

Chapter 5 Problems

1. Use SUPCRT92 to calculate the enthalpy and Gibbs free energy of formation and the entropy of halite (NaCl) from 25°C to 700°C at one bar at 100 degree intervals (25, 100, 200, 300...700°C).
2. Using the Maier-Kelley heat capacity coefficients which are given in the SUPCRT92 output, calculate the enthalpy of formation of halite at the same temperatures and compare with the tabulated output. They should be exactly the same. Why?
3. Convert the SUPCRT92 enthalpies and Gibbs energies of halite to Joules and plot them and the RHF values together. Why are they so different?
4. Convert the SUPCRT92 entropies of your mineral to Joules and compare with those from RHF. Why are they not so different?
5. Use a spreadsheet to calculate the (“traditional”) enthalpy of formation from the elements of halite, using the heat capacity formulas for both the elements (Na and Cl) and the mineral (halite) from the RHF tables, and compare with the values in the RHF tables. They should be very similar, but not identical. Why?
6. Sketch a diagram showing absolute enthalpy vs. $T(K)$ for halite and its elements. No numbers can appear on the enthalpy axis, but differences between halite and its elements can be shown, from 298 to 1000 K.
7. Use SUPCRT92 to calculate $\Delta_r H^\circ$ at 968 K, 1 bar for the reaction in which andalusite is formed from the oxides, i.e.



What is the enthalpy change ($\Delta_{\text{transition}}H$) for the $\alpha - \beta$ quartz transition?

8. Holm and Kleppa¹ made some calorimetric determinations of the heats of formation of kyanite, andalusite, and sillimanite from their constituent oxides (quartz and corundum) in an oxide melt calorimeter at 968 K. For andalusite, the result for the reaction in Question 7 was $\Delta_r H_{968}^\circ = -1.99 \text{ kcal mol}^{-1}$, and from this they calculated $\Delta_r H_{298.15}^\circ = -0.60 \text{ kcal mol}^{-1}$ using drop calorimetry data available at that time. Calculate $\Delta_r H_{968}^\circ$ for this reaction using values of $\Delta_f H_{298}^\circ$ and C_p° values from the RHF tables, and compare this with the Holm and Kleppa value, and the value from SUPCRT92 in Question 7.

Holm and Kleppa used their calorimetry data to calculate a phase diagram for the aluminum silicates. Compare their diagram with the one from Question 6, Chapter 6.

Note that RHF do not use the Maier-Kelley formulation for C_p° . They use

$$C_p^\circ = \Delta a T^{-2} + \Delta b T^{-0.5} + \Delta c T^0 + \Delta d T + \Delta e T^2$$

¹Holm, J.L., and Kleppa, O.J., The thermodynamic properties of the aluminum silicates. Amer. Mineral., v. 51, pp. 1608–1622, 1966.

for which $\int \Delta C_p^\circ dT$ results in

$$\begin{aligned} \Delta_r H_T^\circ - \Delta_r H_{T_r}^\circ = & -\Delta a(1/T - 1/T_r) - 2\Delta b(T^{0.5} - T_r^{0.5}) + c(T - T_r) \\ & + \frac{\Delta d}{2}(T^2 - T_r^2) + \frac{\Delta e}{3}(T^3 - T_r^3) \end{aligned}$$

In most cases, some of the terms are zero.

9. Modeling programs treat data in various ways. One important difference is the source of $\log K$ values, and their variation with temperature. SUPCRT92 is virtually unique, in that it manipulates fundamental thermodynamic quantities, and calculates $\log K$ and other values at any T and P “from scratch”. Many other programs use data from SUPCRT92, rather than from the primary literature. However, they do not duplicate the SUPCRT92 calculations. Rather, they take the calculated $\log K$ values at a series of temperatures, and fit these values with some equation. They then use this equation to evaluate $\log K$ at requested input temperatures.

EQ3/6, REACT, and PHREEQC all use $\log K$ values, from SUPCRT92 and many other sources, at eight temperatures;

0, 25, 60, 100, 150, 200, 250, and 300°C.

The equation that PHREEQC uses is

$$\log K_T = A_1 + A_2 T + \frac{A_3}{T} + A_4 \log(T) + \frac{A_5}{T^2} \quad (1)$$

where A_1 to A_5 are fit coefficients.

However, PHREEQC only uses this equation if the fit coefficients are in the database. If they are not there, PHREEQC calculates $\log K$ values at temperatures other than 25°C (298.15 K) using the Van’t Hoff method,

$$\log K_T = \log K_{298} - \frac{\Delta_r H_{298}^\circ}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \quad (2)$$

This of course assumes that $\Delta_r H_{298}^\circ$ is constant over the range 298.15 to T K.

The fact is that phreeqc.dat has very few species with fit coefficients, while llnl.dat has far more species as well as fit coefficients for all of them. To illustrate this, consider the equilibrium constant for one of the most fundamental reactions in any sulfide solubility problem,



- (a) Get the fit coefficients for this reaction from llnl.dat, to use in equation (1).
- (b) Get the value of $\Delta_r H_{298}^\circ$ for this reaction from phreeqc.dat, to use in equation (2).
- (c) The eight $\log K$ values that were used to get the fit coefficients in llnl.dat are

$T/^{\circ}\text{C}$	$\log K$
0	-7.4159
25	-6.9877
60	-6.6467
100	-6.4827
150	-6.4960
200	-6.6831
250	-7.0225
300	-7.5536

- Calculate $\log K$ at the eight temperatures above using equations (1) and (2)
- Plot $\log K$ vs. T or $1/T$ (or both) for each equation, and
- Plot the eight “real” $\log K$ values on the same graph.

Remember that if you want the Van’t Hoff results to look like a straight line, you must plot $\log K$ vs. $1/T$.

After looking at these results, you will probably be more careful about accepting results from complex programs, without some knowledge of what they are doing.

But of course the question remains, are these the “best” data for this reaction? It’s your decision. My own opinion is that for this particular reaction, the best data are in Suleimenov and Seward (1997).² These data are in `llnl.dat`, but are commented out. If you do a search for “Suleimenov”, you will find them. You could “uncomment” these lines, comment out the other H_2S data, and do some of the calculations again, to see the difference.

²Suleimenov & Seward (1997), A photometric study of hydrogen sulphide ionisation in aqueous solution to 350°C. *Geochim. Cosmochim. Acta*, v. 61, p. 5187–5198.