

A. PROBLEMS

[1] a. Show that $(\partial S/\partial V)_U = P/T$.

b. Verify the above equation for an ideal gas by evaluating $(\partial S/\partial V)_U$ directly.

Hint: For part a, make use of the total differential for U expressed as a function of S and V; i.e. start with $U(S,V)$ and write out dU. [... do something to it in between...] Then consider the first law.

[2] a. Consider an isothermal process in which 2 mole of O_2 at 1.00 bar at $0^\circ C$ is compressed from 22.71 l to 2.25 l. Calculate ΔG for this process assuming ideal gas behaviour. [Express your answer in units of kJ.]

b. Consider another isothermal process in which the pressure on a 3 mole sample of NaCl is changed from 1 bar to 334 bar. Estimate ΔG for this process. For NaCl at $25^\circ C$, $\bar{V} = 27.0 \times 10^{-6} \text{ m}^3/\text{mol}$. [Express your answer in units of kJ.]

[3] Consider the following dissociation reaction: $NH_4Cl(s) = NH_3(g) + HCl(g)$

The pressure of the gaseous products in equilibrium with the solid reactant is 608 kPa at $427^\circ C$, but has risen to 1115 kPa at $459^\circ C$.

a. Calculate the equilibrium constant at the two temperatures.

b. Calculate $\Delta H_{427^\circ C}^\ominus$ and $\Delta S_{427^\circ C}^\ominus$. Assume that the vapour behaves as an ideal gas and that ΔH^\ominus and ΔS^\ominus are independent of temperature in the range given. [Express your answers in units of kJ/mol and J/K/mol, respectively.]

[4] Determine the number of components and the variance for the following systems. Identify the plausible thermodynamic variables that make up the variance.

a. A mixture of solid, liquid and gaseous acetone in equilibrium.

b. An aqueous solution of acetone in equilibrium with crushed ice.

c. An aqueous solution of HCl and HI in equilibrium with its vapour.

d. An equimolar mixture of nicotine and water that separates into two layers (each consisting of a saturated solution) in equilibrium with a vapour phase.

[5] The vapour pressure (in mm Hg) of solid ammonia is given by the relation:

$$\ln P = 23.03 - (3754K)/T, \quad \text{where } T \text{ is the absolute temperature (in K).}$$

The vapour pressure (in mm Hg) of liquid ammonia is given by the relation:

$$\ln P = 19.49 - (3063K)/T.$$

a. What is the temperature of the triple point?

b. Compute the latent heat of vaporization (boiling) at the triple point. [Express your answer in cal/mole.]

Note: We can approximate the behaviour of the vapour by treating it as an ideal gas, and may use the fact that the density of the vapour is negligibly small compared to that of a solid.

c. The latent heat of sublimation at the triple point is 7508 cal/mole. What is the latent heat of fusion (melting) at the triple point?

[6] In an ice-skating rink, skating could become unpleasant (i.e. falling frequently) if the temperature is too cold so that the ice becomes too hard. Estimate the lowest temperature of the ice on a skating rink for which ice skating for a young person of normal weight would be possible and enjoyable.

Given: (1) The latent heat of fusion for ice is 80 cal/g. (2) Water expands by $0.091 \text{ cm}^3/\text{g}$ when it freezes. (3) The triple point of water is at 273.16 K and 1 atm. (4) The equivalent pressure exerted by a young person with normal weight is about 3 atm.

B. READING ASSIGNMENT — McQuarrie and Simon, Ch 16, 19-22.