CHEM 311 PHYSICAL CHEMISTRY
Homework Assignment # 4

1. The following data are given for chloroform ($CHCl_3$). Calculate its absolute entropy at 1 bar and 500 K.

| | |
|---|---|
| $S^\circ$ at 10 K (J $K^{-1}$ $mol^{-1}$) | 1.142 |
| $C_{P,m}$ of solid phase (J $K^{-1}$ $mol^{-1}$) | 52.34 |
| $\Delta_{fus}H^\circ$ (kJ $mol^{-1}$) | 8.8 at 210.2 K |
| $C_{P,m}$ of liquid phase (J $K^{-1}$ $mol^{-1}$) | 114.25 |
| $\Delta_{vap}H^\circ$ (kJ K-1 mol-1) | 31.4 at 334.3 K |
| $C_{P,m}$ of gas phase (J $K^{-1}$ $mol^{-1}$) | $44.24 + 114.67 \times 10^{-3}T - 5.228 \times 10^5/T^2$ |

**Answer**

The third law of thermodynamics allows us to calculate the absolute entropy at 1 bar and 500 K as follows:

$$\begin{aligned} S^\circ_{500} =& S^\circ_{10} + \int_{10}^{210.2} \frac{C_{P,m(s)}}{T} dT + \frac{\Delta_{fus}H^\circ}{210.2 \text{ K}} + \int_{210.2}^{334.3} \frac{C_{P,m(l)}}{T} dT \\ &+ \frac{\Delta_{vap}H^\circ}{334.3 \text{ K}} + \int_{334.3}^{500} \frac{C_{P,m(v)}}{T} dT. \end{aligned}$$

Substituting and integrating, we get:

$$\begin{aligned} \int_{10}^{210.2} \frac{C_{P,m(s)}}{T} dT =& 52.34 \text{ J K}^{-1}\text{mol}^{-1} \ln\left(\frac{210.2}{10.0}\right) = 159.4 \text{ J K}^{-1}\text{mol}^{-1}. \\ \frac{\Delta_{fus}H^\circ}{210.2 \text{ K}} =& \frac{8,800 \text{ J mol}^{-1}}{210.2 \text{ K}} = 41.865 \text{ J K}^{-1}\text{mol}^{-1}. \\ \int_{210.2}^{334.3} \frac{C_{P,m(l)}}{T} dT =& 114.25 \ln\left(\frac{334.3}{210.2}\right) = 53.010 \text{ J K}^{-1}\text{mol}^{-1}. \\ \frac{\Delta_{vap}H^\circ}{334.3 \text{ K}} =& \frac{31400 \text{ J mol}^{-1}}{334.3 \text{ K}} = 93.928 \text{ J K}^{-1}\text{mol}^{-1}. \\ \int_{334.3}^{500} \frac{C_{P,m(v)}}{T} dT =& \int_{334.3}^{500} \left[\frac{44.24}{T} + 114.67 \times 10^{-3} - \frac{5.228 \times 10^5}{T^3}\right] dT \\ =& 44.24 \ln\left(\frac{500}{334.3}\right) + 114.67 \times 10^{-3} (500 - 334.3) \\ &+ \frac{5.228 \times 10^5}{2} \left(\frac{1}{500^2} - \frac{1}{334.3^2}\right) \\ =& 17.81 + 19.001 - 1.2934 = 35.518 \text{ J K}^{-1}\text{mol}^{-1}. \end{aligned}$$

Therefore, the absolute entropy at 500 K and 1 bar is

$$1.142 + 159.4 + 41.865 + 53.010 + 93.928 + 35.518 = 384.86 \text{ J K}^{-1}\text{mol}^{-1}.$$

2. The area of a rectangle may be considered a function of the breadth, $b$, and the length $l$, since $a = bl$. Then, $b$ and $l$ are considered independent variables and $a$ is the dependent variable. Other possible dependent variables are the perimeter $p = 2b + 2l$, and the diagonal, $d = \sqrt{b^2 + l^2}$. Evaluate the following partial derivatives in terms of $b$ and $l$, or obtain a numerical answer:

   (i) $\left(\frac{\partial a}{\partial l}\right)_b$, (ii) $\left(\frac{\partial p}{\partial l}\right)_b$, (iii)$\left(\frac{\partial l}{\partial b}\right)_d$ (iv) $\left(\frac{\partial l}{\partial b}\right)_p$.

   **Answer**

   (i) $a = bl$; Therefore, $(\partial a/\partial l)_b = b$.

   (ii) $p = 2l + 2b$. Therefore, $(\partial p/\partial l)_b = 2$.

   (iii) $d = \left(b^2 + l^2\right)^{1/2}$. Therefore,

$$\frac{\partial d}{\partial b} = \frac{b}{\left(b^2 + l^2\right)^{1/2}} + \frac{l}{\left(b^2 + l^2\right)^{1/2}} \left(\frac{\partial l}{\partial b}\right).$$

   Requiring $d$ to be constant, the left hand side vanishes. Therefore, we get

$$0 = \frac{b}{\left(b^2 + l^2\right)^{1/2}} + \frac{l}{\left(b^2 + l^2\right)^{1/2}} \left(\frac{\partial l}{\partial b}\right)_d.$$

$$\left(\frac{\partial l}{\partial b}\right)_d = -b/l.$$

   (iv) From $p = 2l + 2b$, $\partial p/\partial b = 2(\partial l/\partial b) + 2$. Requiring $p$ to be constant, the left hand side vanishes. Therefore, $(\partial l/\partial b)_p = -1$.

3. Starting from Eq. (3-126), and making use of Eq. (C-11), show that $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\alpha}{\kappa}\right) - P$, where $\alpha$ and $\kappa$ are, respectively, the thermal expansivity and the isothermal compressibility.

   **Answer**

   From Equation (3-126), following the text book, we get

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial A}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T.$$

   Using the relation (3-118) and the Maxwell's relation (3-124), we get

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V.$$

   Now, from Eq. (C-11), we get $\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}$. Using the definitions $\alpha = (\partial V/\partial T)_P/V$ and $\kappa = -(\partial V/\partial P)_T/V$, we therefore obtain $-\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \alpha/\kappa$, and thus,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\alpha}{\kappa}\right) - P.$$

4. A gas obeys the equation of state

$$\left(P - \frac{a}{V_m}\right) V_m = RT.$$

Evaluate the fugacity of the gas at 500 K and 20 bar, if $a$ = 0.786 L bar.

**Answer**

Let us try the working expression derived in class first, which gives

$$\ln\left(\frac{f}{P^\circ}\right) = \int_0^P \left(\frac{Z-1}{P}\right) dP.$$

From the given equation of state, we get

$$\begin{aligned} P &= \frac{RT}{V_m} + \frac{a}{V_m} \\ Z &= \frac{PV_m}{RT} = 1 + \frac{a}{RT}. \\ \ln\left(\frac{f}{P^\circ}\right) &= \frac{a}{RT}\int_0^P \frac{dP}{P} = \frac{a}{RT}\ln\left(\frac{P}{0}\right)! \end{aligned}$$

Obviously, we cannot go any further with this. [In case you are wondering, I copied the wrong equation of state into this problem, and didn't catch my mistake until it was too late.] Just for kicks, let us see if we can find the fugacity the round-about way (also discussed in class).

$$\begin{aligned} dG &= V\,dP, \text{ at constant } T \\ \Delta G_m &= \int_{P_1}^{P_2} V_m dP \end{aligned}$$

From the equation of state, we get

$$\begin{aligned} PV_m - a &= RT, \\ V_m &= \frac{RT + a}{P}. \end{aligned}$$

Therefore,

$$\begin{aligned} \Delta G &= \int_{P_1}^{P_2} \left(\frac{RT + a}{P}\right) dP \\ &= (RT + a)\ln\left(\frac{P_2}{P_1}\right) \end{aligned}$$

Now, let us set $P_1 = P^\circ = 1\,\text{bar}$. Then,

$$\begin{aligned} \Delta G &= \left[8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 500 \text{ K} + 0.786 \text{ L bar} \times \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}} \times \frac{10^5 \text{ Pa}}{1 \text{ bar}}\right)\right] \ln\left(\frac{20}{1}\right) \\ &= 12.689 \text{ kJ mol}^{-1} \end{aligned}$$

Now, we require the same free energy change to be given by the expression

$$\Delta G = RT\ln\left(\frac{f}{P^\circ}\right) = 12689 \text{ J mol}^{-1},$$

where we are assuming that $f_1 \simeq P_1 = P^\circ$, and setting $f_2 = f$. Solving for $f$, we get

$$\begin{aligned} \ln\left(\frac{f}{P}\right) &= \frac{12689}{8.3145 \times 500} = 3.0523 \\ f &= P^\circ \exp(3.0523) = 21.164 \text{ bar} \end{aligned}$$

What does the subtraction of the $a/V_m$ term from $P$ tell us about the nature of the gas? How is that reflected in the fugacity?