

Chemistry 431  
Exam Number 3  
Fall 2023  
50 Minutes  
Solutions

$$R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$$

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

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

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

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

$$1 \text{ kg} = 1000. \text{ g}$$

$$1 \text{ L} = 10^3 \text{ cm}^3$$

$$10^2 \text{ cm} = 1 \text{ m}$$

$$T = t + 273.15$$

$$0.001 \text{ m}^3 \text{ L}^{-1}$$

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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:**

$$dU = TdS - PdV$$

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

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

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

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

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

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

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

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

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

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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



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:** At 238 K

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

At  $P = 2.13 \times 10^3$  bar

$$0 - \Delta_{r,m}G^\ominus = \left( \frac{\text{L}}{1170 \text{ g}} - \frac{\text{L}}{921 \text{ g}} \right) \left( \frac{18.0 \text{ g}}{\text{mol}} \right) (2.13 \times 10^3 \text{ bar} - 1 \text{ bar}) \left( \frac{8.3144 \text{ J}}{0.083144 \text{ L bar}} \right)$$

$$\Delta_{r,m}G^\ominus(238) = 886. \text{ J mol}^{-1}$$

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

$$\frac{\Delta_{r,m}G^\ominus(273)}{273 \text{ K}} - \frac{886. \text{ J mol}^{-1}}{238 \text{ K}} = -752.4 \text{ J mol}^{-1} \left( \frac{1}{273 \text{ K}} - \frac{1}{238 \text{ K}} \right)$$

$$\Delta_{r,m}G^\ominus(273) = 1127 \text{ J mol}^{-1}$$

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



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  $\text{BrF}_{5(g)}$

	$n_{\text{BrF}_5}$	$n_{\text{BrF}_3}$	$n_{\text{F}_2}$
initial	$n_0$	0	0
change	$-\alpha n_0$	$\alpha n_0$	$\alpha n_0$
equilibrium	$n_0(1 - \alpha)$	$\alpha n_0$	$\alpha n_0$

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

$$K_P = \frac{\frac{P_{\text{BrF}_3}}{P^\ominus} \frac{P_{\text{F}_2}}{P^\ominus}}{\frac{P_{\text{BrF}_5}}{P^\ominus}} = \frac{\left(\frac{\alpha}{1 + \alpha} \frac{P}{P^\ominus}\right)^2}{\frac{1 - \alpha}{1 + \alpha} \frac{P}{P^\ominus}} = \frac{\alpha^2}{1 - \alpha^2} \frac{P}{P^\ominus}$$

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

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

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

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

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

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

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

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

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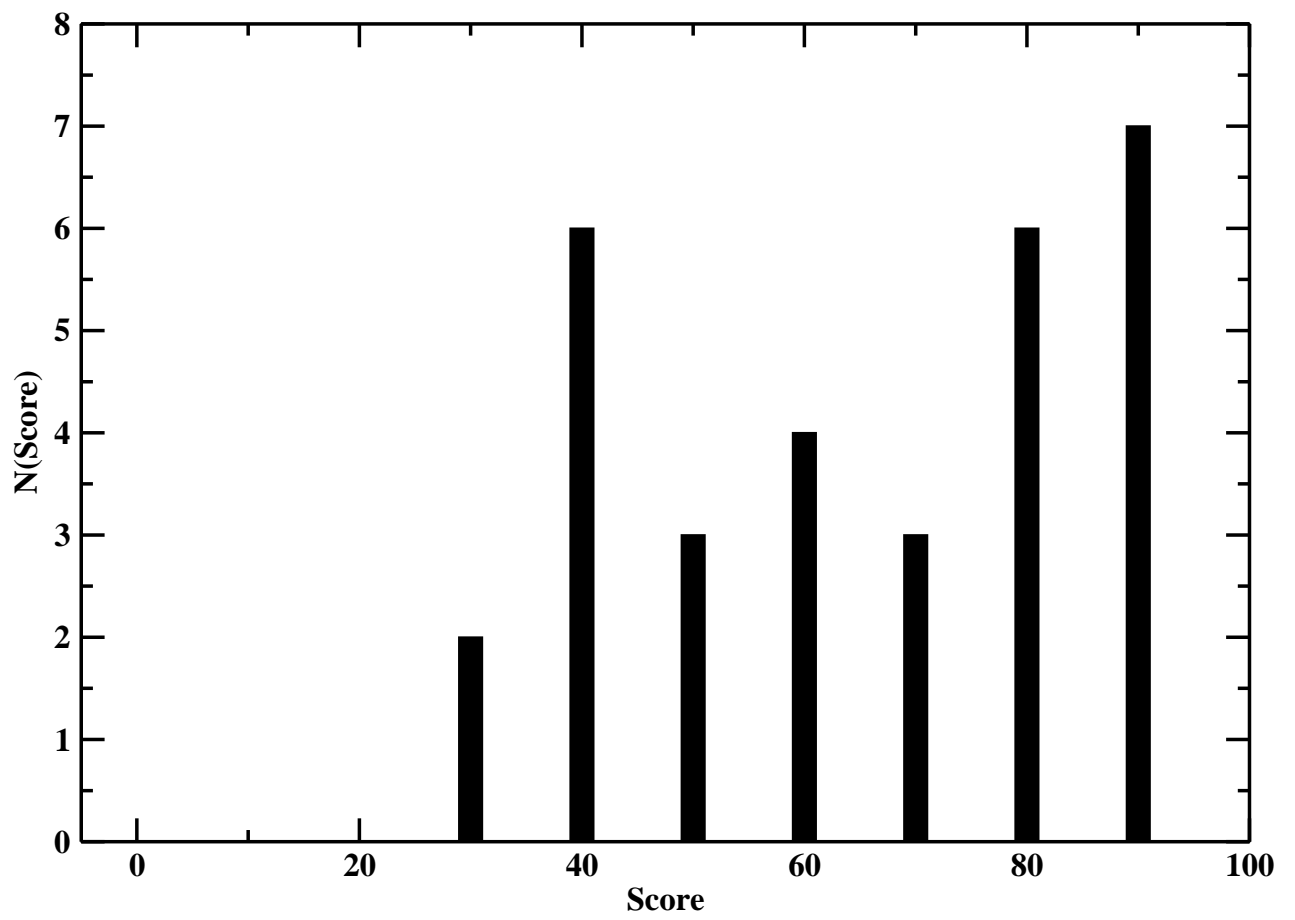


Figure 1: **High** = 100, **Median** = 72, **Mean** = 70