

Chapter 5 Part 2

Dr. Turner

Activities

- We normally put partial pressures of gases or concentrations of aqueous solutions into equilibrium constant expressions. However, we can generalize what goes into equilibrium constant expressions as activities such that

$$Q = \frac{\prod_{\text{i products}} a_i^{|v_i|}}{\prod_{\text{j reactants}} a_j^{|v_j|}}$$

- For gases activity is related to the fugacity of the gas and the standard pressure

$$a_{\text{gas}} = \frac{f_{\text{gas}}}{p^\circ}$$

Activities of phases

- For gases activity is related to the fugacity of the gas and the standard pressure but is normally approximated as to assume ideal behavior

$$a_{gas} = \frac{f_{gas}}{p^\circ} \approx \frac{p_{gas}}{p^\circ}$$

- For solids and liquids, activity is generally approximated to equal 1, but is formally expressed as

$$\ln a_{\text{liquid/gas}} = \frac{\bar{V}}{RT} (p - 1) \approx 1$$

- For aqueous solutions, activity equals the activity coefficient, γ times the molality, m . For dilute solutions, molality is roughly equal to molarity, M .

$$a_{aq} = \frac{\gamma \cdot m}{m^\circ} \approx \frac{\gamma \cdot M}{M^\circ}$$

Determining the activities of solids and liquids

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$$\ln a_i = \frac{\left(18.07 \frac{\text{cm}^3}{\text{mol}}\right) \left(\frac{1 \text{ L}}{1000 \text{ cm}^3}\right)}{\left(0.08314 \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}}\right) (298 \text{ K})} (100 \text{ bar} - 1 \text{ bar}) = 0.0722$$
$$a_i = e^{0.0722} = 1.07$$

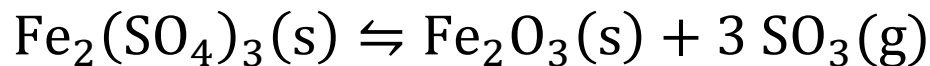
Writing Equilibrium Constant Expressions

What is the general expression for the equilibrium constant, in terms of activities using pressures, for the following chemical equilibrium? Assume that conditions are ideal and near standard pressure.



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$$K = \left(\frac{p_{\text{SO}_3}}{p^\circ} \right)^3$$

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$$K = \frac{\left(\frac{\gamma_{\text{H}^+} m_{\text{H}^+}}{m^\circ}\right)^4 \left(\frac{\gamma_{\text{NO}_3^-} m_{\text{NO}_3^-}}{m^\circ}\right)^4}{\left(\frac{p_{\text{NO}}}{p^\circ}\right)^4 \left(\frac{p_{\text{O}_2}}{p^\circ}\right)^3}$$

Relating K , T , and $\Delta_{rxn}H$

- From the Gibbs-Helmholtz equation, one can derive the equation below, which relates equilibrium constants and different temperatures to $\Delta_{rxn}H$.

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_{rxn}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Relating K , T , and $\Delta_{rxn}H$

The dimerization of a protein has the following equilibrium constant at the given temperatures: $K(4^\circ\text{C}) = 1.3 \times 10^7$, $K = (15^\circ\text{C}) = 1.5 \times 10^5$. Estimate the standard enthalpy of reaction for this process.

Relating K , T , and ΔH

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$$\ln \frac{1.3 \times 10^7}{1.5 \times 10^5} = \frac{\Delta_{rxn}H}{8.314 \times 10^{-3} \frac{\text{kJ}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{288 \text{ K}} - \frac{1}{277 \text{ K}} \right)$$

$$\Delta_{rxn}H = 8.63 \frac{\text{kJ}}{\text{mol}}$$

Return of the ICE Tables

In a previous example, the equilibrium partial pressures of I_2 and I in the gas phase were 0.235 and 0.515 atm, with an equilibrium constant value of 1.13 in 1.00 L. Suppose the volume were suddenly decreased to 0.500 L at the same temperature, effectively doubling the pressure. What are the new equilibrium partial pressures? Are the new values consistent with Le Chatelier's principle?

