

Chapter 18 Answers

1. First order; $k = 0.000490 \text{ s}^{-1}$.
2. The calculated sulfide solubilities are shown in spreadsheet sulfide_solubilities.xls. These were produced by the various PHREEQC input files shown here. Note, however, that this was done some time ago, and the data may have changed.
3. With $R = 8.31451 \text{ J mol}^{-1}$, equation (18.65) is

$$\begin{aligned} \mathbf{G}_{ideal \text{ sol'n}} - (\mu_{\text{N}_2}^{\circ} + 3\mu_{\text{H}_2}^{\circ}) &= \xi (-97116.2 + 213.536 \text{ TK}) \\ &+ 8.31451 \text{ TK} \left[(1 - \xi) \ln \left(\frac{1 - \xi}{4 - 2\xi} \right) \right. \\ &\left. + (3 - 3\xi) \ln \left(\frac{3 - 3\xi}{4 - 2\xi} \right) + 2\xi \ln \left(2 \frac{\xi}{4 - 2\xi} \right) \right] \end{aligned}$$

where $TK = T^{\circ}\text{C} + 273.15$. The derivative is

$$\begin{aligned} \frac{d \left(\mathbf{G}_{ideal \text{ sol'n}} - (\mu_{\text{N}_2}^{\circ} + 3\mu_{\text{H}_2}^{\circ}) \right)}{d\xi} &= -97116.2 + 213.536 \text{ TK} \\ &+ 8.31451 \text{ TK} \left[-\ln \left(\frac{1 - \xi}{4 - 2\xi} \right) \right. \\ &+ \left(-(4 - 2\xi)^{-1} + 2 \frac{1 - \xi}{(4 - 2\xi)^2} \right) (4 - 2\xi) \\ &- 3 \ln \left(\frac{3 - 3\xi}{4 - 2\xi} \right) \\ &+ \left(-3 (4 - 2\xi)^{-1} + 2 \frac{3 - 3\xi}{(4 - 2\xi)^2} \right) (4 - 2\xi) \\ &+ 2 \ln \left(2 \frac{\xi}{4 - 2\xi} \right) \\ &\left. + \left(2 (4 - 2\xi)^{-1} + 4 \frac{\xi}{(4 - 2\xi)^2} \right) (4 - 2\xi) \right] \end{aligned}$$

Equating the right hand side to zero and entering various values of TK , we get

$T^{\circ}\text{C}$	ξ
25	0.9699437225
100	0.7895223979
200	0.2524553561
300	0.04289091069

4. The equation to solve is

$$0 = K_{18.54} - \frac{x_{\text{NH}_3}^2}{x_{\text{N}_2} x_{\text{H}_2}^3}$$

$$= K_{18.54} - \frac{\left(\frac{1-x_i}{4-2\xi}\right)^2}{\left(\frac{3-3\xi}{4-2\xi}\right) \left(\frac{2\xi}{4-2\xi}\right)^3}$$

and the results are

$T^\circ\text{C}$	ξ
25	0.9682334670
100	0.7925621002
200	0.2575056716
300	0.04095043966

as shown in Table 18.4.