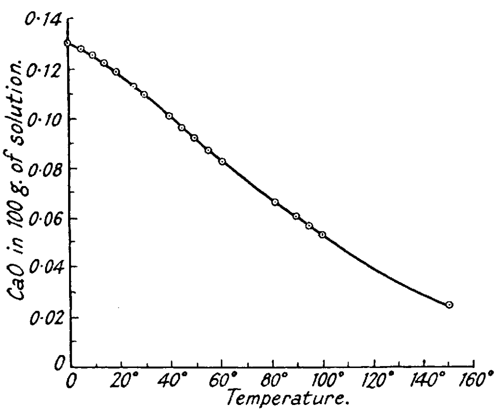
276. *Notes on the System Lime–Water, and on the Determination of Calcium.*

By Henry Bassett.

In spite of many investigations of the solubility of calcium hydroxide there are still points in the behaviour of the system lime–water which are obscure. The relevant literature has been summarised by certain recent workers (*e.g.*, Haslam, Calingaert, and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 308; Johnston and Grove, *ibid.*, 1931, **53**, 3976). Of the earlier workers, Lamy (*Compt. rend.*, 1878, **86**, 333; *Ann. Chim. Phys.*, 1878, **14**, 145) studied the solubility of lime with most thoroughness, and with curious results. Most later workers overlooked his paper, so the main reason for the wide divergence in the results obtained by different investigators has only recently been appreciated.

Lamy determined the solubility of coarsely crystalline calcium hydroxide and of freshly slaked pure lime, and found that the latter was much the more soluble. Since calcium hydroxide is normally obtained by slaking calcium oxide, and because its solubility in water is low and decreases with rise of temperature, its particle size is usually very small. For the same reasons the average particle size only increases very slowly in contact with the saturated solution.

The calcium hydroxide of small particle size comes into equilibrium with water quickly enough for the same value for the solubility to be found after one hour's shaking as after 24. Although such solutions are supersaturated with respect to coarse particles, growth of the particles occurs so slowly that the effect due to it is scarcely apparent when the usual tests are made to see whether true equilibrium between solid and solution has been attained. Hence, although many of those who have determined the solubility of calcium hydroxide applied such tests, their results are too high and do not correspond to the limiting values for coarse particles. Miller and Witt (*J. Physical Chem.*, 1929, **33**, 285) appear to have been the first to appreciate the influence of particle size on the solubility of calcium hydroxide, but, in spite of that, their one measurement, at 30°, seems to be 10% too high. Johnston and Grove (*loc. cit.*) also realised the position and made one very careful determination with coarsely crystalline hydroxide at 25°. They found that 100 g. of saturated solution contained 0·111 g. of CaO, but the present author considers that this is probably slightly low and that 0·113 g. is a better value. It is difficult to get complete saturation of the solution with the dense coarse crystals.



No complete series of determinations over the range 0—100° has hitherto been published in which the influence of particle size has been taken into account. The author's results for this range are shown in Table I, in which are also given for comparison the results of Moody and Leyson (J., 1908, **93**, 1767) and of Haslam, Calingaert, and Taylor (*loc. cit.*); these appear to be the most satisfactory figures hitherto published. Shenstone and Cundall (J., 1883, **43**, 550) made two determinations of the solubility, at 19° and 150°, in a special platinum apparatus. These appear to be very good results and are included in Table I and in the Fig.

The data in col. 3 are based on some dozens of experiments and give the true solubility of calcium hydroxide, *i.e.*, the solubility of preparations in which the individual crystals are large enough for the effect of particle size to have been eliminated. These values fall on a smooth curve shown in the Fig., which has a point of inflexion at a temperature of about 60°. The higher solubilities of very fine particles of calcium hydroxide are naturally not very reproducible owing to the general instability of such systems. Col. 4 of Table I gives values obtained for the freshly slaked lime; values which are 10—15% higher than the limiting values are readily obtained. The limiting value of the cryohydric temperature is — 0·116°, whereas for freshly slaked lime the value — 0·123° was obtained.

TABLE I.

Temp.	Solid phase.	True sol. of coarse $Ca(OH)_2$.	Sol. of fine $Ca(OH)_2$.	Values of M. and L.	Values of H., C., and T.
		G. CaO per 100 g. solution.			
−0·088°	Ice	0·100			
−0·090	,,	0·102			
−0·123	Ice and $Ca(OH)_2$		0·144, 0·140		
−0·116	,,	0·130			
0	$Ca(OH)_2$	0·130	0·151, 0·143		
2	,,			0·130	
5	,,	0·128	0·142		
10	,,	0·125	0·138	0·127	0·131
15	,,	0·122	0·133	0·124	
19 *	,,	0·118			
20	,,			0·120	
25	,,	0·113	0·129	0·115	
30	,,	0·109	0·121	0·110	
40	,,	0·100	0·107	0·101	
42	,,				0·102
45	,,	0·0962			
48	,,				0·0957
50	,,	0·0917	0·0968	0·0923	
55	,,	0·0861			
56	,,				0·0884
60	,,		0·0917	0·0847	
60·8	,,	0·0818			0·0842
66	,,				0·0802
70	,,		0·0800	0·0784	0·0762
80	,,			0·0731	0·0673
81·7	,,	0·0657			
90	,,	0·0591			
95·3	,,	0·0561			
99	,,	0·0523			
150 *	,,	0·0246			

* Shenstone and Cundall (*loc. cit.*).

EXPERIMENTAL.

The calcium hydroxide was obtained by slaking lime, prepared by ignition in platinum of pure precipitated calcium carbonate, made from exhausted carbon dioxide Kipp liquor which had been carefully neutralised with some of the same white marble used for the Kipp filling. The neutralised liquor was shaken for several days with a small excess of lime prepared from marble, and then filtered in order to remove traces of iron, magnesium, etc. The calcium carbonate was precipitated by slow addition of ammonium carbonate. After standing for about a day with occasional stirring, it was very thoroughly washed by decantation and finally on a Buchner funnel, and then dried in the oven. It was distinctly crystalline and only contained 0·008% of chlorine.

The saturated solutions were obtained by mechanically shaking 0·75—1·5 g. of hydroxide with 100 c.c. of water for a sufficient length of time in thermostats at the desired temperature. The solutions were contained in bottles of either silver or platinum, the latter being that referred to in J., **1917**, **111**, 632 : it was possible to fit a small condenser around the neck. At the lower temperatures the bottles were tightly closed with well-waxed corks. At higher temperatures, the long narrow neck of the flask, closed by a good, tightly fitting, unwaxed cork, was allowed to project above the thermostat liquid.

The time of shaking required varied with circumstances. Freshly slaked lime which had been boiled with solution in the platinum flask for 4 days (1 g. CaO to 100 c.c. water) gave the same solubility at 25° or other temperatures as large crystals of hydroxide, prepared by heating large volumes of cold saturated lime water to 50° or by slow evaporation over sulphuric acid at room temperature. Calcium hydroxide prepared by the boiling process was used for the majority of the experiments, and only required about 6 hours' shaking at the lower temperature for attainment of equilibrium.

The high solubility given by the finely divided freshly slaked lime at any temperature gradually diminishes at a rate which depends upon (*a*) the temperature, (*b*) the relative proportion of solid hydroxide and solution, and (*c*) the vigour of shaking or stirring. Under the conditions of experiment, the limiting value of the solubility was reached at 100° in less than 4 days, but about a month was required at 50°.

Although the hydroxide prepared from the pure precipitated carbonate reaches its condition of minimum solubility after boiling in platinum for about 4 days, the crystals are still very minute. The interesting observation was made, however, that if calcium hydroxide prepared by slaking quicklime made from chalk (Upper Chalk from Purley, Surrey) was similarly boiled, it became relatively coarsely crystalline (crystals up to 1 mm. in diameter). It would seem that the small amount of argillaceous material present facilitates crystallisation in some way.

At higher temperatures the solids were allowed to settle in the thermostat, and the clear solutions withdrawn for analysis by means of a warmed pipette. At lower temperatures they were generally filtered through a jacketed filter tube or one immersed in the thermostat. The filtering medium (asbestos and a disc of filter-paper) was shown to have no measurable effect on the concentration of the solution on account of adsorption effects.

The equilibrium solid phase was always examined both microscopically and analytically. It was dried by washing with alcohol (or acetone) and ether, and always found to be $Ca(OH)_2$. No evidence has been found for the existence of any hydrate of this compound or of more than one crystalline modification. The matter has been studied with some care owing to various dubious statements in the literature. The possibility that the washing with alcohol might have decomposed a hydrate has, of course, been borne in mind.

Ashton and Wilson's careful crystallographic examination of calcium hydroxide prepared by various methods (*Amer. J. Sci.*, 1927, **13**, 209) seems to have proved that the hydroxide has only been obtained crystallised in the hexagonal system. The idea that it is dimorphic which has crept into the literature seems to be due partly to the fact that crystalline preparations may show either hexagonal plates or small rhombohedra, and partly to a misunderstanding. The fact that the two forms may occur in the same preparation and coexist indefinitely (cf. Nogareda, *Anal. Fis. Quim.*, 1931, **29**, 556) indicates that they are not dimorphic forms. The idea seems to originate in a suggestion by Glinka (*J. Russ. Phys. Chem. Soc.*, 1885, **17**, 451; *Bull. Soc. franç. Min.*, 1887, **10**, 63) that the crystals probably did not belong to the hexagonal system, as had been previously thought, but to the orthorhombic. Glinka himself did not suggest that the hydroxide was dimorphic.

The high initial solubilities of freshly slaked lime might have been due to the existence of an unstable hydrate, and many years ago the author examined the relationship between the water content of freshly slaked lime and the water vapour pressure. Typical adsorption isotherms were obtained which showed that less than 0·5% of the extra water was at all firmly held, though slight adsorption effects were detectable up to about 10% of extra water. The curves gave no indication of any definite hydrate. All attempts by Haslam, Calingaert, and Taylor (*loc. cit.*) to prepare a monohydrate failed. Nogareda (*loc. cit.*, p. 33) has recently examined the dehydration curves of mixtures ranging from $CaO,5H_2O$ to CaO,H_2O with similar results. He concludes, however, that there is a definite monohydrate as a result of density determinations of the hydroxide and of a solid of the composition $Ca(OH)_2,H_2O$. The molecular volume for the extra molecule of water so obtained was found to be 15·6 in one case and 16·1 in another.

These figures are considered by Nogareda to approximate to the value 14·5, which, according to Moles and Crespi (*Anal. Fis. Quim.*, 1927, **25**, 549; *Z. physikal. Chem.*, 1927, **130**, 337), is characteristic of all but the first molecule of water in various hydrated sulphates. It should be noted that, according to Thorpe and Watts (J., 1880, **37**, 116), the molecular volumes of the water molecules in hydrates of the magnesium sulphate type have approximately the following values: in monohydrate, 10·7; difference between mono- and di-hydrate, 13·3; between di- and tri-, 14·5; between tri- and tetra-, 15·4; and between hexa- and hepta-, 16·2. It is evident that the molecular volume of water in hydrates tends to increase with the degree of hydration.

In the case of the lime products under consideration, it appears to the author that the effects of adsorption, which extend over the first molecule of extra water contained in the hydroxide preparations, might well cause its molecular volume to be rather less than that of the water in much wetter mixtures. In any case it is very difficult to determine the true value of the density of such material, and Nogareda's values are not much nearer to 14·5 than to the value 18 of ordinary water.

Notes on the Determination of Calcium.—Several analytical methods were employed in obtaining the results summarised in this paper. Many determinations were made gravimetrically as oxide after precipitation as oxalate; in other cases the calcium oxalate precipitate was titrated with standard permanganate, and in still other cases the alkalinity was determined with standard acid. With due precautions all these methods give good results, but in the gravimetric estimation as CaO it is essential to apply a correction for moisture absorption; from the weight of CaO actually found, 0·0005 g. was deducted from small weights of CaO, and 0·0007 g. from larger weights (up to 0·1 g.) (see p. 1275).

There appears to be a general belief that the volumetric estimation of calcium with permanganate, after precipitation as oxalate, is unreliable, but by use of the simple modification given below it may be made very accurate. As usually carried out, the method is liable to give slightly low results, but the correct explanation of this has not been given even in the most recent long paper on the subject (Hahn and Weiler, *Z. anal. Chem.*, 1927, **70**, 1). These authors concluded that the low results were due to slight decomposition (hydrolysis) of the precipitated calcium oxalate with removal of oxalic acid during the washing, but they did not prove this. The error is, in fact, due to the small, true, solubility of calcium oxalate, as shown by the following experiments.

(*a*) Pure calcium oxalate, prepared in a similar manner to the carbonate previously described, was used for the experiments. It had been air-dried after thorough washing with water, followed by absolute alcohol; it contained the merest trace of chlorine and was quite air-stable with reference to its water content during several years.

Calcium was determined by conversion of a weighed amount into sulphate, and oxalate by titration with permanganate standardised against sodium oxalate. The two results calculated as CaO were 38·03% and 38·02% respectively (Calc. for CaC_2O_4,H_2O: CaO, 38·39%). The air-dried material thus contains 13·18% of water (calc., 12·33%). The extra water was lost after drying over-night at 110°. The analysis shows that the lengthy washing of the preparation had not caused any disturbance to the CaO/C_2O_4 ratio.

(*b*) 0·5 G. of the same preparation of oxalate was washed on a 9-cm. ashless filter-paper with three successive amounts of 300 c.c. of distilled water, each 300 c.c. being collected and analysed separately: (1) 50 c.c. were titrated by 0·0186*N*-permanganate, and (2) 200 c.c. were evaporated with sulphuric acid, and the calcium sulphate weighed.

	(1)		(2)		
	$KMnO_4$, c.c.	G. of CaO per 200 c.c. soltn.	$CaSO_4$, g.	=	CaO, g.
(i)	0·47	0·00100	0·0010		0·00041
(ii)	0·38	0·00079	0·0014		0·00058
(iii)	0·40	0·00083	0·0018		0·00074

Within the limits of error of such determinations, these figures indicate that the calcium oxalate is dissolving as such, not that oxalic acid is being preferentially dissolved. The mean of the six values for CaO corresponds to 0·00082 g. CaC_2O_4 in 100 c.c. of solution.

(*c*) Numerous attempts were made to find whether small amounts of calcium oxalate became basic after prolonged extraction with water, and whether there were any indications that earlier extracts had a lower CaO/C_2O_4 ratio which increased in later extracts as the surface of the oxalate particles might be supposed gradually to become more basic. Entirely negative results were obtained.

(*d*) The solubility of the calcium oxalate was determined at 25° both in water and in dilute aqueous ammonia. The same result was obtained after 4 weeks' shaking as after one.

Solvent.	C.c. 0·0186*N*-$KMnO_4$ for 50 c.c. soltn.	Equiv. CaO in 100 c.c., g.	$CaSO_4$, g., from *x* c.c. soltn., g.	Equiv. CaO in 100 c.c., g.	CaC_2O_4 in 100 c.c. soltn., g.
Water	0·34	0·00035	150 c.c. gave 0·0016	0·00038	0·00082
1·99*N*-NH_3	1·20	0·00125	100 c.c. gave 0·0034	0·00140	0·00297
2·12*N*-NH_3	1·83	0·00191	125 c.c. gave 0·0046	0·00152	0·00385

The conclusions to be drawn from these results are that: (i) The values obtained from the oxalate and the calcium determinations are the same within the limits of accuracy of the experiments, which again shows that the calcium oxalate dissolves as such both in water and in dilute ammonia. (ii) The solubility in pure water at 25° is the same as that previously found by percolation at room temperature; water, percolating over calcium oxalate on a filter paper during an ordinary filtration, thus becomes approximately saturated with calcium oxalate. (iii) Calcium oxalate is much more soluble in dilute ammonia than in pure water (this is the normal enhanced solubility caused by electrolytes not yielding an ion in common with the substance being dissolved); it is evidently better to wash calcium oxalate precipitates with pure water rather than dilute aqueous ammonia as is sometimes suggested.

The solubility of calcium oxalate in water at 25° has previously been determined by Richards, McCaffrey, and Bisbee (*Z. anorg. Chem.*, 1901, **28**, 71), who found 0·00068 g. per 100 g. of solution.

It becomes evident from the above results that the ideal washing liquid for calcium oxalate precipitates is distilled water saturated with calcium oxalate. This can be used whether the precipitate is to be subsequently weighed as carbonate, oxide, or sulphate, or whether it is to be titrated with permanganate. It is better than the dilute solution of ammonium oxalate, suggested by Richards, McCaffrey, and Bisbee (*loc. cit.*) and by Hillebrand and Lundell ("Quantitative Inorganic Analysis, etc."); this is often used in gravimetric estimations but is clearly inadmissible for volumetric work.

It is noteworthy that, owing to the error due to moisture absorption by lime (see below), a more accurate result will be obtained when calcium is weighed as lime if no attempt is made to prevent solution of calcium oxalate during the washing. This is probably one reason why washing with dilute ammonia (which increases the solubility) has been found satisfactory, or even washing with warm or hot water, or hot ammonium oxalate solution, as is recommended in some text-books (*e.g.*, Clowes and Coleman, "Quantitative Chemical Analysis," 13th Ed., 1931, p. 81).

The simplest way of applying the method is to place a few g. of the bulk sample of pure dry calcium oxalate on a filter-paper and allow distilled water to flow through it, the solution so obtained being used to wash the calcium oxalate precipitate in the actual estimation. Excellent results are thus obtainable, as shown by the following example.

Two portions of pure calcium carbonate (0·125 g.), prepared as previously described, were dissolved in dilute hydrochloric acid and precipitated in the usual way as oxalate. The one precipitate was washed with cold distilled water (50 c.c.) until all chloride had been removed; the other was washed first with 2·5 c.c. of distilled water, then with 50 c.c. of the calcium oxalate solution obtained as above. The preliminary wash with 2·5 c.c. of water was to obviate any danger of slight additional precipitation of oxalate by interaction of the ammonium oxalate in the mother-liquor and the washing solution: it is not really necessary. The washed precipitates were dissolved in hot 2*N*-sulphuric acid and titrated with permanganate standardised against sodium oxalate. In the two experiments, the CaO content was found to be respectively 55·88 and 56·01% of the carbonate (calc.: 56·04%). For every additional 50 c.c. of water used for washing, the CaO value found would have been lower by about 0·13%. It is therefore essential to wash calcium oxalate precipitates with a saturated aqueous solution of this salt.

The gravimetric estimation of calcium as oxide after precipitation as oxalate is subject to several sources of error. In the author's experience it is practically impossible to obtain the correct weight of ignited lime, owing to moisture absorption, even when using a very rapid air-damped balance. It seems as though the ignited lime absorbs moisture during the cooling in the desiccator—even if this contains phosphoric oxide—probably from the adsorbed film on the glass surface which is renewed to some extent every time the desiccator is opened. Ignition in a platinum crucible over a good Bunsen burner appears to be sufficient to convert calcium carbonate or oxalate completely into oxide. The sole effect of subsequent ignition over the blow-pipe seems to be to make the surface of the lime slightly less sensitive to moisture.

The amount of moisture absorbed by the lime during the cooling and the weighing is largely determined by the rate at which it reaches the solid by diffusion, and so is more or less independent of the weight of lime. The error caused thereby is therefore far more serious with small weights of lime than with larger. The above points are illustrated by the following data obtained with a rapid air-damped balance, 25 minutes' cooling being allowed in a desiccator containing phosphoric oxide.

Pure $CaCO_3$ used, g.	1·0068	0·2042
Calc. wt. of CaO, g.	0·5641 (56·04% of $CaCO_3$)	0·1144 (56·04%)
CaO after 35 mins.' ignition over good Bunsen burner, g.	0·5648 (56·10% of $CaCO_3$)	0·1156 (56·61%)
After further 10 mins. over blow-pipe, g.	0·5639 (56·01% of $CaCO_3$) rising to 0·5644 (56·06%) after 1 min. on balance pan.	0·1149 (56·29%) rising very rapidly to 0·1152 (56·42%)

The solubility effect already discussed helps to counteract the effect due to absorption of moisture during weighing. The latter effect generally predominates, and for weights of lime up to 0·1 g., the weight found is too great by about 0·0005—0·0007 g. when the weighings are done as rapidly as possible on the ordinary analytical balances and when the oxalate precipitate has been washed with cold water. A third source of error, which also causes a high result, may arise from the use of ammonia solutions which have stood for a long time in the bottles. These may contain considerable amounts of silica, a small proportion of which is carried down by the calcium oxalate. In such circumstances, as much as 1% of what is regarded as lime after the ignition may consist of silica. In view of all the sources of error it would seem that the estimation of calcium by weighing as lime should be discarded.

Use of Pure Calcium Carbonate as a Volumetric Standard.—The use of Iceland spar as an independent standard in acidimetry has been described by Orme Masson (*Chem. News*, 1900, **81**, 73) but has not come into general use owing to the time taken for the last traces of acid to be neutralised before the loss of weight of the spar can be determined. It has been found, however, that the pure precipitated calcium carbonate, prepared as described in this paper, can be readily used for standardising any of the strong mineral acids in the following way.

An amount of the carbonate, capable of neutralising 25—50 c.c. of the acid, is accurately weighed into a platinum crucible and then ignited to lime over a good Bunsen burner. The residue is tipped into a clean dry beaker, and 20—50 c.c. water rapidly added. No mechanical loss due to the slaking process normally occurs, but difficulty may arise with the relatively large amounts of lime required for standardising *N*-acid; the trouble may be overcome by introducing steam into the beaker containing the lime for some time before adding the water. The calcium hydroxide is then titrated with the acid to be standardised in presence of either methyl-orange or methyl-red, the crucible being rinsed out with a little of the acid and then with water. The hydroxide dissolves readily as acid is added, and by cautious addition of the acid towards the end, and crushing of small lumps with a glass rod, very accurate determinations of the end-point are possible. Even *N*-sulphuric acid can be standardised in this way, but owing to the separation of $CaSO_4,2H_2O$, care must be taken that all lumps of hydroxide have completely dissolved.

Hydrochloric and sulphuric acid standardised in this way were found to be 0·0979*N* and 1·013*N* respectively, whilst by weighing as silver chloride and barium sulphate respectively, the values found were 0·0980*N* and 1·012*N*.

SUMMARY.

The increased solubility of fine particles is the chief source of uncertainty in previous determinations of the solubility of calcium hydroxide.

Steps have been taken to eliminate this source of error, and the solubility has been determined from the cryohydric point (— 0·116°) to 100°.

There appears to be no sound evidence for the existence either of a hydrate of calcium hydroxide or of more than one crystalline form.

Some of the sources of error in the determination of calcium have been examined.

The solubility of calcium oxalate in water has been shown to be an important source of error in all methods.

The volumetric determination with permanganate is shown to be the most accurate and convenient if the calcium oxalate precipitate is washed with water saturated with this salt instead of with pure water.

A method is given for using pure precipitated calcium carbonate as an independent standard in acidimetry.

I wish to thank Dr. W. L. Bedwell for carrying out some of the experiments on the volumetric estimation of calcium and on the solubility of calcium oxalate.

THE UNIVERSITY, READING. [*Received, May 29th*, 1934.]