Exam 3, Chemistry 481, 6 Dec 2019

SHOW ALL WORK/EXPLAIN YOUR ANSWERS FOR FULL CREDIT

YOU CAN USE THE BLANK PAGE AT THE END FOR SCRATCH WORK

Possibly useful relations:

 $k_B = 1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}; R \text{ (molar gas constant)} = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

- In this problem, you will receive very little credit if you just give the correct answer(s) without any derivation.
 - a. Derive expressions for V and S in terms of derivatives of G. (10 pts) From thermodynamics we know dG = -SdT + VdP. From mathematics, we know that $dG = (\partial G/\partial T)_P dT + (\partial G/\partial P)_T dP$. Equating these two gives

$$S = -(\partial G/\partial T)_P \tag{1}$$

and

$$V = (\partial G / \partial P)_T \tag{2}$$

b. From the definition of G derive the equation which relates $(\partial H/\partial P)_T$ to the equivalent derivatives of G and S. (10 pts) We know that G = H - TS, so that the differential dG = dH - TdS - SdT. At constant temperature dT = 0, so that

$$(\partial G/\partial P)_T = (\partial H/\partial P)_T - T(\partial S/\partial P)_T \tag{3}$$

Rearranging gives

$$(\partial H/\partial P)_T = (\partial G/\partial P)_T + T(\partial S/\partial P)_T \tag{4}$$

c. Then derive the thermodynamic equation of state which relates $(\partial H/\partial P)_T$ to the three fundamental physical variables V, T, and P. (15 pts) We need to replace the derivatives of G and S on the right hand side ("RHS") of Eq. (4) with derivatives involving V, T, and/or P The first term on the RHS of Eq. (4) is given by Eq. (2). The derivative in the 2nd term is a Maxwell relation, and can be obtained by equating the mixed second derivatives of G with respect to T and P. From Eqs. (1) and (2), we find for the desired Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Thus, finally, Eq. (4) becomes

$$(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P \tag{5}$$

2. One Maxwell relation is

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

The van der Waals equation of state is

$$P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

where a and b are constants. Use this information to determine the change in entropy when 1 mole of a van der Waals gas expands isothermally from V to 2V. (10 pts) The change in entropy is (using the given Maxwell relation)

$$\Delta S = \int_{V}^{2V} \left(\frac{\partial S}{\partial V}\right)_{T} dV = \int_{V}^{2V} \left(\frac{\partial P}{\partial T}\right)_{V} dV$$

For a van der Waals gas the derivative of P with respect to T is $(\partial P/\partial T)_V = nR/(V - nb)$. Thus

$$\Delta S = \int_{V}^{2V} \frac{nR}{V - nb} dV = nR \ln(2V - nb) - nR \ln(V - nb) = nR \ln \frac{2V - nb}{V - nb}$$

3. Some thermodynamic and physical properties of solid and gasous ethanol are given in the following table (the superscript (o) implies 298 K and 1 bar) Answer the following questions:

quantity	$C_2H_5OH(l)$	$C_2H_5OH(g)$
$\Delta H_f^{(o)} (\text{kJ/mol})$	-276.2	-234.0
$C_P (\mathrm{J/mol}\cdot\mathrm{K})$	114.1	65.49
S^o (J/mol·K)	161.2	191.6
$\bar{V} \ (\mathrm{cm}^3)$	36.35	ideal gas

a. Determine an expression for the enthalpy of vaporization at temperature T and a pressure of 1 bar. Give your answer in terms of T, $T_o = 298K$, and the heats of formation and specific heats of both phases. You can assume that the specific heats are independent of temperature. (10 pts)

We know that $(\partial H/\partial T)_P = C_P$. Thus $H(T) = H_{T_o} + \int_{T_o}^T C_P dT$. Using this equation for the liquid and for the vapor gives

$$\Delta H_v(T) = H_v(T) - H_l(T) = H_v(T_o) - H_l(T_o) = \Delta H_f^{(o)}(v) - \Delta H_f^{(o)}(l) + \int_{T_o}^T \Delta C_p(T) dT$$
(6)

- b. At 1 bar the boiling point of ethanol is 351K. Determine $\Delta_{\text{vap}}\bar{G}$ at this point. (Justify your answer) (10 pts). At the boiling point, the liquid and vapor have identical free energies. Thus $\Delta_{\text{vap}}\bar{G} = 0$.
- c. At a temperature of 355K will $\Delta_{\text{vap}}\bar{G} \equiv \bar{G}_v \bar{G}_l$ be positive or negative? (Justify your answer) (10 pts) Above the boiling point, at the same pressure, the free energy of the vapor will be lower. Thus $\Delta_{\text{vap}}\bar{G}$ will be negative.
- d. Derive the equation

$$\left[\frac{\partial}{\partial T} \left(\frac{A}{T}\right)\right]_V = -\frac{U}{T^2}$$

which is a Gibbs-Helmholtz equation for A. (15 pts) We know that A = U - TS, and, thereby A/T = U/T - S Differentiation with respect to T gives

$$\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{V} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V} - \frac{1}{T^{2}}U - \left(\frac{\partial S}{\partial T}\right)_{V}$$
(7)

From a comparison of the mathematical and thermodynamic definition of dU we know

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = TdS - PdV$$

thus at constant V (dV = 0)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = TdS$$

This equation can be rearranged as

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT$$

or, at constant ${\cal V}$

$$\frac{dS}{dV} \equiv \left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V$$

Substitution into Eq. (7), an equality at constant pressure, gives the desired result, since the $(\partial S/\partial T)_V$ terms cancel.

4. The isothermal compressibility is defined as

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)$$

and the coefficient of thermal expansion is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)$$

a. In terms of these two quantities determine an expression for $(\partial P/\partial T)_V$. (10 pts) We know that the product of three partial derivatives is

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

or

$$\left(\frac{\partial z}{\partial y}\right)_x = -\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z$$

Here, let x = V, y = P, and z = T, so corrected 12/6 14:41

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = \alpha V \times \frac{1}{\kappa V} = \alpha/\kappa$$