Hall's Notes and Queries

NQ9

The solubility of gypsum in water

In WT3e [1], App C (Table C.2), we compiled some information on the solubility of the minerals calcite, dolomite, gypsum and portlandite in the temperature range 0–35 °C. This was to support our occasional remarks elsewhere in the book on the long-term chemical action of capillary water flows; and in particular the comment on p324 that in London conditions water flow in brick masonry driven by rising damp and evaporation is sufficient to dissolve 2 kg of calcitic limestone per m length of structure in 100 years.

More generally, we wanted to note that materials often regarded as more or less insoluble (such as calcite and dolomite) are really not. Gypsum and portlandite (an important constituent of hardened but uncarbonated concrete) are certainly appreciably soluble – a small teaspoon of either dissolves completely in a litre of water. We also gave (in Table C.1) the solubility of several common salts, including familiar sodium chloride and sodium sulphate: these all show high solubility in water, with vivid consequences in efflorescence and salt crystallization damage in brick, stone and concrete.

The purpose of this NQ is to further analyse the solubility of gypsum. Why gypsum? Because as a hydrated mineral of moderate solubility it provides an excellent example of what we know of solubility and the underpinning calculation methods.

Preamble

The plain-language meaning of solubility is that it is the answer to the question 'How much solid X can I dissolve in, say, 1 kg water?' The technical convention is to determine how much X is in solution (at equilibrium) in contact with an excess of solid X. This arrangement ensures that the solution is truly saturated. (That there is a well defined maximum amount that dissolves in a given amount of water is a consequence of the chemist's phase rule.) For most substances, the amount of X that I have dissolved and the amount of X I find in solution are necessarily the same. There is however an exception when X is a salt hydrate such as gypsum $CaSO_4 \cdot 2\,H_2O$. When 1 mol $CaSO_4 \cdot 2\,H_2O$ dissolves in water, it releases 2 mol H_2O as liquid water, and this adds to the 1 kg of water that we started with. It is therefore conventional (and better) to define the solubility of $CaSO_4 \cdot 2\,H_2O$ as the amount of $CaSO_4$ in a total of 1 kg water at saturation.[1]

Most substances become more soluble in water as the temperature rises. There are exceptions. Portlandite is one such, where the *retrograde* solubility falls as the temperature increases. Gypsum is unusual in reaching a maximum solubility at about 40 °C, its solubility decreasing slightly at higher temperatures (see Fig 1).

Gypsum solubility

The solubility of almost everything has been measured. Direct mea-

---

[1] If n mol $CaSO_4 \cdot 2\,H_2O$ is added to 1 kg water to make a saturated solution, then the solution contains n mol $CaSO_4$, but the mass of water (kg) is now $1 + 2nM_w$, where M_w is the molar mass of water (0.01802 kg/mol). Therefore the solubility (mol/kgw) as conventionally defined is $b_s = n/(1 + 2nMw)$, which of course is always less than n.

surement is usually analytically straightforward, and data have accumulated since the first days of quantitative chemistry in the nineteenth century. Early data are collated in the ICT volumes [2] edited by Ernest Washburn (an individual much mentioned in WT3e [1]). New data, not always better, appear from time to time. Gypsum solubility has often been measured. Several sources are listed in [3]; [4] and [5] point to some different sources. Taken together, the data are broadly consistent but show a little scatter, even when obvious outliers are excluded. Still, one can form some kind of mean of the retained data, and perhaps fit an interpolating equation to show how the solubility changes over a range of temperature. Such an equation was given in [4]. My own selection of data is plotted in Fig 1 together with the interpolating equation. If the aim is to find a good value for the solubility of gypsum in pure water at a certain temperature then the experimental data alone provide that value. Nordstrom in a brief review of gypsum data [11] concludes that the solubility at 25°C is 0.01528 mol $CaSO_4$/kgw; taking a simple mean of the data from Fig 1 gives the same value.

Gypsum solubility – thermodynamics

Over recent decades solubility has increasingly been seen as a property not just to be measured but to be understood in the framework of electrolyte solution theory. This has two interwoven aspects. First, the extent of dissolution of a solid X in water is to be related directly to the thermodynamic properties of the solid, the solvent (water) and the dissolved species. Equilibrium is assumed. Thus for gypsum (Gp) in water

$$\mathrm{CaSO_4 \cdot 2\,H_2O = Ca^{2+}(aq) + {SO_4}^{2-}(aq) + 2\,H_2O\,(l)} \tag{1}$$

we define an equilibrium constant for dissolution K_{sp} (the *solubility*

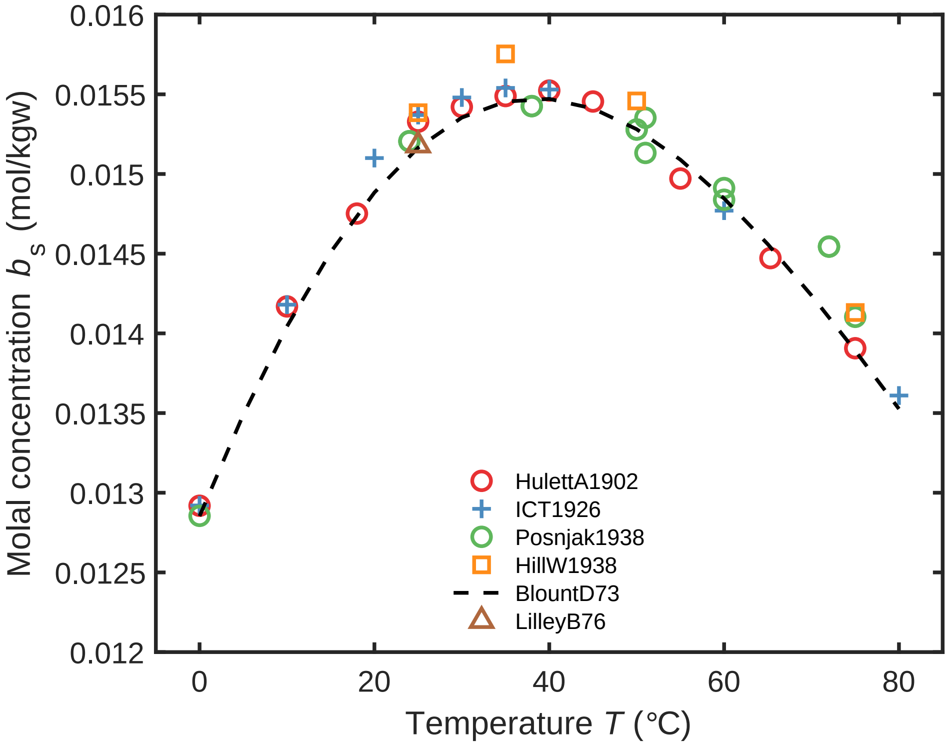

Figure 1: The measured solubility b_s (mol/kgw) of gypsum in pure water in the temperature range 0–80 °C. Data from [2, 4, 6–9]. The interpolating equation of [4] is $\ln b = -4.354 + 0.0105T - 1.700 \times 10^{-4}T^2 + 0.584 \times 10^{-6}T^3$ at 1 atm pressure. Note that gypsum is metastable at temperatures above about 42 °C [10].

product) as

$$K_\mathrm{sp} = \frac{a_+ a_-}{a_\mathrm{Gp}} = \gamma_\pm^2 b_s^2 \tag{2}$$

where a_+, a_- are the activities of the ions in a saturated solution of molal concentration b_s [12]. The activity of Gp solid is 1 by definition. The quantity $\gamma_\pm$ is the mean ionic activity coefficient. The link to the thermodynamics is through the equation

$$\ln K_\mathrm{sp} = -\Delta_\mathrm{r} G^\circ / \mathbf{R}T \tag{3}$$

where $\Delta_{\mathrm{r}}G^\circ$ is the standard state Gibbs energy of dissolution at absolute temperature T. In turn, we obtain $\Delta_{\mathrm{r}}G^\circ$ from the standard state Gibbs energy of formation of each of the species in eqn 1. Thus

$$\Delta_{\mathrm{r}}G^\circ = \Delta_{\mathrm{f}}G^\circ_{\mathrm{Gp}} - \Delta_{\mathrm{f}}G^\circ_{\mathrm{Ca}^{2+}} - \Delta_{\mathrm{f}}G^\circ_{\mathrm{SO_4}^{2-}} - 2\Delta_{\mathrm{f}}G^\circ_{\mathrm{H_2O}} \tag{4}$$

Each of the quantities $\Delta_{\mathrm{f}}G^\circ$ is calculated from the enthalpy $\Delta_{\mathrm{f}}H^\circ$ and entropy $\Delta_{\mathrm{f}}S^\circ$ of formation of the species. For gypsum we have

$$\Delta_{\mathrm{f}}G^\circ_{\mathrm{Gp}} = \Delta_{\mathrm{f}}H^\circ_{\mathrm{Gp}} - T\Delta_{\mathrm{f}}S^\circ_{\mathrm{Gp}} \tag{5}$$

$$\Delta_{\mathrm{f}}G^\circ_{\mathrm{Ca}^{2+}} = \Delta_{\mathrm{f}}H^\circ_{\mathrm{Ca}^{2+}} - T\Delta_{\mathrm{f}}S^\circ_{\mathrm{Ca}^{+2}} \tag{6}$$

$$\Delta_{\mathrm{f}}G^\circ_{\mathrm{SO_4}^{2-}} = \Delta_{\mathrm{f}}H^\circ_{\mathrm{SO_4}^{2-}} - T\Delta_{\mathrm{f}}S^\circ_{\mathrm{SO_4}^{2-}} \tag{7}$$

$$\Delta_{\mathrm{f}}G^\circ_{\mathrm{H_2O}} = \Delta_{\mathrm{f}}H^\circ_{\mathrm{H_2O}} - T\Delta_{\mathrm{f}}S^\circ_{\mathrm{H_2O}} \tag{8}$$

Finally these quantities are calculated from the known standard state enthalpies and entropies of the element from which each species is formed.

Just as for solubility, the thermodynamic properties have been measured by various means (calorimetric, spectroscopic, ...) over many years. Available results were first collated in the mammoth eight-part NBS Technical Note 270, revised in SI units in 1982 [13]. There are other more recent sources, of which [14, 15] provide data on many mineral materials (including calcite, dolomite and portlandite, although not gypsum) and [16] data on cement minerals. By combining enthalpy and entropy properties of the components to obtain the Gibbs energy of dissolution, we then apply Eqn 2 to obtain the solubility product K_{sp}. For gypsum, the various quantities are given in Table 1. Putting the values for the standard Gibbs energies from Table 2 into Eqn 4 gives a value of −26.15 kJ/mol for the Gibbs energy of dissolution $\Delta_r G^\circ$. Then from Eqn 3 we obtain $\ln K_{\mathrm{sp}} = -4.58$.

Table 1: Thermodynamic quantities (at 25.0°C and 1 bar pressure) to calculate the solubility product of gypsum (all data from [16]).

Species	$\Delta_f G^\circ$ kJ/mol	$\Delta_f H^\circ$ J/(mol K)	$\Delta_f S^\circ$ J/(mol K)
Note	(1)	(2)	(3)
Gp	-1797.76	-2023.36	-756.67
Ca^{2+}(aq)	-552.79	-543.07	32.60
${SO_4}^{2-}$(aq)	-744.46	-909.70	-554.22
H_2O(l)	-237.18	-285.88	-163.34

Notes: (1) Calculated from Eqns 5-8. (2) Generally determined from calorimetric data. (3) Calculated by combining absolute entropy S° of species and elements from the following list: Gp 193.8, Ca^{2+}(aq) -56.48, ${SO_4}^{2-}$(aq) 18.83, Ca 41.42, S 32.05, H_2 130.684, O_2 205.14, H^+ 0.0 (J/(mol K).

Nordstrom [11] finds 'best' values of 26.162 ± 0.132 for $\Delta_r G^\circ$ and -4.576 ± 0.048 for $\ln K_{\mathrm{sp}}$.

Why should we go to all this trouble? It is because to use Eqn 2 to find the amount of gypsum that dissolves (b_{s}) we need to know the activity coefficient of the ions in solution, expressed as $\gamma_\pm$. This requires some calculation based on the theory of electrolyte solutions. It is also because we need the full machinery of activity coefficient estimation to stand any chance of describing the solubility in multicomponent solutions. Gypsum in pure water is rarely an adequate description of our systems of interest: more often, we are confronted with gypsum in contact with several other minerals and dissolved salts, perhaps also atmospheric CO_2 and perhaps at a defined pH. In such a complicated mixture, the simple solubility provides no guide.

Gypsum – the computed solubility

Today, we generally make use of software solvers to calculate activities in chemical systems of interest. The most widely employed is PhreeqC, which can be used with more than a dozen thermodynamic data files (TDFs) [5] which provide solubility products and thermodynamic data, together with temperature coefficients. Activity coefficients can be computed using several theoretical models. Table 2 brings together the main results of computing the solubility of gypsum in water at 25°C using seven different TDFs. The results are generally consistent, but we note (1) that the $\log_{10} K_{\rm sp}$ values are not all the same; (2) that the range in estimated solubility is 6 percent; and (3) that with only three TDFs is the solution density computed, and with only two is the osmotic coefficient computed (although all compute the water activity). The mean solubility, $b_{\rm s}$, 0.01546 ± 0.00034 mol/kgw agrees (within the uncertainties) with the Nordstrom value [11] 0.01528 ± 0.0008 mol/kgw. The gypsum case is rather favourable since the solution concentration is low.

More serious shortcomings are apparent if the solubility is calculated over the temperature range 10–50 °C, as shown in Fig 2. As noted in [5], the existence of the solubility maximum is not predicted by all TDFs: here minteq.v4.dat predicts that the solubility increases linearly with rising temperature. Perhaps more striking are the considerable differences in the predicted solubility even when a maximum is found. Clearly, the closest agreement with the measured solubility is achieved using phreeqc.dat, pitzer.dat and frezchem.dat.

Gypsum – solubility in mixtures

It is also interesting to ask about the solubility of gypsum in sodium

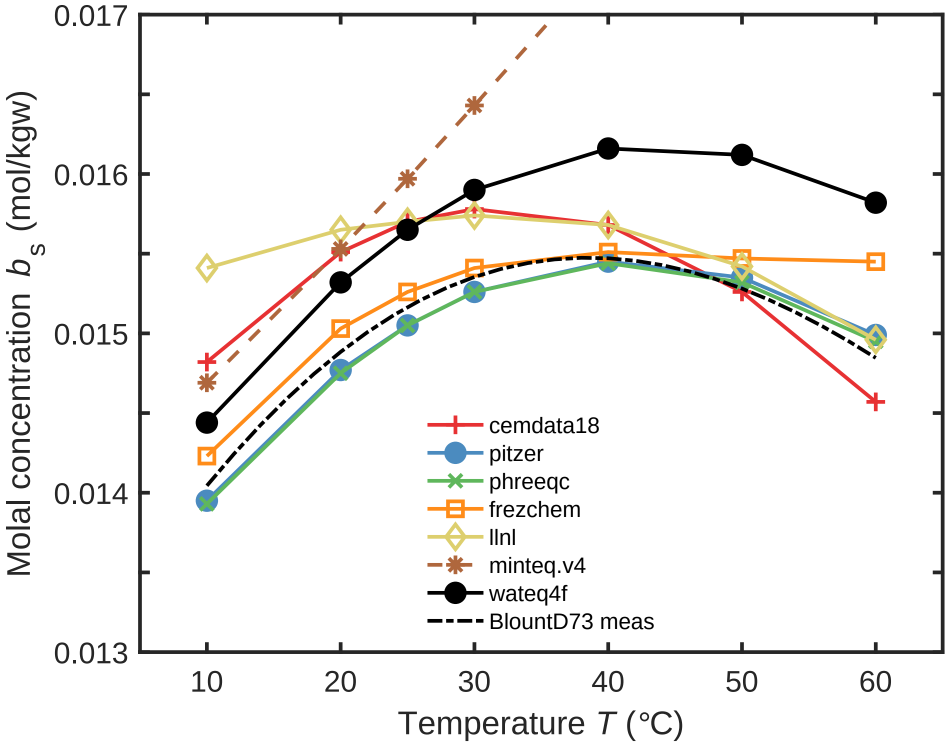

Figure 2: The calculated solubility b_s (mol/kgw) of gypsum in pure water in the temperature range 10–60 °C. The dashed line is the interpolation of experimental data [4] shown in Fig 1.

sulphate solutions of different concentration. Sodium sulphate is often present in building materials and is itself highly soluble. A simple common-ion argument suggests that increasing quantities of dissolved sulphate ion must suppress gypsum dissolution. This is not what was found experimentally many years ago [17]. Fig 3 shows the measured gypsum solubility in sodium sulphate solutions up to 1.57 molal. After decreasing at low sodium sulphate concentrations, gypsum becomes more soluble as the concentration further increases. The explanation lies in the detailed speciation of the solution, which shows that at higher sulphate concentrations the neutral ion pair $CaSO_4$(aq) is increasingly formed. In this case, calculations

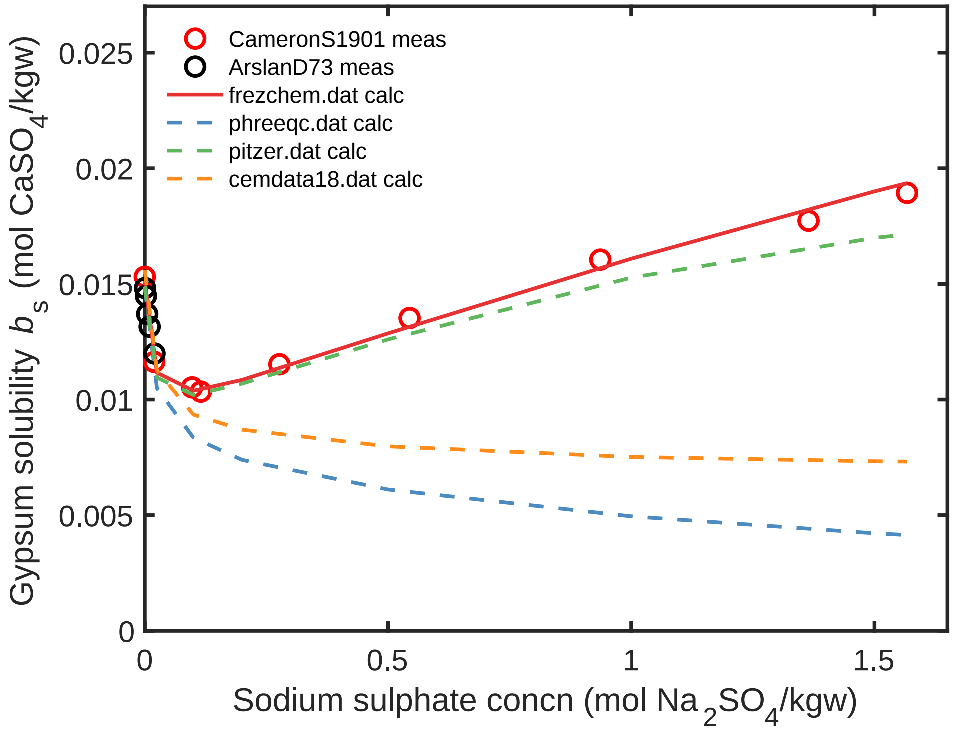

Figure 3: The calculated solubility b_s (mol/kgw) of gypsum in sodium sulphate aqueous solutions of various concentrations at 22 °C, compared with experimental data [17, 18]; the solubility of mirabilite $Na_2SO_4 \cdot 10\,H_2O$ in this system is 1.567 mol Na_2SO_4/kgw.

using frezchem.dat predict more or less exactly the measured solubility, with estimates from using pitzer.dat in good agreement only at lower concentrations. The Pitzer activities do not explicitly identify the species present at higher concentrations as these are rolled up into the activity coefficients.

Gypsum solubility – the numbers

I now return to the gypsum solubilities mentioned at the start of this NQ and included in Table C.1 of WTB3e [1]. It is clear from Fig 2 that to take these solubilities from PhreeqC calculations using the wateq4f.dat TDF was not the best choice. A better choice is to use either phreeqc.dat, or pitzer.dat (frezchem.dat is optimised for temperatures $\leqslant 25\,^\circ\mathrm{C}$). An alternative is to use the interpolating equation of [4] based directly on the aggregate of experimental data. In addition, as noted earlier, the solubility is to be expressed as the weight of $CaSO_4$ per kg water, rather than the weight of Gp. These improved numbers are collated in Table 3.

Table 2: Comparison of thermodynamic data files and computed results for gypsum solubility b_{s} in water at 25 °C.

TDF	$\log_{10}(K_{\mathrm{sp}})$	$10^2 b_{\mathrm{s}}$ mol/kgw	Density $\mathrm{kg/m^3}$	ϕ
Note	(1)	(2)	(3)	
phreeqc	-4.58	1.505	999.08	–
llnl	-4.482	1.570	–	–
minteq.v4	-4.61	1.597	–	–
pitzer	-4.58	1.505	999.12	0.695
frezchem	–	1.526	999.15	0.693
cemdata18	-4.581	1.570	–	–
wateq4f	-4.58	1.565	–	–

Notes: (1) Calculated from Eqns 5-8. (2) Generally determined from calorimetric data. (3) Calculated by combining absolute entropy S° of species and elements from the following list: Gp 193.8, Ca^{2+}(aq) -56.48, ${SO_4}^{2-}$(aq) 18.83, Ca 41.42, S 32.05, H_2 130.684, O_2 205.14, H^+ 0.0 (J/(mol K).

Table 3: Solubility of gypsum in water over temperature range 0–35 °C.

	Mb_s (g $CaSO_4$/kgw)				
T(°C)	frezchem	phreeqc	pitzer	Cemdata18	Measured
0	1.762	1.741	1.748	1.869	1.750
5	1.858	1.823	1.828	1.949	1.836
10	1.937	1.896	1.899	2.018	1.912
15	2.000	1.958	1.960	2.072	1.975
20	2.046	2.008	2.011	2.111	2.026
25	2.077	2.049	2.049	2.137	2.064
30	2.098	2.077	2.077	2.148	2.090
35	2.107	2.095	2.095	2.148	2.104

Note: M is the molar mass of $CaSO_4$ = 136.134 g/mol, b_s is the molality of $CaSO_4$ in the saturated solution (unit mol $CaSO_4$/kg water).

References

[1] Christopher Hall and William D Hoff. *Water Transport in Brick, Stone and Concrete*. Third edn. CRC Press, 2021.

[2] E.W. Washburn. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*. Vol. 4. National Bureau of Standards, 1926.

[3] G Azimi and VG Papangelakis. "The solubility of gypsum and anhydrite in simulated laterite pressure acid leach solutions up to 250 °C". In: *Hydrometallurgy* v102 (2010), pp. 1–13.

[4] Charles W Blount and Frank W Dickson. "Gypsum-anhydrite equilibria in systems $CaSO_4-H_2O$ and $CaSO_4-NaCl-H_2O$". In: *American Mineralogist* v58 (1973), pp. 323–331.

[5] Peng Lu et al. "Comparison of thermodynamic data files for PHREEQC". In: *Earth-Science Reviews* v225 (2022), 103888.

[6] George A Hulett and Lucius E Allen. "The solubility of gypsum". In: *Journal of the American Chemical Society* v24 (1902), pp. 667–679.

[7] E Posnjak. "The system $CaSO_4-H_2O$". In: *American Journal of Science* v5 (1938), pp. 247–272.

[8] Arthur E Hill and John H Wills. "Ternary systems. XXIV. Calcium sulfate, sodium sulfate and water". In: *Journal of the American Chemical Society* v60 (1938), pp. 1647–1655.

[9] TH Lilley and Charles C Briggs. "Activity coefficients of calcium sulphate in water at 25 °C". In: *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences* v349 (1976), pp. 355–368.

[10] A Elena Charola, Josef Pühringer, and Michael Steiger. “Gypsum: a review of its role in the deterioration of building materials”. In: *Environmental Geology* v52 (2007), pp. 339–352.

[11] D Kirk Nordstrom. “Improving internal consistency of standard state thermodynamic data for sulfate ion, portlandite, gypsum, barite, celestine, and associated ions”. In: *Procedia Earth and Planetary Science* v7 (2013), pp. 624–627.

[12] Gregor Munro Anderson and David A Crerar. *Thermodynamics in Geochemistry: the Equilibrium Model*. Oxford University Press, 1993.

[13] Donald D Wagman et al. “The NBS tables of chemical thermodynamic properties (NBS Technical Note 270)”. In: *Journal of Physical and Chemical Reference Data* 11 (1982), Supplement 2.

[14] Richard A Robie and Bruce S Hemingway. *Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 Pascals) pressure and at higher temperatures. US Geological Survey Bulletin 2131*. Washington DC: US Government Printing Office, 1995.

[15] TJB Holland and R Powell. “An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids”. In: *Journal of Metamorphic Geology* v29 (2011), pp. 333–383.

[16] Barbara Lothenbach et al. “Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials”. In: *Cement and Concrete Research* v115 (2019), pp. 472–506.

[17] Frank K. Cameron and Atherton Seidell. “Solubility of gypsum in aqueous solutions of certain electrolytes”. In: *The Journal of Physical Chemistry* v5 (1901), pp. 643–655.

[18] A Arslan and GR Dutt. “Solubility of gypsum and its prediction in aqueous solutions of mixed electrolytes”. In: *Soil Science* v155 (1993), pp. 37–47.

Christopher Hall
v3 (minor edits)
1 May 2025

To cite this NQ: C Hall, The solubility of gypsum in water, *Hall’s Notes and Queries* NQ9