

Chemistry 431
Problem Set 11
Fall 2023

Solutions

1. Seven grams of ice at -10.0°C are dropped into 80.0 g of water at $30.^{\circ}\text{C}$ and the system is allowed to reach equilibrium adiabatically. Calculate the final temperature of the system. The specific heat of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$, the specific heat of ice is $2.09 \text{ J g}^{-1} \text{ K}^{-1}$, and the heat of fusion of ice is 334.7 J g^{-1} .

Answer:

$$\begin{aligned}q_1 + q_2 &= 0 \\(7 \text{ g})(2.09 \text{ J K}^{-1}\text{g}^{-1})(10 \text{ K}) + (7 \text{ g})(334.7 \text{ J g}^{-1}) \\+ (7 \text{ g})(T - 273 \text{ K})(4.18 \text{ J g}^{-1}\text{K}^{-1}) + (80 \text{ g})(4.18 \text{ J g}^{-1}\text{K}^{-1})(T - 303 \text{ K}) &= 0 \\T &= 293.7 \text{ K} = 20.7 \text{ C}\end{aligned}$$

2. One mole of liquid water is originally contained in a capsule that is enclosed in an evacuated tank of fixed volume that is thermostated to $100.^{\circ}\text{C}$. The capsule is broken and the liquid water is allowed to evaporate into the previously evacuated tank. After equilibrium is established at $100.^{\circ}\text{C}$, the pressure of the water vapor in the tank is found to be 0.5 atmospheres. Assuming the water vapor to be an ideal gas and neglecting the volume of the liquid water compared to that of the vapor, calculate ΔU , ΔH , ΔS , ΔA , ΔG , q and w for the process. The enthalpy of vaporization of water at $100.^{\circ}\text{C}$ and 1. atmospheres pressure is $44. \text{ kJ mol}^{-1}$.

Answer:

$$\begin{aligned}w &= 0 \quad \Delta H = 44000 \text{ J} \\ \Delta U &= \Delta H - \Delta(PV) = \Delta H - (P_2V_2 - P_1V_1) \approx \Delta H - P_2V_2 \\ &= \Delta H - nRT = 44000 \text{ J} - (1 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(373 \text{ K}) = 40899 \text{ J} \\ q &= \Delta U = 40899 \text{ J} \\ \Delta S &= \frac{\Delta H}{T} + nR \ln \frac{P_i}{P_f} \\ &= \frac{44000 \text{ J}}{373 \text{ K}} + (1 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{1}{0.5} = 124 \text{ J K}^{-1} \\ \Delta G &= \Delta H - T\Delta S = 44000 \text{ J} - (373 \text{ K})(124 \text{ J K}^{-1}) = -2252 \text{ J} \\ \Delta A &= \Delta U - T\Delta S = 40899 \text{ J} - (373 \text{ K})(124 \text{ J K}^{-1}) = -5353 \text{ J}\end{aligned}$$

Notice that $\Delta A < 0$ because the process is spontaneous at constant T and V . ΔG is unrestricted in sign for such a process.

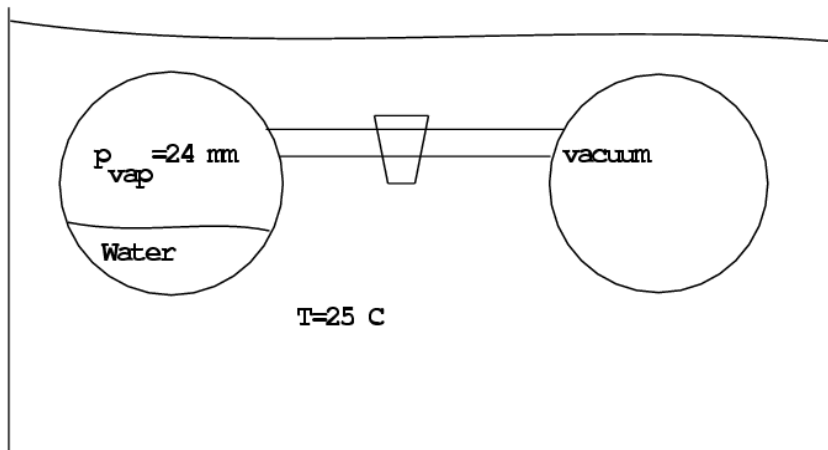


Figure 1: A representation of the flask discussed in problem 3

3. In the container pictured in Figure 1, the left hand side initially consists of water in equilibrium with its vapor and the right hand side is evacuated. The two sides, each of volume 20. liters, are connected with a closed stop-cock and the entire system is placed in a heat bath thermostated to 25. °C. The vapor pressure of water at 25. °C is 24. mm and the enthalpy of vaporization of water is 44. kJ mol⁻¹. If the stopcock is opened, calculate ΔU , ΔH , ΔS , ΔA , ΔG , q and w when equilibrium is reached. You may assume some liquid water remains on the left hand side at the end of the process, and you may neglect the volume of the liquid compared to the vapor. You may also assume the vapor obeys the ideal gas law.

Answer:

$$n = \frac{PV}{RT} = \frac{(0.03158 \text{ atm})(20 \text{ L})}{(0.0821 \text{ L atm mol}^{-1}\text{K}^{-1})(298 \text{ K})} = 0.02582 \text{ mol}$$

$$\Delta H = (0.02582 \text{ mol})(44000 \text{ J mol}^{-1}) = 1136 \text{ J}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{1136 \text{ J}}{298 \text{ K}} = 3.81 \text{ J K}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = 0$$

$$\begin{aligned} \Delta U &= \Delta H - \Delta(PV) = \Delta H - nRT \\ &= 1136 \text{ J} - (0.02582 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) = 1072 \text{ J} \end{aligned}$$

$$\Delta A = \Delta U - T\Delta S = 1072 \text{ J} - (298 \text{ K})(3.81 \text{ J K}^{-1}) = -64 \text{ J}$$

$$w = 0 \quad q = \Delta U = 1072 \text{ J}$$

As with the previous problem, the process is spontaneous and constant T and V . $\Delta A < 0$ and ΔG can be anything.

4. A 10.0 g sample of liquid water at 373 K is placed in a capsule, and the capsule containing the water is put in a large, evacuated tank of fixed volume. The capsule is broken at a fixed temperature of 373 K, and the pressure of the water vapor in the previously evacuated tank is found to be 0.500 bar. During the evaporation of the liquid water heat is absorbed from the surroundings, and a measurement of the heat finds $q = 22.7$ kJ. Assuming the enthalpy of vaporization of water to be independent of temperature, use the data to calculate the vapor pressure of water at 50.0°C.

Answer:

$$\Delta U = 22700 \text{ J} \quad n = \frac{10.0 \text{ g}}{18.0 \text{ g mol}^{-1}} = 0.556 \text{ mol} \quad \Delta_m U = \frac{22700 \text{ J}}{0.556 \text{ mol}} = 40860 \text{ J mol}^{-1}$$

$$\Delta_m H = \Delta_m U + \Delta(PV) = \Delta_m U + RT = 40860 \text{ J mol}^{-1} + (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(373 \text{ K}) = 44000 \text{ J mol}^{-1}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{P}{1.01 \text{ bar}} = \frac{44000 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left(\frac{1}{373 \text{ K}} - \frac{1}{323 \text{ K}} \right)$$

$$P = 0.112 \text{ bar}$$

5. The vapor pressure of solid ammonia is given by

$$\ln P = 23.03 - \frac{3754}{T}$$

and that of liquid ammonia is given by

$$\ln P = 19.49 - \frac{3063}{T}$$

where the pressure is expressed in millimeters of mercury.

- (a) What is the temperature of ammonia at the triple point?

Answer:

$$19.49 - \frac{3063}{T} = 23.03 - \frac{3754}{T}$$

$$T = 195.2 \text{ K}$$

- (b) What are the latent enthalpies of sublimation and vaporization of ammonia at the triple point?

Answer:

$$\ln P = -\frac{\Delta H}{RT} + \text{constant}$$

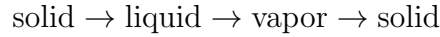
$$\frac{\Delta_{sub,m}H}{R} = 3754 \text{ K}$$

$$\Delta_{sub,m}H = (3754 \text{ K})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) = 31.14 \text{ kJ mol}^{-1}$$

$$\Delta_{vap,m}H(3063 \text{ K})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) = 25.47 \text{ kJ mol}^{-1}$$

(c) What is the latent heat of fusion of ammonia at the triple point?

Answer:



so that

$$\begin{aligned}\Delta_{\text{fusion},m}H &= \Delta_{\text{sub},m}H - \Delta_{\text{vap},m}H \\ &= (31.14 - 25.47)\text{kJ mol}^{-1} = 5.67\text{kJ mol}^{-1}\end{aligned}$$

6. The vapor pressure of solid SO_2 is 1.32×10^{-3} atm at 177.0K and 1.32×10^{-2} atm at 195.8K. The vapor pressure of liquid SO_2 is 4.39×10^{-2} atm at 209.6K and 1.32×10^{-1} atm at 225.3K. Calculate the temperature of sulfur dioxide at the triple point.

Answer:

$$\begin{aligned}\ln \frac{P_2}{P_1} &= \frac{\Delta_{\text{sub},m}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{1.32 \times 10^{-3}}{1.32 \times 10^{-2}} &= \frac{\Delta_{\text{sub},m}H}{R} \left(\frac{1}{195.8 \text{ K}} - \frac{1}{177.0 \text{ K}} \right) \\ \frac{\Delta_{\text{sub},m}H}{R} &= 4245. \text{ K} \\ \ln \frac{P_2}{P_1} &= \frac{\Delta_{\text{vap},m}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{4.39 \times 10^{-2}}{1.32 \times 10^{-1}} &= \frac{\Delta_{\text{vap},m}H}{R} \left(\frac{1}{225.3 \text{ K}} - \frac{1}{209.6 \text{ K}} \right) \\ \frac{\Delta_{\text{vap},m}H}{R} &= 3311. \text{ K} \\ \ln P_{\text{solid}} &= -\frac{4245. \text{ K}}{T} + K_{\text{solid}} \\ \ln(1.32 \times 10^{-3}) &= -\frac{4245.}{177.0} + K_{\text{solid}} \quad K_{\text{solid}} = 17.35 \\ \ln P_{\text{liquid}} &= -\frac{3311. \text{ K}}{T} + K_{\text{liquid}} \\ \ln(1.32 \times 10^{-1}) &= -\frac{3311.}{225.3} + K_{\text{liquid}} \quad K_{\text{liquid}} = 12.67\end{aligned}$$

At the triple point

$$\begin{aligned}-\frac{4245. \text{ K}}{T} + 17.35 &= -\frac{3311. \text{ K}}{T} + 12.67 \\ T &= 200. \text{ K}\end{aligned}$$

7. The density of liquid bismuth is 10. kg liter⁻¹, and the density of solid bismuth is 9.67 kg liter⁻¹. The normal melting point of bismuth is 270. °C and the enthalpy of fusion of bismuth is 52.718 kJ kg⁻¹. Calculate the melting point of bismuth under 100. atmospheres pressure.

Answer:

$$\begin{aligned}
 P_2 - P_1 &= \frac{\Delta_{fus,m}H}{\Delta_{fus,m}V} \ln \frac{T_2}{T_1} \\
 \ln \frac{T_2}{T_1} &= \frac{\Delta_{fus,m}V}{\Delta_{fus,m}H} (P_2 - P_1) \\
 &= \frac{(0.1 \text{ L kg}^{-1} - 0.1034 \text{ L kg}^{-1})(100\text{atm} - 1 \text{ atm})}{52718\text{J kg}^{-1}} \\
 &= -6.409 \times 10^{-6} \frac{\text{L atm}}{\text{J}} \left(\frac{8.3144\text{J}}{0.0821 \text{ L atm}} \right) \\
 &= -6.49 \times 10^{-4} \\
 T_2 &= 543\text{K} \exp(-6.49 \times 10^{-4}) = 542.6\text{K}
 \end{aligned}$$

8. The temperature at the triple point of xenon is 161.40K and the normal boiling point of xenon is 165.11K. Given that the vapor pressure of liquid xenon is 0.912 atmospheres at 163.0K, calculate the vapor pressure of xenon at the triple point. Assume the enthalpy of vaporization of xenon is temperature independent.

Answer:

$$\begin{aligned}
 \ln \frac{P_2}{P_1} &= \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\
 \ln \frac{1}{0.912} &= \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{163.0 \text{ K}} - \frac{1}{165.11 \text{ K}} \right) \\
 \frac{\Delta_{vap,m}H}{R} &= 1174.9 \text{ K} \\
 \ln \frac{P}{1 \text{ atm}} &= 1174.9 \text{ K} \left(\frac{1}{165.11 \text{ K}} - \frac{1}{161.40 \text{ K}} \right) \\
 P &= 0.849 \text{ atm}
 \end{aligned}$$

9. The enthalpy of vaporization of water is 44. kJ mol⁻¹, and the enthalpy of fusion of ice is 6. kJ mol⁻¹. If the vapor pressure of ice at 0. °C is 6.016 × 10⁻³ atmospheres, what is the vapor pressure of ice at -20. °C?

Answer:

$$\begin{aligned}
 \Delta_{sub,m}H &= \Delta_{vap,m}H + \Delta_{fus,m}H \\
 &= (6 + 44)\text{kJ mol}^{-1} = 50\text{kJ mol}^{-1} \\
 \ln \frac{P}{6.016 \times 10^{-3}\text{atm}} &= \frac{50000\text{J mol}^{-1}}{8.3144\text{J mol}^{-1}\text{K}^{-1}} \left(\frac{1}{273\text{K}} - \frac{1}{253\text{K}} \right) \\
 P &= 1.06 \times 10^{-3}\text{atm}
 \end{aligned}$$

10. The triple point of methane(CH₄) occurs at $T_t=90.70$ K and $P_t=0.1170$ bar. The critical point of methane occurs at $T_c=190.6$ K and $P_c=46.10$ bar. Given the enthalpy of sublimation of methane is $\Delta_{sub,m}H=9.700$ kJ mol⁻¹, calculate the melting temperature of methane when the total pressure is 1.000 bar. The densities of liquid and solid methane are respectively $\rho_\ell = 0.4340$ g cm⁻³ and $\rho_s=0.5020$ g cm⁻³. You can assume the densities of the liquid and solid are pressure and temperature independent, and you can assume the enthalpies of fusion, sublimation and vaporization are also temperature and pressure independent.

Answer:

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{46.10}{0.1170} = \frac{\Delta_{vap,m}H}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left(\frac{1}{90.70 \text{ K}} - \frac{1}{190.6 \text{ K}} \right) \quad \Delta_{vap,m}H = 8600. \text{ J mol}^{-1}$$

$$\Delta_{fus,m}H = \Delta_{sub,m}H - \Delta_{vap,m}H = 1100. \text{ J mol}^{-1}$$

$$P_2 = P_1 + \frac{\Delta_{fus,m}H}{\Delta_{fus,m}V} \ln \frac{T_2}{T_1}$$

$$1.000 \text{ bar} = 0.1170 \text{ bar} + \frac{(1100. \text{ J mol}^{-1}) \left(\frac{0.08314 \text{ L bar}}{8.3144 \text{ J}} \right) \ln \left(\frac{T}{90.70 \text{ K}} \right)}{\left(\frac{\text{cm}^3}{0.4340 \text{ g}} - \frac{\text{cm}^3}{0.5020 \text{ g}} \right) \left(\frac{\text{L}}{10^3 \text{ cm}^3} \right) \left(\frac{16.00 \text{ g}}{\text{mol}} \right)}$$

$$T = 90.74 \text{ K}$$

11. The triple point of argon is $T_t = 83.80$ K and $P_t = 0.6889$ bar, and the critical point of argon is $T_c = 150.69$ K and $P_c = 48.63$ bar. At $T = 81.44$ K, the vapor pressure of solid argon is measured to be $P = 0.500$ bar. Assuming the enthalpy changes for all phase transition in argon are temperature independent, and given the densities of solid and liquid argon are respectively $\rho_{solid} = 1.616$ g cm⁻³ and $\rho_{liquid} = 1.400$ g cm⁻³, calculate the standard freezing point of argon.

Answer:

$$\text{liquid-vapor : } \ln \frac{P_2}{P_1} = \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{48.63}{0.6889} = \frac{\Delta_{vap,m}H}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left(\frac{1}{83.80 \text{ K}} - \frac{1}{150.69 \text{ K}} \right) \quad \Delta_{vap,m}H = 6680 \text{ J mol}^{-1}$$

$$\text{solid-vapor : } \ln \frac{0.6889}{0.500} = \frac{\Delta_{sub,m}H}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left(\frac{1}{81.44 \text{ K}} - \frac{1}{83.80 \text{ K}} \right) \quad \Delta_{sub,m}H = 7700 \text{ J mol}^{-1}$$

$$\Delta_{fus,m}H = \Delta_{sub,m}H - \Delta_{vap,m}H = 1020 \text{ J mol}^{-1}$$

$$\text{solid-liquid : } P_2 - P_1 = \frac{\Delta_{fus,m}H}{\Delta_{fus,m}V} \ln \frac{T_2}{T_1}$$

$$1 \text{ bar} - 0.6889 \text{ bar} = \frac{1020 \text{ J mol}^{-1} \left(\frac{0.083144 \text{ L bar}}{8.3144 \text{ J}} \right)}{\left(\frac{\text{cm}^3}{1.400 \text{ g}} - \frac{\text{cm}^3}{1.616 \text{ g}} \right) \left(\frac{39.9 \text{ g}}{\text{mol}} \right) \left(\frac{\text{L}}{10^3 \text{ cm}^3} \right)} \ln \frac{T}{83.80 \text{ K}}$$

$T = 83.80 \text{ K}$

12. (a) Using an Euler-Maxwell relation, show that

$$\left(\frac{\partial \gamma}{\partial P} \right)_{\sigma, T} = \left(\frac{\partial V}{\partial \sigma} \right)_{P, T}$$

Answer:

$$dG = -SdT + VdP + \gamma d\sigma$$

$$\left(\frac{\partial \gamma}{\partial P} \right)_{\sigma, T} = \left(\frac{\partial V}{\partial \sigma} \right)_{T, P}$$

(b) For a spherical bubble of radius, r , show that

$$\left(\frac{\partial V}{\partial \sigma} \right)_{P, T} = \frac{r}{2}.$$

Answer:

$$V = \frac{4}{3}\pi r^3$$

$$dV = 4\pi r^2 dr$$

$$\sigma = 4\pi r^2$$

$$d\sigma = 8\pi r dr$$

$$\left(\frac{\partial V}{\partial \sigma} \right)_{T, P} = \frac{4\pi r^2 dr}{8\pi r dr} = \frac{r}{2}$$

(c) Use parts “a” and “b” to derive the Laplace equation

$$P_{in} - P_{out} = \frac{2\gamma}{r}.$$

Answer:

$$\left(\frac{\partial \gamma}{\partial P} \right)_{\sigma, T} = \frac{r}{2}$$

$$d\gamma = \frac{r}{2} dP$$

$$dP = \frac{2d\gamma}{r}$$

or

$$P_{in} - P_{out} = \frac{2\gamma}{r}$$

13. What is the ratio of the vapor pressure of mercury above the meniscus of a capillary 10^{-7} meters in radius to the vapor pressure of mercury above a flat surface at 20°C ? The surface tension of mercury is $47. \times 10^{-2} \text{ N m}^{-1}$, and the density of mercury is 13.6 gm cm^{-3} . Assume a zero contact angle (mercury has a convex meniscus).

Answer:

$$\ln \frac{P_v}{P_{v_0}} = \frac{V_{m,l} 2\gamma}{RT r}$$

$$= \frac{2(\text{cm}^3/13.6\text{g})(200.59 \text{ g mol}^{-1})(\text{m}/10^2 \text{ cm})^3(47 \times 10^{-2}\text{N/m})}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(293 \text{ K})(10^{-7} \text{ m})} = 0.0569$$

$$\frac{P_v}{P_{v_0}} = 1.058$$

14. Use the data of problem number 13 to predict the capillary depression of mercury in a tube 1. mm diameter at $20.^\circ\text{C}$.

Answer:

$$h = \frac{2\gamma}{\rho g r}$$

$$\rho = \left(\frac{13.6 \text{ g}}{\text{cm}^3} \right) \left(\frac{\text{kg}}{10^3 \text{ g}} \right) \left(\frac{10^2 \text{ cm}}{\text{m}} \right)^3 = 13.6 \times 10^3 \text{ kg m}^{-3}$$

$$h = \frac{(2)(47 \times 10^{-2} \text{ kg s}^{-2})}{(13.6 \times 10^3 \text{ kg m}^{-3})(9.8 \text{ m s}^{-2})(0.5 \times 10^{-3} \text{ m})} = 0.0141 \text{ m} = 1.41 \text{ cm}$$

15. A sample of benzene of mass 100. grams is dispersed as droplets of radius $1.0 \mu\text{m}$. The surface tension of benzene is $2.8 \times 10^{-2} \text{ N m}^{-1}$ and its density is 0.88 gm cm^{-3} . What is the change in the Helmholtz free energy for the dispersal? What is the minimum work necessary to bring about the dispersal?

Answer:

$$dA = -SdT - PdV + \gamma d\sigma$$

$$\Delta A = \gamma \Delta \sigma \quad \text{constant } T \text{ and } V$$

Let N be the number of droplets. The volume of the droplets is

$$N \frac{4}{3} \pi r^3 = \frac{m}{\rho}$$

where m is the mass and ρ is the density of the fluid. Then

$$N = \frac{3m}{4\pi r^3 \rho}$$

The surface area of the droplets is

$$\sigma = N 4\pi r^2$$

$$= \frac{3m}{4\pi r^3 \rho} 4\pi r^2$$

$$= \frac{3m}{r\rho} = \Delta\sigma \quad \text{ignoring the surface area of the initial sample}$$

Then

$$w = \Delta A = \gamma \Delta\sigma$$

$$= \frac{3(2.8 \times 10^{-2} \text{ kg s}^{-2})(0.1 \text{ kg})}{(10^{-6} \text{ m})(0.88 \times 10^{-3} \text{ kg}/10^{-3} \text{ m}^3)} = 9.5 \text{ J}$$

16. By how much is the vapor pressure of benzene changed when it is dispersed in the form of small droplets of radius

(a) $10 \mu\text{m}$;

(b) $0.10 \mu\text{m}$;

both at $25.^\circ\text{C}$?

Answer:

$$P_{mist} = P_{bulk} \exp \left\{ \frac{2\gamma V_{m,l}}{rRT} \right\}$$

$$V_{m,l} = \frac{78.12 \text{ g}}{0.88 \text{ g cm}^{-3}} = 89 \text{ cm}^3 \text{ mol}^{-1}$$

$$\frac{2\gamma V_{m,l}}{RT} = \frac{(2)(2.8 \times 10^{-2} \text{ N m}^{-1})(89 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{(2.48 \times 10^3 \text{ J mol}^{-1})} = 2.01 \times 10^{-9} \text{ m}$$

For $r = 1. \times 10^{-5} \text{ m}$

$$\frac{P_{mist}}{P_{bulk}} = \exp \left\{ \frac{2.01 \times 10^{-9} \text{ m}}{1.0 \times 10^{-5} \text{ m}} \right\} = 1.0002$$

For $r = 1. \times 10^{-7} \text{ m}$

$$\frac{P_{mist}}{P_{bulk}} = \exp \left\{ \frac{2.01 \times 10^{-9} \text{ m}}{1.0 \times 10^{-7} \text{ m}} \right\} = 1.020$$

17. The vapor pressure of liquid methanol (CH_3OH) is 0.521 bar at 50.0°C , the standard boiling point of methanol is 64.3°C , the surface tension of methanol at $298.\text{K}$ is 0.02207 N m^{-1} , and the density of methanol at $298.\text{K}$ is 0.793 g cm^{-3} . Assuming the enthalpy of vaporization of methanol is temperature independent, calculate the vapor pressure of methanol at $298.\text{K}$ when the liquid is dispersed into droplets of radii 1.0×10^{-8} meters.

Answer:

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\begin{aligned}
\ln \frac{0.521}{1} &= \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{337.3 \text{ K}} - \frac{1}{323 \text{ K}} \right) \\
\frac{\Delta_{vap,m}H}{R} &= 4967 \text{ K} \\
\ln \frac{P_0}{1} &= 4967 \text{ K} \left(\frac{1}{337.3 \text{ K}} - \frac{1}{298 \text{ K}} \right) \\
P_0 &= 0.143 \text{ bar} \\
P &= P_0 \exp \left\{ \frac{2\gamma V_{m,\ell}}{rRT} \right\} \\
&= (0.143 \text{ bar}) \exp \left\{ \frac{(2)(0.02207 \text{ N m}^{-1}) \left(\frac{\text{cm}^3}{0.793 \text{ g}} \right) \left(\frac{32 \text{ g}}{\text{mol}} \right) \left(\frac{\text{m}}{10^2 \text{ cm}} \right)^3}{(1. \times 10^8 \text{ m})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(298. \text{K})} \right\} \\
&= 0.154 \text{ bar}
\end{aligned}$$

18. Given that for liquid water, the vapor pressure at 298.K is 0.0319 bar, the enthalpy of vaporization is 40670 J mol⁻¹, the surface tension is 0.0720 N m⁻² and the density is 1.00 g cm⁻³, calculate the temperature at which water droplets of radii 1.00 × 10⁻⁸ m have a vapor pressure of 0.500 bar. Assume that the enthalpy of vaporization, the density and the surface tension of water are all temperature independent.

Answer:

$$\begin{aligned}
\ln \frac{P_{flat}(T)}{P_{flat}(298)} &= \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{298 \text{ K}} - \frac{1}{T} \right) \\
P_{flat}(T) &= P_{flat}(298) \exp \left\{ \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{298. \text{ K}} - \frac{1}{T} \right) \right\} \\
P_{drop}(T) &= P_{flat}(T) \exp \left\{ \frac{2\gamma V_{m,\ell}}{rRT} \right\} \\
&= P_{flat}(298) \exp \left\{ \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{298. \text{ K}} - \frac{1}{T} \right) + \frac{2\gamma V_{m,\ell}}{rRT} \right\} \\
(0.500 \text{ bar}) &= (0.0319 \text{ bar}) \exp \left\{ \frac{40670 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1} \text{K}^{-1}} \left(\frac{1}{298. \text{ K}} - \frac{1}{T} \right) \right. \\
&\quad \left. + \frac{2(0.0720 \text{ N m}^2) \left(\frac{1.00 \text{ cm}^3}{\text{g}} \right) \left(\frac{\text{m}}{10^2 \text{ cm}} \right)^3 \left(\frac{18.00 \text{ g}}{\text{mol}} \right)}{(1.00 \times 10^{-8} \text{ m})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})T} \right\} \\
T &= 356. \text{ K}
\end{aligned}$$

19. At 298 K the surface tension and density of ethanol (C_2H_5OH) are respectively $\gamma = 0.02205$ J m⁻² and $\rho = 0.7852$ g cm⁻³. When 10.0 g of liquid ethanol are dispersed into small spherical droplets, the change in the Helmholtz free energy is measured to be $\Delta A = 84.26$ J and the vapor pressure of the dispersed droplets is found to be 7.309×10^{-2} bar. Calculate the vapor pressure of the bulk sample of liquid ethanol at 298K when the sample is *not* dispersed into droplets.

Answer:

$$\Delta A = N4\pi r^2\gamma \quad N = \frac{\Delta A}{4\pi r^2\gamma}$$

$$M\rho^{-1} = N\frac{4}{3}\pi r^3 = \frac{4}{3}\pi r^3 \frac{\Delta A}{4\pi r^2\gamma}$$

$$r = \frac{3M\gamma}{\rho\Delta A} = \frac{3(10.0 \text{ g}) \left(\frac{\text{cm}^3}{0.7852 \text{ g}}\right) \left(\frac{\text{m}}{10^2 \text{ cm}}\right)^3 (0.02205 \text{ J m}^{-2})}{84.26 \text{ J}} = 1.00 \times 10^{-8} \text{ m}$$

$$P = P_{flat} \exp \left[\frac{2\gamma V_{m,\ell}}{rRT} \right]$$

$$7.309 \times 10^{-2} \text{ bar} = P_{flat} \exp \left[\frac{2(0.02005 \text{ J m}^{-2}) \left(\frac{\text{cm}^3}{0.7852 \text{ g}}\right) \left(\frac{46.0 \text{ g}}{\text{mol}}\right) \left(\frac{\text{m}}{10^2 \text{ cm}}\right)^3}{(1.00 \times 10^{-8} \text{ m})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})} \right]$$

$$P_{flat} = 6.585 \times 10^{-2} \text{ bar}$$

20. The normal boiling point of liquid ethanol (C_2H_5OH) is 78.4°C and the vapor pressure of liquid ethanol is 0.132 atm at 34.9°C. When liquid ethanol is dispersed into small spherical droplets all having the same radius at 25.0°C, the vapor pressure of the mist is 8.52×10^{-2} atm. Given that at 25.0°C the surface tension of liquid ethanol is 0.0224 N m⁻¹ and the density of liquid ethanol is 0.785 g cm⁻³, calculate the radii of the spherical droplets.

Answer:

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{1}{0.132} = \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{307.9 \text{ K}} - \frac{1}{351.4 \text{ K}} \right) \quad \frac{\Delta_{vap,m}H}{R} = 5037 \text{ K}$$

$$\ln \frac{P_{flat}}{0.132 \text{ atm}} = 5037 \text{ K} \left(\frac{1}{307.9 \text{ K}} - \frac{1}{298 \text{ K}} \right) \quad P_{flat} = 7.66 \times 10^{-2} \text{ atm}$$

$$P_{drop} = P_{flat} \exp \left(\frac{2\gamma V_{m,\ell}}{rRT} \right)$$

$$8.52 \times 10^{-2} = 7.66 \times 10^{-2} \exp \left(\frac{2(0.0224 \text{ N m}^{-1}) \left(\frac{\text{cm}^3}{0.785 \text{ g}}\right) \left(\frac{\text{m}}{10^2 \text{ cm}}\right)^3 \left(\frac{46.0 \text{ g}}{\text{mol}}\right)}{r(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})} \right)$$

$$r = 9.96 \times 10^{-9} \text{ m}$$

21. 1.00 moles of liquid water at 25.0°C are dispersed into spherical droplets, and it is found the vapor pressure of the droplets is exactly 4 times the vapor pressure of water above a flat surface. Given the density of water is 1.00 g cm⁻³ and the surface tension of water is 0.072 N m⁻¹, calculate the radii of the water droplets and the change in the Helmholtz free energy associated with the dispersal.

Answer:

$$P = P_0 \exp \left\{ \frac{2\gamma V_{m,\ell}}{rRT} \right\}$$

$$\ln \frac{P}{P_0} = \frac{2\gamma V_{m,\ell}}{rRT} \quad r = \frac{2\gamma V_{m,\ell}}{RT \ln(P/P_0)}$$

$$= \frac{(2)(0.072 \text{ N m}^{-1}) \left(\frac{\text{cm}^3}{\text{g}} \right) \left(\frac{18 \text{ g}}{\text{mol}} \right) \left(\frac{\text{m}}{10^2 \text{ cm}} \right)^3}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) \ln 4} = 7.5 \times 10^{-10} \text{ m}$$

$$\Delta A = N\gamma\Delta\sigma = N\gamma 4\pi r^2$$

$$N \frac{4}{3} \pi r^3 = \frac{m}{\rho}$$

$$N = \frac{3m}{4\pi r^3 \rho} = \frac{(3)(18 \text{ g})}{4\pi (7.5 \times 10^{-10} \text{ m})^3 \left(\frac{1 \text{ g}}{\text{cm}^3} \right) \left(\frac{10^2 \text{ cm}}{\text{m}} \right)^3} = 1.02 \times 10^{22}$$

$$\Delta A = (1.02 \times 10^{22})(0.072 \text{ N m}^{-1})(4\pi)(7.5 \times 10^{-10} \text{ m})^2 = 5191 \text{ J}$$