

Tutorials 6 Thermodynamics 2, 2025/2026

Exercise 22

Calculate the solubility s as a molality (in mol/kg) of HgCl_2 in water at 298.15 K and $P = P^\ominus$.

Hint: Use the Gibbs free energy of formation for the components given in the table and the dissolution reaction to calculate the equilibrium constant K . Assume that the solubility is small enough to approximate the activity of the ions by their molalities, and check the poor solubility afterwards.

	$\Delta_f G^\ominus$ (kJ/mol)
$\text{HgCl}_2(\text{s})$	-178.6
$\text{Hg}^{2+}(\text{aq})$	164.40
$\text{Cl}^-(\text{aq})$	-131.23

Exercise 23

Calculate the ionic strength of a solution which consists of 0.20 mol/kg KCl and 0.10 mol/kg FeCl_3 .

Exercise 24

We determine the change in solubility of the poorly soluble salt AgCl in water at 298.15 K ($s = 1.274 \cdot 10^{-5}$ mol/kg) when we increase the ionic strength by adding 0.00200 mol/kg K_2SO_4 .

- Calculate the equilibrium constant for dissolving AgCl in a saturated solution in the absence of K_2SO_4 using the Debye-Hückel limiting law.
- Calculate the ionic strength of the solution with K_2SO_4 but without AgCl .
- Calculate the mean activity coefficient of the Ag^+ and Cl^- ions in the K_2SO_4 -solution using the Debye-Hückel limiting law and the result of b), i.e. by neglecting the ionic strength of the AgCl in the solution.
- Calculate the solubility of AgCl in the K_2SO_4 -solution with the result of c) and a).
- In part b) the ionic strength calculation only included the ions of K_2SO_4 . This is a reasonable approximation since AgCl is poorly soluble compared to K_2SO_4 . Determine the solubility of AgCl in the solution with K_2SO_4 if we include the result of d) in the calculation of the ionic strength of the (whole) solution (i.e. use the solubility found in d) to recalculate the ionic strength and with that result the solubility).

Exercise 25

The standard potential (in V) of the $\text{Ag}/\text{AgCl}/\text{Cl}^-$ electrode as a function of the temperature at 1 bar is

$$E^\ominus = 0.23659 - 4.8564 \cdot 10^{-4}t - 3.4205 \cdot 10^{-6}t^2 + 5.869 \cdot 10^{-9}t^3,$$

where t is the temperature in $^\circ\text{C}$.

- Derive a Maxwell relation between E , T , S and q .
- Use the Maxwell relation to determine $\Delta_r G^\ominus$, $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ at $T = 25^\circ\text{C}$ for an electrochemical so-called Harned cell with a silver chloride- and a standard hydrogen electrode. For a Harned cell the two half cells are directly coupled via the solution, so there is no weak link between the two, they share the same solution (see Figure 1).
Hint: Use $\Delta_r G^\ominus = -\nu FE^\ominus$ and use the Maxwell relation of a) to find $\Delta_r S^\ominus$.

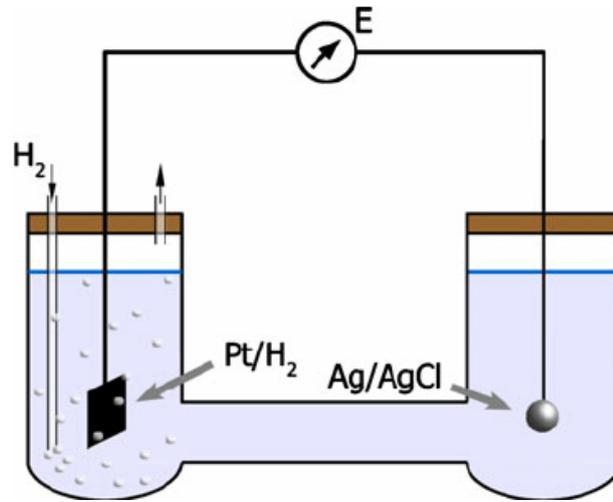


Figure 1: The Harned cell configuration, with joined solution for both half cells.

- c) An unknown quantity of completely dissolved KCl is added to the Harned cell of b) at standard conditions at a temperature of 323.2 K. As a result the potential of the cell turns out to be increased by 0.1000 V as compared to the situation of the cell at $T = 25\text{ }^\circ\text{C}$, without the added KCl. Estimate the amount of KCl added using the Debye-Hückel limiting law. Hint: Standard conditions only implies $P = P^\ominus$ and $b_{\text{Cl}^-} = b_{\text{H}^+} = b^\ominus \equiv 1\text{ mol/kg}$, *i.e.* the temperature is (as always) *not* set by standard conditions.