

Effect of temperature on distribution coefficient for Zn²⁺

Student worksheet

Principle

The soil-water distribution coefficient has the symbol K_d . It has no units.

$$K_d = \frac{[\text{Metal ions adsorbed in the soil}]_{\text{eq}}}{[\text{Metal ions dissolved in water}]_{\text{aq}}} = \frac{C_{\text{soil}} (\text{mg kg}^{-1} \text{ of soil})}{C_{\text{aq}} (\text{mg dm}^{-3} \text{ of solution})}$$

In this experiment you will prepare solutions of zinc sulfate and leave them in contact with soil for a few days at different temperatures. You will then filter the solutions and determine the concentration of Zn²⁺ ions in them using a zincon assay. You will use the data that you record to find out about the effect of temperature on the distribution coefficient for zinc ions and to determine the enthalpy change, entropy change and the free energy of the equilibrium between zinc ions adsorbed on the soil and zinc ions dissolved in water.

Equipment and materials

- Soil (0.1 g)
- Electronic balance
- Boiling tube x 3
- 5 cm³ pipette
- 1 cm³ pipette
- Hot water baths x 3
- -10 – 110 °C thermometer
- Filter funnel and filter paper
- Zinc sulfate solution containing 0.01 g dm⁻³ Zn²⁺ (10 ppm) (15 cm³)
- Equipment and materials for zincon assay (see *Zinc by zincon assay*)

Method

Care: Wear eye protection.

1. Weigh 0.1 g samples of solid growing medium into three boiling tubes labelled '25 °C', '50 °C' and '75 °C'.
2. Using pipettes add 5.0 cm³ of a solution of zinc sulfate (containing 10 ppm Zn²⁺) to both boiling tubes, followed by 1.0 cm³ of deionised water.
3. Leave the tubes for 3-4 days standing in hot water baths set at the appropriate temperatures, occasionally shaking them.
4. Filter the contents of the tubes through folded paper in a funnel.
5. Use a zincon assay to determine the concentration of zinc ions in the filtered solutions (see *Zinc by zincon assay*).

Calculations

1. Calculate the mass (in mg) of zinc ions in 5 cm³ of each filtrate.
2. Calculate the mass (in mg) of zinc ions bound to the growing medium in both samples.
3. Calculate K_d for zinc ions and soil at 25 °C, 50 °C and 75 °C.

Calculation of thermodynamic quantities

You can use the data that you have recorded to calculate a value for the enthalpy change and the entropy change for the equilibrium between metal ions adsorbed on the soil and metal ions dissolved in water. You can also use the information to calculate a value for the free energy of the equilibrium between metal ions adsorbed on the soil and metal ions dissolved in water.

The relationship between an equilibrium constant such as K_d and the change in free energy, ΔG° is:

$$\text{Equation 1} \quad \Delta G^\circ = -RT \ln K_d$$

where R is the universal gas constant, $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, and T is the temperature in Kelvin.

The change in free energy, ΔG° , depends on the magnitude of the enthalpy change, ΔH° , and the entropy change, ΔS° :

$$\text{Equation 2} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Combining equations 1 and 2 gives:

$$-RT \ln K_d = \Delta H^\circ - T\Delta S^\circ$$

This equation may be rearranged to give:

$$\ln K_d = -\Delta H^\circ / (RT) + \Delta S^\circ / R$$

This is the Van't Hoff equation (see figure on right).

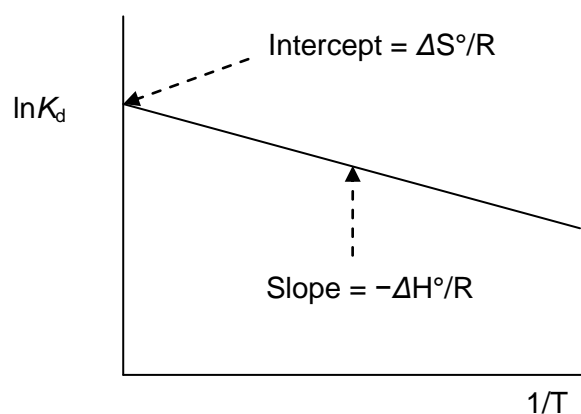


Figure The Van't Hoff equation has the form ' $y = mx + c$ '. A plot of $\ln K_d$ against $1/T$ is linear, with a slope of $-\Delta H^\circ/R$, and a y -intercept of $\Delta S^\circ/R$.

1. Use your data to plot a graph of $\ln K_d$ against $1/T$ and calculate values for ΔH° and $T\Delta S^\circ$.

2. Then use the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

to calculate ΔG° .