by substitution for a counterpoise similar in material, shape, and volume, and during the actual weighing of both the pentoxide tube and its counterpoise, one stopcock was always open in order to avoid irregularities from changing atmospheric conditions.

The volume of air passed over the salt was found by measuring the water run out of the aspirator in a large bottle, the volume of which had been determined very carefully by weighing its water content. At the beginning of the experiment the aspirator was always filled to the top with water, which had been allowed to come to room temperature before the air current was started. Thus no change in the volume of the water could take place during the experiment. The volume of the connecting tubes between the saturating tube and the aspirator was so small that changing atmospheric conditions could not have introduced any appreciable error in the measurement of the volume of the air.

In order to make certain that saturation really was reached in the saturating tube, the rate at which the air was passed over the salt was varied between comparatively wide limits, the maximum rate being not far from 4 liters per hour, the minimum rate about $^1/_4$ of this. Within these limits it was not possible to detect any certain difference in the results, so that it seems reasonably sure that equilibrium was really reached in the saturating tube and that the moisture was completely absorbed in the weighing tube.

Since in no case was the observed vapor pressure as high as that of water at the temperature of the room, condensation could not have occurred between the saturating and absorbing tubes. Obviously this condition limits the temperature at which the foregoing method may be used, unless the connection between the tubes is immersed in the thermostat. Such a modification has been successfully used in later experiments of the same nature.

Temperatures were determined to a few hundredths of a degree by comparison of the thermometers with accurate standards. The thermostats were thoroughly stirred and the temperature control by means of toluene regulators was as accurate as the thermometric readings. The thermostat at 0° was chilled by means of a layer of several inches of cracked ice. At 25°, an electric light bulb and on warm days a coil of cold water in addition served satisfactorily, while the bath was maintained at 50° by the method recently proposed by Derby[1] of passing a current through the water of the bath between carbon electrodes.

From the weight of water found in the absorbing tube was calculated its theoretical volume under standard conditions, upon the assumption that a mol occupies 22.41 liters. The volume of air in the aspirator was

---

[1] THIS JOURNAL, 35, 1767 (1913).

TABLE I.

$H_2C_2O_4.2H_2O$.

Temp. ° C.	Wt. of water. G.	Volume of dry air at 0° and 760 mm. Cc.	Rate per hour. Liters.	Average interior pressure. Mm.	Aqueous pressure. Mm.
0	0.0028	7199	1.5	765.7	0.37
	0.0029	7231	1.5	765.0	0.38
	0.0027	7401	1.5	765.4	0.35
	0.0031	7303	1.6	764.5	0.40
					Av., 0.38
15	0.0081	7339	2.7	763.2	(1.05)
	0.0094	7582	2.8	764.2	1.18
	0.0094	7535	3.7	764.4	1.18
	0.0085	7292	3.6	764.6	1.10
	0.0092	7374	2.1	759.4	1.18
	0.0085	7130	2.0	759.4	1.12
					Av., 1.15
25	0.0198	7157	1.8	760.4	2.61
	0.0198	7070	1.7	761.4	2.64
	0.0200	7098	1.4	761.0	2.66
	0.0199	7016	1.6	760.4	2.67
	0.0199	6903	2.9	755.1	2.70
	0.0197	7066	1.6	762.7	2.64
					Av., 2.65
40	0.0627	7352	2.2	743.4	7.80
	0.0614	7216	2.5	743.2	7.78
	0.0629	7336	2.4	742.3	7.83
	0.0610	7220	2.2	742.5	7.72
	0.0634	7415	2.6	742.2	7.81
	0.0621	7285	2.0	743.0	7.80
					Av., 7.79
50	0.1228	7396	2.0	764.6	15.47
	0.1190	7172	1.8	764.9	15.47
	0.1262	7483	1.6	761.9	15.66
	0.1223	7246	1.5	762.3	15.68
	0.1178	7175	1.1	761.4	(15.24)
	0.1231	7379	2.6	759.5	15.44
	0.1192	7147	2.7	759.4	15.43
	0.1254	7491	1.2	761.1	15.53
	0.1216	7247	1.3	761.6	15.57
	0.1257	7501	2.1	761.0	15.54
	0.1221	7271	2.1	761.2	15.57
	0.1231	7352	1.6	766.6	15.64
					Av., 15.55
		$SrCl_2.6H_2O$.			
0	0.0088	6993	1.6	763.7	1.20
	0.0092	6869	1.7	764.2	1.27
	0.0094	7241	2.0	762.8	1.24
	0.0092	7135	2.0	763.3	1.22

TABLE I (*continued*).

Temp. °C.	Wt. of water G.	Volume of dry air at 0° and 760 mm. Cc.	Rate per hour. Liters.	Average interior pressure. Mm.	Aqueous pressure. Mm.
	0.0092	6609	2.7	761.1	1.31
	0.0096	7507	2.4	750.0	1.19
	0.0094	7383	2.7	749.7	1.19
	0.0097	7330	2.8	744.6	1.22
	0.0095	7200	2.3	744.6	1.22
					Av., 1.23
15	0.0327	7501	2.4	765.0	4.13
	0.0313	7230	1.9	764.7	4.10
	0.0322	7455	2.8	764.6	4.09
	0.0303	7201	2.2	764.2	3.98
	0.0317	7414	2.8	763.4	4.04
	0.0297	7170	2.7	762.4	3.91
	0.0321	7298	2.6	746.0	4.06
	0.0311	7133	2.5	745.3	4.02
	0.0315	7374	2.6	745.5	3.94
	0.0306	7202	2.0	745.7	3.92
	0.0316	7304	2.8	744.3	3.98
	0.0303	7186	2.7	744.0	3.88
	0.0317	7520	2.4	748.6	3.91
	0.0309	7384	2.5	748.4	3.88
					Av., 3.99
25	0.0642	6988	1.6	757.7	8.56
	0.0634	7038	2.3	756.0	8.39
	0.0638	7157	1.4	762.9	8.37
	0.0622	7115	1.2	760.6	8.18
	0.0626	7020	1.4	760.2	8.34
	0.0643	7205	1.7	764.6	8.39
	0.0631	7108	1.6	765.1	8.36
	0.0653	7272	1.7	762.1	8.42
	0.0649	7198	2.0	762.2	8.45
	0.0643	7243	1.6	761.8	8.32
	0.0654	7405	1.5	767.1	8.34
					Av., 8.37
		$Na_2SO_4.10H_2O$.			
0	0.0213	7340	1.6	765.0	2.75
	0.0208	7082	2.2	765.1	2.78
	0.0209	7166	2.4	764.6	2.76
	0.0204	6912	1.6	759.8	2.78
	0.0208	7088	1.6	759.5	2.76
					Av., 2.77
15	0.0714	7268	2.3	764.3	9.23
	0.0721	7359	2.3	764.7	9.21
	0.0745	7595	2.8	763.7	9.21
	0.0718	7346	3.1	764.3	9.18
					Av., 9.21

TABLE I (*continued*).

Temp. ° C.	Wt. of water. G.	Volume of dry air at 0° and 760 mm. Cc.	Rate per hour. Liters.	Average interior pressure. Mm.	Aqueous pressure. Mm.
25	0.1506	7224	1.6	760.8	19.23
	0.1488	7114	2.0	760.9	19.30
	0.1442	6916	2.6	759.1	19.19
	0.1475	7106	1.2	761.5	19.17
	0.1457	7006	1.3	761.9	19.21
	0.1490	7191	1.6	761.1	19.13
	0.1517	7299	1.7	761.1	19.18
	0.1497	7208	1.6	761.2	19.17
					Av., 19.20

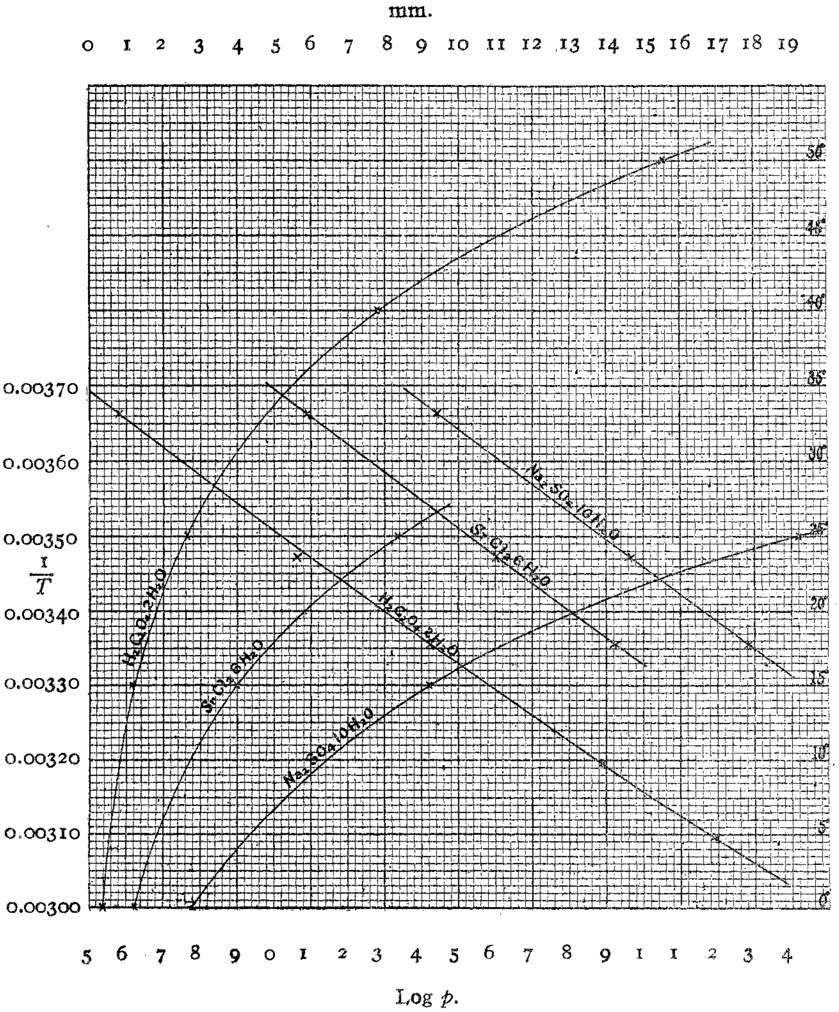

Fig. 1.

TABLE II.

$H_2C_2O_4.2H_2O$.

Temp.	Observed. Mm.	Calculated. Mm.	Difference. Mm.
—25°	. . .	0.05	. .
—15	. . .	0.11	. .
0	0.38	0.38	0.00
15	1.15	1.24	+0.09
25	2.65	2.65	0.00
40	7.79	7.80	+0.01
50	15.55	15.56	0.0
60	. . .	30.34	. .
70	. . .	57.95	. .

$SrCl_2.6H_2O$.[a]

Temp.	Observed. Mm.	Calculated. Mm.	Difference. Mm.
—25°	. .	0.14	. .
—15	. .	0.35	. .
0	1.23	1.23	0.00
15	3.99	3.99	0.00
25	8.37	8.37	0.00
40	. .	23.99	. .
50	. .	46.56	. .

$Na_2SO_4.10H_2O$.[b]

Temp.	Observed. Mm.	Calculated. Mm.	Difference. Mm.
—25°	. . .	0.27	. .
—15	. . .	0.72	. .
0	2.77	2.77	0.00
15	9.21	9.21	0.00
25	19.20	19.19	—0.01
40	. . .	52.97	. .
50	. . .	98.85	. .

[a] Frowein, *Z. physik. Chem.*, **1**, 5 (1887).

Temperature.	Mm.
14.75°	3.29
20.34	5.14
25.66	7.82
30.01	10.87
34.66	15.33
39.45	21.57

Andreae, *ibid.*, **7**, 260 (1891).

Temperature.	Mm.
19.7°	5.61
25.6	8.72
29.9	11.84
34.1	15.83
37.55	19.86

[b] Lescoeur, *Ann. chim. phys.*, [6] **21**, 529 (1890).

Temperature.	Mm.
0°	3.8
5	5.2
10	7.0
15	9.7
20	13.9
25	19.0
29	24.0

corrected to the same conditions, after allowing for a slight difference in pressure inside and outside the aspirator, determined with an open-arm water manometer attached to the aspirator bottle. The volume of the water vapor, divided by the volume of dry air plus the volume of the water vapor, and multiplied by the total interior pressure, yields the aqueous pressure of the salt under the conditions of the experiment. The results are given in the tables.

On the accompanying curves the aqueous pressure is plotted against the temperature, and the logarithm of the aqueous pressure is plotted against the reciprocal of the absolute temperature. In the latter case the points lie very nearly upon straight lines, almost exactly so with sodium sulfate. These lines are represented very closely by the following equations:[1]

$$H_2C_2O_4.2H_2O \qquad \log p = 18.053 - \frac{9661}{T + 250}$$

$$SrCl_2.6H_2O \qquad \log p = 15.081 - \frac{6371}{T + 152}$$

$$Na_2SO_4.10H_2O \qquad \log p = 10.566 - \frac{2794.1}{T + 3}$$

In Table II the observed values are compared with those calculated from the equations. The concordance is such as to inspire confidence in results obtained by extrapolation over a moderate temperature range.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE UNIVERSITY OF BRISTOL.]

COLLOIDAL ELECTROLYTES. SOAP SOLUTIONS AND THEIR CONSTITUTION.[2]

BY JAMES W. McBAIN AND C. S. SALMON.

Received June 11, 1918.

Colloidal electrolytes are salts in which an ion has been replaced by a heavily hydrated polyvalent micelle that carries an equivalent sum-total of electrical charges and conducts electricity just as well or even better than the simple ion it replaces. This is the conclusion to which our 6 years study of soap solutions has led us.

---

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

[2] This is the paper referred to by McBain, *Trans. Faraday Soc.*, **9**, 99 (1913); *Kolloid-Z.*, **13**, 56 (1913); and *Trans. Chem. Soc.*, **105**, 957 (1914), whose publication has been delayed owing to the outbreak of war. The work was completed in the early Summer of 1914. Previous papers from this laboratory on the constitution of soap solutions commence with McBain and Taylor, *Ber.*, **43**, 321 (1910); *Z. physik. Chem.*, **76**, 179; (1912); further papers, *Trans. Chem. Soc.*, **99**, 191 (1911); *Z. physik. Chem.*, **99**, 191 (1911); **101**, 2042 (1912); **105**, 417, 957 (1914); *Trans. Faraday Soc.*, **9**, 99 (1913); *Kolloid-Z.*, **12**, 256 (1913).