Chemistry 431
Exam Number 4
Fall 2023
Solutions

R =8.3144 J mol^{-1} K^{-1}

R=.08314 L bar mol^{-1} K^{-1}

k=1.381 $\times 10^{-23}$ J molecule^{-1}K^{-1}

h=6.626 $\times 10^{-34}$ Js

$N_A = 6.022 \times 10^{23}$ molecules mol^{-1}

1 kg = 1000. g

1 L = 10^3 cm^3

10^2 cm = 1 m

$T = t + 273.15$

0.001 m^3 L^{-1}

1 atmosphere = 1.01 bar

g=9.8 m s^{-2}

Name:

1. A certain gas obeys the equation of state

$$P = \frac{RT}{(V_m - b)} - \frac{a}{(V_m)^n}$$

where a and b are a numerical constants, V_m is the molar volume and n is an integer that is greater than one. Derive an expression for the critical volume of the gas in terms of b and n. (33 Points)

Answer:

$$\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{(V_m - b)^2} + \frac{na}{(V_m)^{n+1}} = 0$$

at

$$T_c = \frac{na}{(V_c)^{n+1}} \frac{(V_c - b)^2}{R}$$

$$\left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = \frac{2RT}{(V_m - b)^3} - \frac{n(n+1)a}{(V_m)^{n+2}} = 0$$

at

$$\frac{2RT_c}{(V_c - b)^3} = \frac{n(n+1)a}{(V_c)^{n+2}}$$

$$\frac{2R}{(V_c - b)^3} \frac{na}{(V_c)^{n+1}} \frac{(V_c - b)^2}{R} = \frac{n(n+1)a}{(V_c)^{n+2}}$$

$$(n^2 + n - 2n)V_c = (n^2 + n)b \qquad V_c = \frac{n+1}{n-1}b$$

Name:

2. The density of liquid mercury is 13.6 g cm^{-3}, the standard boiling point of liquid mercury is 630. K and the vapor pressure of liquid mercury at 523 K is 0.100 bar. When liquid mercury at 600. K is dispersed into droplets of radii $r = 1.00 \times 10^{-8}$ m, the vapor pressure of the droplets is found to be 0.752 bar. Calculate the surface tension of liquid mercury. Assume the surface tension, density and enthalpy of vaporization of mercury are temperature independent. (33 Points)

Answer:

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

$$\ln \frac{1.00}{0.100} = \frac{\Delta_{vap,m}H}{R}\left(\frac{1}{523 \text{ K}} - \frac{1}{630 \text{ K}}\right) \qquad \frac{\Delta_{vap,m}H}{R} = 7090 \text{ K}$$

$$\ln \frac{P_{600}}{0.100 \text{ bar}} = 7090 \text{ K}\left(\frac{1}{523 \text{ K}} - \frac{1}{600 \text{ K}}\right) \qquad P_{600} = 0.570 \text{ bar}$$

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

$$0.752 = 0.570 \exp\left[\frac{2\gamma\left(\frac{\text{cm}^2}{13.6 \text{ g}}\right)\left(\frac{200.6 \text{ g}}{\text{mol}}\right)\left(\frac{\text{m}}{10^2 \text{ cm}}\right)^3}{(1.00 \times 10^{-8} \text{ m})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(600 \text{ K})}\right]$$

$$\gamma = 0.468 \text{J m}^{-2}$$

Name:

3. The enthalpy of fusion of mercury us 2.29 kJ mol^{-1}, the enthalpy of fusion of silver is 11.28 kJ mol^{-1}, the normal melting point of mercury is 234 K and the normal melting point of silver is 1235 K. Assuming silver forms an ideal solution with mercury, calculate the molal solubility of silver in liquid mercury at 298 K. (34 Points)

Answer:

$$\chi_{Ag} = \exp\left[-\frac{\Delta_{fus,m}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right]$$

$$= \exp\left[-\frac{11280 \text{ J mol}^{-1}}{8.3144 \text{ J mol}^{-1}\text{K}}\left(\frac{1}{298 \text{ K}} - \frac{1}{1235 \text{ K}}\right)\right] = 0.0316$$

$$= \frac{m}{m + \dfrac{1000. \text{ g}}{200.6 \text{ g mol}^{-1}}}$$

$$m = 0.163 \text{ molal}$$

Name:

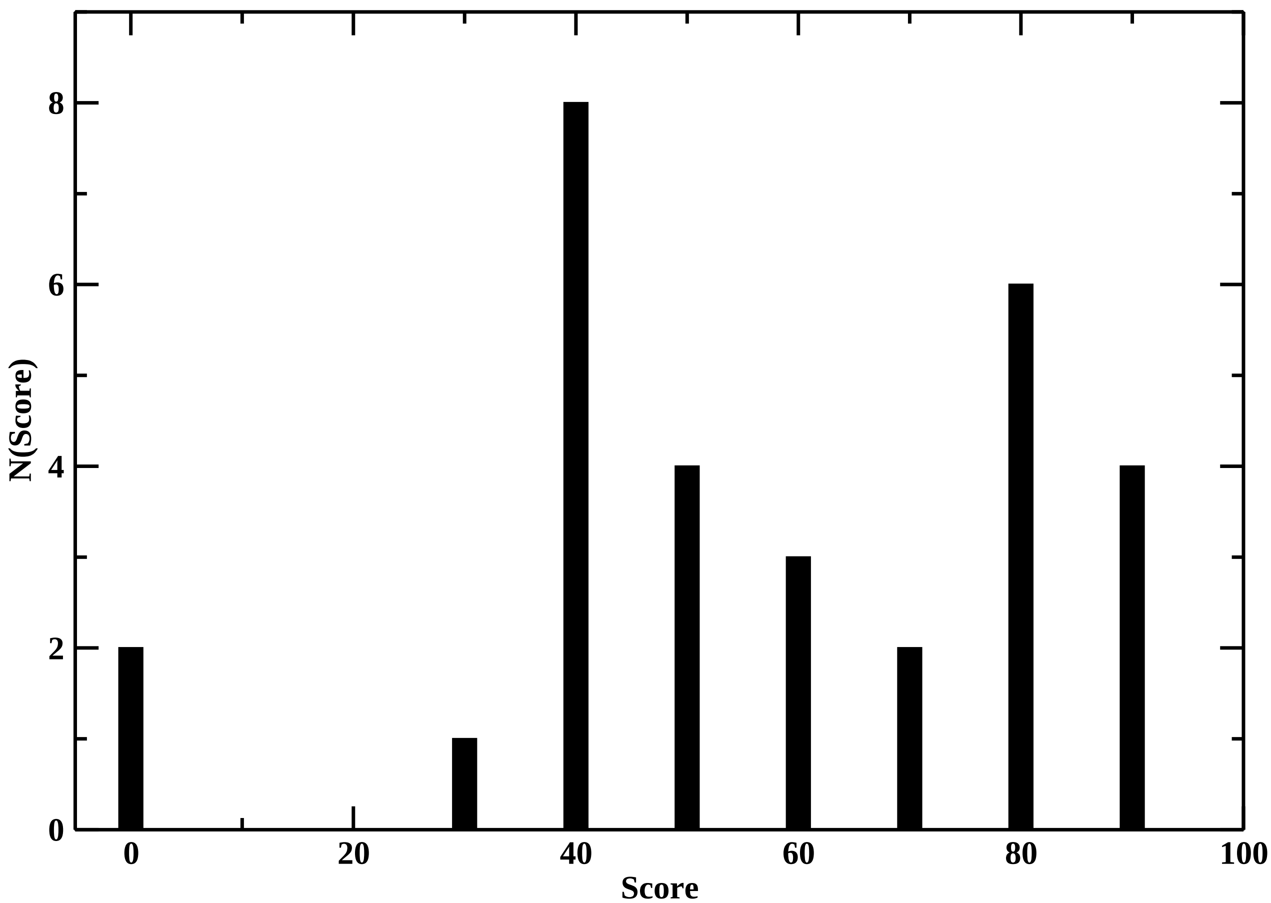

Figure 1: **High = 100, Median = 62, Mean = 62**