Problem Set 7
Solutions

Due 10-30-15

14 pts.

1. $\underline{\Delta G \text{ for Change in } P}$ (2 pts)

   Calculate the change in Gibbs energy of 35 g of ethanol (mass density 0.789 g cm^{-3}) when the pressure is increased isothermally from 1 atm to 3000. atm. Report your answer to 2 significant figures.

   GIVEN: ASSUME incompressible fluid

   $m = 35\,g \Rightarrow 2$ Sig Figs

   $\rho = 0.789 g\,cm^{-3}$

   $V = \frac{m}{\rho} = \frac{35\,g}{0.789\,g\,cm^{-3}} = 44.35995\,cm^3 = \underline{4.435995 \times 10^{-5} m^3}$

   isothermal, $\Delta T = 0, dT = 0$

   $P_i = 1\,atm \qquad P_f = 3000\,atm$

   $\Delta P = 2999\,atm = \underline{3.038737 \times 10^8\,Pa}$

   FIND: $\Delta G(P)$

   Start with the Fundamental equation for G

   $$dG \;=\; -S\,dT + V\,dP$$

   isothermal, so $dT = 0$

   $$dG \;=\; +V\,dP$$

   integrate

   $$\Delta G \;=\; +\int_{P_i}^{P_f} V\,dP$$

   V is constant since we are assuming incompressible fluid

   Therefore, V comes out of the integral

   $$
   \begin{aligned}
   \Delta G \;&=\; +V\,\Delta P \\
   &=\; 4.435995 \times 10^{-5} m^3 \times 3.038737 \times 10^8\,Pa \\
   &=\; +1.347982 \times 10^4\,Pa\,m^3 = +1.347982 \times 10^4\,J
   \end{aligned}
   $$

   $$\boxed{\Delta G = +1.3 \times 10^4\,J = +1.3\,kJ}$$

2. <u>Gibbs-Helmholtz</u> (3 pts)

Calculate $\Delta_r \overline{G}^\circ (375\,K)$ for the reaction $2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g)$ from the value of $\Delta_r \overline{G}^\circ (298\,K)$, $\Delta_r \overline{H}^\circ (298\,K)$ and the Gibbs-Helmholtz equation using the data below.

compound	$\Delta_f \overline{G}^\circ\ (kJ\,mol^{-1})$	$\Delta_f \overline{H}^\circ\ (kJ\,mol^{-1})$
$CO(g)$	-137.17	-110.53
$O_2(g)$	0	0
$CO_2(g)$	-394.36	-393.51

GIVEN: ASSUME $\Delta_r \overline{H}^\circ$ is constant over the temperature range

$T_f = 375\,K$

FIND: $\Delta_r \overline{G}^\circ (375\,K)$

First, compute $\Delta_r \overline{G}^\circ (298\,K)$ and $\Delta_r \overline{H}^\circ (298\,K)$

$$\Delta_r \overline{X}^\circ = \sum \nu \Delta_f \overline{X}^\circ$$

$$\Delta_r \overline{G}^\circ (298\,K) = [\{2\,(-394.36)\} - \{2\,(-137.17) + 1\,(0)\}]\ kJ\,mol^{-1}$$
$$= [-788.72 - -274.34]\ kJ\,mol^{-1}$$
$$\Delta_r \overline{G}^\circ (298\,K) = \underline{-514.38\,kJ\,mol^{-1}}$$

$$\Delta_r \overline{H}^\circ (298\,K) = [\{2\,(-393.51)\} - \{2\,(-110.53) + 1\,(0)\}]\ kJ\,mol^{-1}$$
$$= [-787.02 - -221.06]\ kJ\,mol^{-1}$$
$$\Delta_r \overline{H}^\circ (298\,K) = \underline{-565.96\,kJ\,mol^{-1}}$$

Use the Gibbs-Helmholtz equation

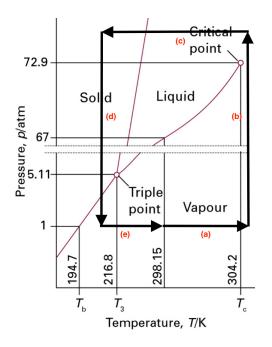$$\Delta_r \overline{G}^\circ (T_f) = \frac{T_f}{T^\circ} \Delta_r \overline{G}^\circ (298\,K) + \Delta_r \overline{H}^\circ (298\,K)\left(1 - \frac{T_f}{T^\circ}\right)$$

$$\Delta_r \overline{G}^\circ (375\,K) = \frac{375\,K}{298\,K}\left(-514.38\,kJ\,mol^{-1}\right) + -565.96\,kJ\,mol^{-1}\left(1 - \frac{375\,K}{298\,K}\right)$$

$$= -647.2903 + +146.2380\,kj\,mol^{-1}$$

$$= \underline{-501.0523\,kJ\,mol^{-1}}$$

$$\boxed{\Delta_r \overline{G}^\circ (375\,K) = -501\,kJ\,mol^{-1}}$$

3. <u>Phase Diagram</u> (2 pts)
   Use the phase diagram below to state what would be observed when a sample of carbon dioxide, initially at 1.0 atm and 298 K, is subjected to the following cycle: (a) isobaric heating to 320. K, (b) isothermal compression to 100. atm, (c) isobaric cooling to 210. K, (d) isothermal decompression to 1.0 atm, (e) isobaric heating to 298 K.

(a) Gas is heated above T_c, but the pressure is still well below P_c, therefore, the sample remains a gas. There is NO phase transition.

(b) The pressure is increased above P_c and temperature remains above T_c. Therefore the gas slowly becomes a supercritical fluid. There is NO phase transition.

(c) The temperature is lowered below T_c. Initially, the supercritical fluid will become a liquid without a phase transition occurring. Then, as the sample is cooled further, the liquid eventually becomes a solid in a phase transition.

(d) The pressure is lowered below the solid–gas coexistence curve. The solid sample sublimes to gas around 3.5 atm. This IS a phase transition.

(e) The gas is heated to return to its original state. There is NO phase transition.

4. **$\Delta_{fus}H$ and $\Delta_{fus}S$** (2 pts)

The molar volume of a certain solid is $161.0\,cm^3\,mol^{-1}$ at $1.00\,atm$ and 350.75 K, it's melting temperature. The molar volume of the liquid at this temperature and pressure is $163.3\,cm^3\,mol^{-1}$. At 100. atm the melting temperature changes to 351.26 K. Calculate the enthalpy and entropy of fusion of the solid.

    GIVEN:

$$P = 1.00\,atm = \underline{101325\,Pa} \Rightarrow 3 \text{ Sig Figs}$$

$$T = 350.75\,K$$

$$\overline{V}_{sol} = 161.0\,cm^3\,mol^{-1}$$

$$\overline{V}_{liq} = 163.3\,cm^3\,mol^{-1}$$

$$\Delta_{fus}\overline{V} = \overline{V}_{liq} - \overline{V}_{sol} = (163.3 - 161.0)\,cm^3\,mol^{-1} = 2.3\,cm^3\,mol^{-1}$$
$$= \underline{2.3 \times 10^{-6}\,m^3\,mol^{-1}}$$

$$P_f = 100\,atm = \underline{10132500\,Pa}$$

$$T_f = 351.26\,K$$

FIND: $\Delta_{fus}\overline{S}$ and $\Delta_{fus}\overline{H}$ at P_f and T_f

    Start by rearranging the Claperyon equation

$$\frac{dP}{dT} = \frac{\Delta_{fus}\overline{S}}{\Delta_{fus}\overline{V}}$$

$$dP = \frac{\Delta_{fus}\overline{S}}{\Delta_{fus}\overline{V}}\,dT$$

    $\Delta_{fus}\overline{V}$ can be assumed T independent

    however, $\Delta_{fus}\overline{S}$ cannot be independent of T

    instead, substitute $\Delta_{fus}\overline{S} = \dfrac{\Delta_{fus}\overline{H}}{T}$

    because $\Delta_{fus}\overline{H}$ can be assumed to be T independent

$$dP = \frac{\Delta_{fus}\overline{H}}{T\,\Delta_{fus}\overline{V}}\,dT$$

    integrate

$$\int_{P}^{P_f} dP = \int_{T}^{T_f} \frac{\Delta_{fus}\overline{H}}{T\,\Delta_{fus}\overline{V}}\,dT$$

    $\Delta_{fus}\overline{V}$ and $\Delta_{fus}\overline{H}$ come out of the integral, assumed T independent

$$\int_{P}^{P_f} dP = \frac{\Delta_{fus}\overline{H}}{\Delta_{fus}\overline{V}} \int_{T}^{T_f} \frac{1}{T}\,dT$$

$$\Delta P \;=\; \frac{\Delta_{fus}\overline{H}}{\Delta_{fus}\overline{V}} \ln\left(\frac{T_f}{T}\right)$$

$$\text{solve for } \Delta_{fus}\overline{H}$$

$$\Delta_{fus}\overline{H} \;=\; \frac{\Delta P \, \Delta_{fus}\overline{V}}{\ln\left(\frac{T_f}{T}\right)}$$

$$=\; \frac{(10132500 - 101325)\, Pa \times (2.3 \times 10^{-6}\, m^3\, mol^{-1})}{\ln\frac{351.26\,K}{350.75\,K}}$$

$$=\; \underline{+1.587898 \times 10^4\, J\, mol^{-1}}$$

$$\boxed{\Delta_{fus}\overline{H} = +1.59 \times 10^4\, J\, mol^{-1} = +15.9\, kJ\, mol^{-1}}$$

$$\Delta_{fus}\overline{S} \;=\; \frac{\Delta_{fus}\overline{H}}{T_f}$$

$$=\; \frac{1.587898 \times 10^4\, J\, mol^{-1}}{351.26\,K}$$

$$=\; \underline{+4.520578 \times 10^1\ J\, K^{-1}\, mol^{-1}}$$

$$\boxed{\Delta_{fus}\overline{S} \;=\; +45.2\ J\, K^{-1}\, mol^{-1}}$$

5. $\underline{T_{trs}(P)}$ (2 pts)

Calculate the melting point of ice under a pressure of 50. bar. Assume that the density of ice under these conditions is approximately 0.92 g cm^{-3} and that of liquid water is 1.00 g cm^{-3}.

GIVEN:

$P = 1\,bar = \underline{1 \times 10^5\,Pa}$

$T = 0°C = \underline{273.15\,K}$

$P_f = 50\,bar = \underline{5.0 \times 10^6\,Pa} \Rightarrow 2$ Sig Figs

$\Delta P = 5.0 \times 10^6\,Pa - 1 \times 10^5\,Pa = \underline{4.9 \times 10^6\,Pa}$

$\rho_{ice} = 0.92\,g\,cm^{-3} = \underline{9.2 \times 10^5\,g\,m^{-3}}$ $\rho_{water} = 1.00\,g\,cm^{-3} = \underline{1.00 \times 10^6\,g\,m^{-3}}$

$\Delta_{fus}\overline{V} = M\,\Delta\left(\frac{1}{\rho}\right) = 18.02\,g\,mol^{-1}\left(\frac{1}{1.00\times10^6\,g\,m^{-3}} - \frac{1}{9.2\times10^5\,g\,m^{-3}}\right)$

$\Delta_{fus}\overline{V} = \underline{-1.566957 \times 10^{-6}\,m^3\,mol^{-1}}$

$\Delta_{fus}\overline{H} = 6.008 \times 10^3\,J\,mol^{-1}$

FIND: T_f at P_f

Substitute $\Delta_{fus}\overline{S} = \frac{\Delta_{fus}\overline{H}}{T}$ into the Clapeyron equation

ASSUME $\Delta_{fus}\overline{H}$ and $\Delta_{fus}\overline{V}$ are independent of T and integrate

$$dP = \frac{\Delta_{fus}\overline{H}}{\Delta_{fus}\overline{V}}\frac{dT}{T}$$

$$\int_P^{P_f} dP = \frac{\Delta_{fus}\overline{H}}{\Delta_{fus}\overline{V}}\int_T^{T_f}\frac{dT}{T}$$

$$\Delta P = \frac{\Delta_{fus}\overline{H}}{\Delta_{fus}\overline{V}}\ln\left(\frac{T_f}{T}\right) \qquad \text{solve for } T_f$$

$$\ln\left(\frac{T_f}{T}\right) = \frac{\Delta P\,\Delta_{fus}\overline{V}}{\Delta_{fus}\overline{H}} \qquad \text{exponentiate both sides}$$

$$\left(\frac{T_f}{T}\right) = \exp\left(\frac{\Delta P\,\Delta_{fus}\overline{V}}{\Delta_{fus}\overline{H}}\right)$$

$$T_f = T\exp\left(\frac{\Delta P\,\Delta_{fus}\overline{V}}{\Delta_{fus}\overline{H}}\right)$$

$$= 273.15\,K\,\exp\left(\frac{(4.9\times10^6\,Pa)\times(-1.566957\times10^{-6}\,m^3\,mol^{-1})}{6.008\times10^3\,J\,mol^{-1}}\right)$$

$$= \underline{2.728011\times10^2\,K} = 272.8\,K$$

$$\boxed{T_f = 2.7\times10^2\,K}$$

6. <u>Slope of Chemical Potential</u> (3 pts)

Calculate the difference in slope of the chemical potential against pressure on either side of (a) the normal freezing point of water and (b) the normal boiling point of water. The densities of ice and water at 0°C are 0.917 g cm^{-3} and 1.000 g cm^{-3}, and those of water and water vapor at 100.°C are 0.958 g cm^{-3} and 0.598 g dm^{-3}, respectively. By how much does the chemical potential of water vapor exceed that of liquid water at 1.2 atm and 100.°C?

GIVEN:

$$M_{H_2O} = 18.02\,g\,mol^{-1} = \underline{18.02 \times 10^{-3}\,kg\,mol^{-1}}$$

$$0°C = 273.15\,K$$
$$\rho_{sol} = 0.917\,g\,cm^{-3} = \underline{9.17 \times 10^2\,kg\,m^{-3}}$$
$$\rho_{liq} = 1.000\,g\,cm^{-3} = \underline{1.000 \times 10^3\,kg\,m^{-3}}$$

$$100°C = 373.15\,K$$
$$\rho_{liq} = 0.958\,g\,cm^{-3} = \underline{9.58 \times 10^2\,kg\,m^{-3}}$$
$$\rho_{vap} = 0.598\,g\,dm^{-3} = \underline{0.598\,kg\,m^{-3}}$$

FIND: Difference in slope of chemical potential, against pressure, on either side of the (a) the solid–liquid phase and (b) the liquid–vapor phase, AND compute the difference in chemical potential between liquid and vapor at 1.2 atm and 100°C.

The difference in the slope against pressure for two phases is just. . .

$$\left.\frac{\partial\mu_\beta}{\partial P}\right|_T - \left.\frac{\partial\mu_\alpha}{\partial P}\right|_T = \overline{V}_\beta - \overline{V}_\alpha = \Delta_{trs}\overline{V}$$

The other equation that you will need is $\overline{V} = \frac{M}{\rho}$ and $\Delta_{trs}\overline{V} = M\left(\frac{1}{\rho_\beta} - \frac{1}{\rho_\alpha}\right)$

(a)

$$\begin{aligned}
\left.\frac{\partial\mu_l}{\partial P}\right|_T - \left.\frac{\partial\mu_s}{\partial P}\right|_T &= \overline{V}_l - \overline{V}_s = \Delta_{trs}\overline{V} = \Delta_{fus}\overline{V}\\
&= M\left(\frac{1}{\rho_l} - \frac{1}{\rho_s}\right)\\
&= 18.02 \times 10^{-3}kg\,mol^{-1}\left(\frac{1}{1.00 \times 10^3kg\,m^{-3}} - \frac{1}{9.17 \times 10^2kg\,m^{-3}}\right)\\
&= \underline{-1.631036 \times 10^{-6}m^3\,mol^{-1}}
\end{aligned}$$

$$\boxed{\left.\frac{\partial\mu_l}{\partial P}\right|_T - \left.\frac{\partial\mu_s}{\partial P}\right|_T = -1.63 \times 10^{-6}m^3\,mol^{-1}}$$

(b)

$$
\begin{aligned}
\left.\frac{\partial \mu_g}{\partial P}\right|_T - \left.\frac{\partial \mu_l}{\partial P}\right|_T &= \overline{V}_g - \overline{V}_l = \Delta_{trs}\overline{V} = \Delta_{vap}\overline{V} \\
&= M\left(\frac{1}{\rho_g} - \frac{1}{\rho_l}\right) \\
&= 18.02 \times 10^{-3} kg\,mol^{-1}\left(\frac{1}{0.598\,kg\,m^{-3}} - \frac{1}{958\,kg\,m^{-3}}\right) \\
&= \underline{+3.011497 \times 10^{-2} m^3\,mol^{-1}}
\end{aligned}
$$

$$
\boxed{\left.\frac{\partial \mu_g}{\partial P}\right|_T - \left.\frac{\partial \mu_l}{\partial P}\right|_T = +3.01 \times 10^{-2} m^3\,mol^{-1}}
$$

(c) Compute the difference of the chemical potential of vapor and liquid at 1.2 atm and 100°C.

$$
\left.\frac{\partial \mu_g}{\partial P}\right|_T - \left.\frac{\partial \mu_l}{\partial P}\right|_T = \overline{V}_g - \overline{V}_l
$$

Since we are at a non-standard pressure, 1.2 atm, we have to integrate first, multiply by dP

$$
d\mu_g - d\mu_l = \left(\overline{V}g - \overline{V}l\right)dP
$$

integrate

$$
\int d\mu_g - \int d\mu_l = \int_{1.0\,atm}^{1.2\,atm}\left(\overline{V}g - \overline{V}_l\right)dP = \int_{1.0\,atm}^{1.2\,atm}\overline{V}_g\,dP - \int_{1.0\,atm}^{1.2\,atm}\overline{V}_l\,dP
$$

assuming incompressible liquid, $\overline{V}_l$ will come out of the integral

assuming ideal gas, we substitute $\dfrac{RT}{P}$ for $\overline{V}_g$

$$
\int d\mu_g - \int d\mu_l = \int_{1.0\,atm}^{1.2\,atm}\frac{RT}{P}\,dP - \overline{V}_l\int_{1.0\,atm}^{1.2\,atm}dP
$$

$$
\begin{aligned}
\mu_g - \mu_l &= RT\ln\frac{1.2\,atm}{1.0\,atm} - \overline{V}_l\Delta P \\
&= 8.314510\,J\,K^{-1}\,mol^{-1} \times 373.15\,K \times \ln 1.2 \\
&\quad -\frac{18.02 \times 10^{-3}kg\,mol^{-1}}{958\,kg\,m^{-3}} \times (1.2\,atm - 1.0\,atm) \times \frac{101325\,Pa}{1\,atm} \\
&= \underline{+5.652796 \times 10^2\,J\,mol^{-1}}
\end{aligned}
$$

$$
\boxed{\mu_g - \mu_l = +5.65 \times 10^2\,J\,mol^{-1}}
$$

Since, μ_g is larger than μ_l this shows that the gas will spontaneously, and irreversibly condense into liquid at 1.2 atm.