

Chem273 test 9/9/09 Thermodynamics and Electrochemistry

Answer TWO questions out of three.

Question 1 (Each part is worth 5 marks)

You are given the equations

$$dU = dq + dw \quad (1)$$

$$dq = TdS \quad (2)$$

$$dw = -pdV \quad (3)$$

$$H = U + pV \quad (4)$$

$$G = H - TS \quad (5).$$

(a) Use equations (1) to (5) to obtain the result

$$dG = Vdp - SdT \quad (7).$$

(b) Explain why it is correct to use equation (2) to substitute for dq in equation (1), even though the second law of thermodynamics clearly states that

$$dS = dq_{\text{reversible}} / T \quad (6).$$

(c) For a system involving two phases, such as water and water vapour which we label phase 1 and phase 2, use equation (7) to show that

$$d(\Delta G) = \Delta V.dp - \Delta S.dT \quad (8),$$

where, for example,

$$\Delta G = G_2 - G_1 \quad (9).$$

(d) Show from equation(8) that, if the two phases are always in equilibrium,

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H_{\text{vap}}}{T \Delta V} \quad (10).$$

(e) Hence obtain the useful result

$$\text{Ln}\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (11)$$

and mention any approximations that you have to make in order to obtain equation (11).

Question 2 (Each part is worth 5 marks)

(a) The Nernst equation can be written in the form

$$E = E_0 - \frac{RT}{zF} \ln(Q) \quad (12).$$

Explain the meanings of all of the symbols in equation (12).

(b) Explain the operation of a glass electrode, as commonly used in a *pH* meter, and obtain an expression for its *emf*. (Do not include the voltage of the counter electrode or of any other electrode that is used to make contact with the solution inside the glass electrode.)

(c) An electrochemical cell comprises two half-cells, each of which consists of a silver wire dipping into a solution of AgNO_3 at a concentration of 0.01 mole/L. The half-cells are connected together by means of a salt bridge. Explain the construction, purpose and mode of operation of the salt bridge.

(d) The silver nitrate in one of the half-cells is titrated with potassium chloride at a concentration of 0.01 mole/L. Derive an expression for the cell *emf* *before* the end-point of the titration.

(e) Explain how values for the solubility product of silver chloride could be obtained by measuring the *emf* of the cell *after* the end-point of the titration.

Question 3 (Each part is worth 5 marks)

(a) Starting with the first law of thermodynamics in the form

$$dU = dq + dw \quad (1),$$

explain why equation (1) reduces to

$$C_v dT = -pdV \quad (13)$$

in the case of an adiabatic expansion of an ideal gas.

(b) Hence obtain the result that

$$TV^{\gamma-1} = \text{constant} \quad (14),$$

during the reversible, adiabatic expansion of an ideal gas, where γ is the ratio of heat capacities C_p/C_v for the gas.

(c) Starting with the result (14), show that

$$pV^\gamma = \text{constant}' \quad (15)$$

and

$$T^\gamma p^{1-\gamma} = \text{constant}'' \quad (16)$$

during the reversible, adiabatic expansion of an ideal gas, where $\text{constant}'$ and $\text{constant}''$ differ by factors of R from the constant in (14).

(d) Explain the heating of the air that is involved in a Canterbury nor-wester, beginning with a parcel of moist air crossing the Tasman sea.

(e) A volume of air over the Southern Alps at a pressure of 500 Torr and a temperature of 270 K descends to the plains where the pressure is 760 Torr. Assuming that the air contains only nitrogen and oxygen, for both of which the ratio of C_p to C_v is 1.4, show that the air temperature over the plains should be about 304 K.