Chemistry 431
Exam Number 3
Fall 2023
50 Minutes
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}

Name:

1. Show that for any substance

$$\left(\frac{\partial U}{\partial S}\right)_P = T - \frac{PT\left(\frac{\partial V}{\partial T}\right)_P}{C_P}$$

where C_P is the constant pressure heat capacity of the substance. (33 Points)
Answer:

$$dU = TdS - PdV$$

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

$$dH = TdS + VdP \qquad \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

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

$$\left(\frac{\partial T}{\partial P}\right)_S\left(\frac{\partial P}{\partial S}\right)_T\left(\frac{\partial S}{\partial T}\right)_P = -1$$

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

$$dG = -SdT + VdP \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$dS = \frac{1}{T}dH - \frac{V}{T}dP \qquad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P}$$

$$\left(\frac{\partial U}{\partial S}\right)_P = T - \frac{PT\left(\frac{\partial V}{\partial T}\right)_P}{C_P}$$

Name:

2. As a function of temperature and pressure, ice takes on many different crystal structures named I_h, I_2, I_3, and so on. Ice I_h, called *hexagonal ice*, is the most stable crystal structure of the system near 273 K and a pressure of 1 bar. At a pressure of 2.13 $\times 10^3$ bar and a temperature of 238 K, crystal structures I_h and I_2 are in equilibrium with each other. Given $\Delta_{r,m}H^{\ominus} = -752.4\text{J mol}^{-1}$ for the process

$$\mathrm{I}_h \longrightarrow \mathrm{I}_2 \tag{1}$$

is independent of temperature and pressure, and given the density of I_h ice and I_2 ice are respectively $\rho_h = 921.\text{g L}^{-1}$ and $\rho_2 = 1170 \text{ g L}^{-1}$, calculate $\Delta_{r,m}G^{\ominus}$ for process (1) at 273 K. (33 Points)

Answer:

$$\Delta_{r,m}G(T_2, P) - \Delta_{r,m}G^{\ominus}(T_2) = \Delta_{r,m}V(P - P^{\ominus})$$

$$\frac{\Delta_{r,m}G^{\ominus}(T_2)}{T_2} - \frac{\Delta_{r,m}G^{\ominus}(T_1)}{T_1} = \Delta_{r,m}H^{\ominus}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Combining

$$\frac{\Delta_{r,m}G(T_2, P)}{T_2} - \frac{\Delta_{r,m}G^{\ominus}}{T_1} - \frac{\Delta_{r,m}V(P - P^{\ominus})}{T_1} = \Delta_{r,m}H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{\Delta_{r,m}G(T_2, P)}{T_2} = 0$$

at equilibrium. Then

$$\Delta_{r,m}G^{\ominus}(273) = -\Delta_{r,m}V(P - P^{\ominus}) - \Delta_{r,m}H\left(\frac{T_1}{T_2} - 1\right)$$

$$= -\left(\frac{\text{L}}{1170 \text{ g}} - \frac{\text{L}}{921 \text{ g}}\right)\left(\frac{18.0 \text{ g}}{\text{mol}}\right)(2130 \text{ bar} - 1\text{bar})\left(\frac{100 \text{ J}}{\text{L bar}}\right) + (752.4 \text{ J mol}^{-1})\left(\frac{273}{238} - 1\right) = 996.\text{ J mol}^{-1}$$

Name:

3. The equilibrium degree of dissociation of gas-phase bromine pentafluoride according to the reaction

$$BrF_{5(g)} \rightleftharpoons BrF_{3(g)} + F_{2(g)}$$

at a total pressure of P_{tot} =3.00 bar is $\alpha_{1000} = 0.121$ at 1000. K and $\alpha_{1100} = 0.278$ at 1100. K. Assuming $\Delta_{r,m}H^{\ominus}$ to be temperature independent, calculate the standard entropy change for the reaction at 1500. K. (34 Points)

Answer:

Let n_0= the initial number of moles of $BrF_{5(g)}$

	n_{BrF_5}	n_{BrF_3}	n_{F_2}
initial	n_0	0	0
change	$-\alpha n_0$	αn_0	αn_0
equilibrium	$n_0(1-\alpha)$	αn_0	αn_0

$$n_{total} = 2\alpha n_0 + (1-\alpha)n_0 = (1+\alpha)n_0$$

$$K_P = \frac{\frac{P_{BrF_3}}{P^{\ominus}}\frac{P_{F_2}}{P^{\ominus}}}{\frac{P_{BrF_5}}{P^{\ominus}}} = \frac{\left(\frac{\alpha}{1+\alpha}\frac{P}{P^{\ominus}}\right)^2}{\frac{1-\alpha}{1+\alpha}\frac{P}{P^{\ominus}}} = \frac{\alpha^2}{1-\alpha^2}\frac{P}{P^{\ominus}}$$

$$K_P(1000) = 4.46 \times 10^{-2} \qquad K_P(1100) = 2.51 \times 10^{-1}$$

$$\ln\frac{K_P(T_2)}{K_P(T_1)} = \frac{\Delta_{r,m}H^{\ominus}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{0.251}{0.0446} = \frac{\Delta_{r,m}H^{\ominus}}{R}\left(\frac{1}{1000\text{ K}} - \frac{1}{1100\text{ K}}\right) \qquad \frac{\Delta_{r,m}H^{\ominus}}{R} = 19000\text{ K}$$

$$\ln\frac{K_P(1500)}{0.0446} = 19000\text{ K}\left(\frac{1}{1000\text{ K}} - \frac{1}{1500\text{ K}}\right) \qquad K_P(1500) = 25.3$$

$$\Delta_{r,m}H^{\ominus} = (19000\text{ K})(8.3144\text{ J mol}^{-1}\text{K}^{-1}) = 158000\text{ J mol}^{-1}$$

$$\Delta_{r,m}G^{\ominus} = -RT\ln K_P = -(8.3144\text{ J mol}^{-1}\text{K}^{-1})(1500\text{ K})\ln(25.3) = -40240\text{ J mol}^{-1}$$

$$\Delta_{r,m}S^{\ominus} = \frac{\Delta_{r,m}H^{\ominus} - \Delta_{r,m}G^{\ominus}}{T}$$

$$= \frac{158000\text{ J mol}^{-1} - (-40240\text{ J mol}^{-1})}{1500\text{ K}} = 132\text{ J mol}^{-1}\text{K}^{-1}$$

Name:

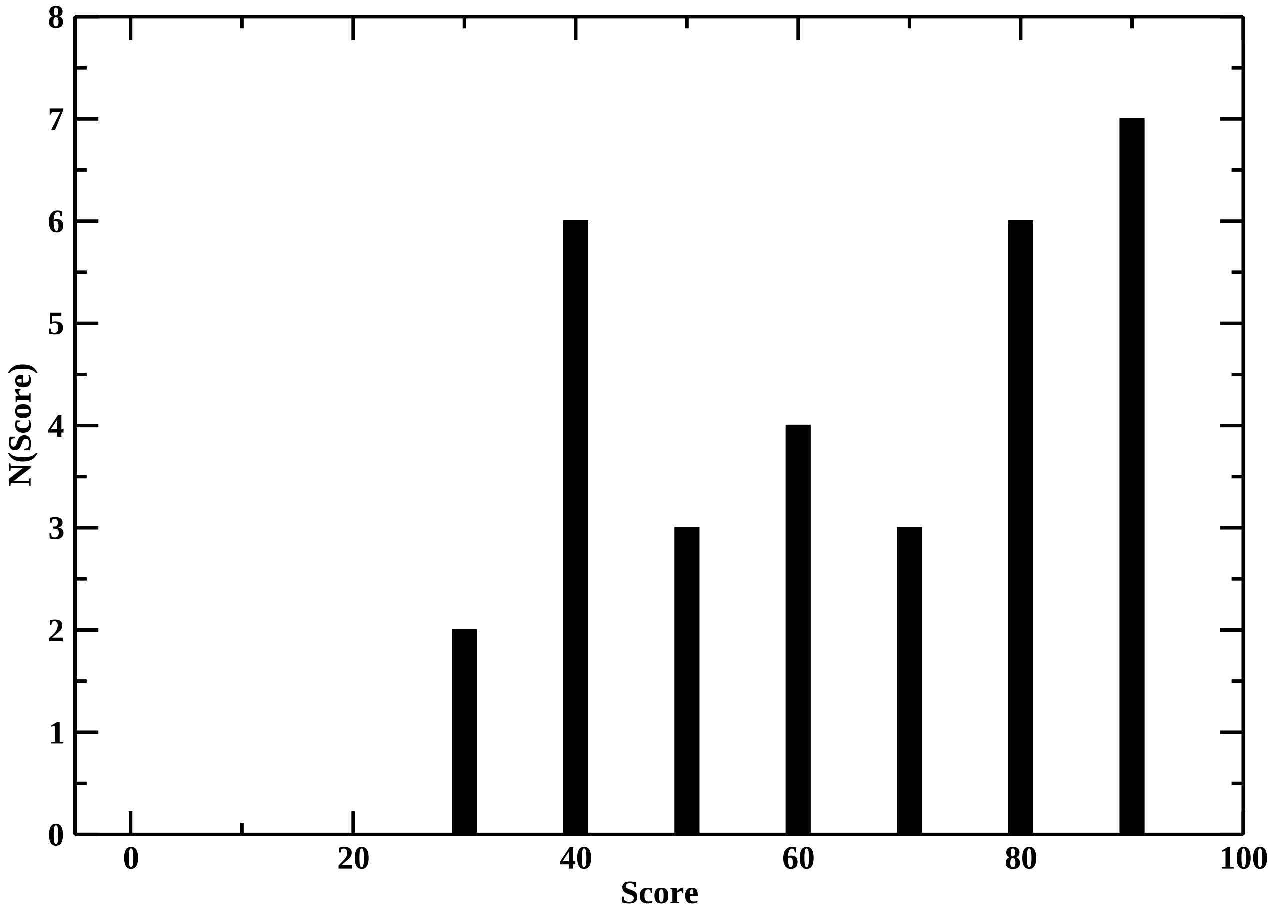

Figure 1: **High = 100, Median = 72, Mean = 70**