Homework 5 Solutions

1. The substance with the lower molar Gibbs energy is the more stable; therefore, rhombic sulfur is more stable. The application of pressure tends to favor the substance with the smaller molar volume (higher density); therefore, rhombic sulfur becomes even more stable relative to monoclinic sulfur as the pressure increases.

 $\Delta G \cong V \Delta p$

 ΔG is less positive for rhombic sulfur than for monoclinic sulfur, so relative to monoclinic sulfur, the Gibbs energy of rhombic sulfur becomes more negative.

For the transition S(rhombic) \rightarrow S(monoclinic), $\Delta G_{\rm m} = +0.33$ kJ mol⁻¹ $\Delta S_{\rm m} = (32.6 - 31.8) = 0.8$ J K⁻¹ mol⁻¹ $\Delta G_{\rm m} = \Delta H_{\rm m} - T\Delta S_{\rm m}$

We assume that $\Delta H_{\rm m}$ and $\Delta S_{\rm m}$ are roughly independent of temperature. We need the change in $\Delta G_{\rm m}$ to be -0.33 kJ mol⁻¹ as a result of the change in temperature:

 $-(T_{\rm f} - T_{\rm i})\Delta S_{\rm m} = -0.33 \text{ kJ mol}^{-1}$ $T_{\rm f} = (330 \text{ J mol}^{-1})/(0.8 \text{ J K}^{-1} \text{ mol}^{-1}) + 298.15 \text{ K} = 710.65 \text{ K}$

2. $dG_m = -S_m dT$ (at constant pressure)

For this relatively small temperature change we may assume that S_m is constant. Then we may write after integration

$$\int_{T_i}^{T_f} dG_m = \int_{T_i}^{T_f} (-S_m) dT$$

$$\Delta G_m = -S_m (T_f - T_i) = -S_m \Delta T = -173.3 \text{ J K}^{-1} \text{ mol}^{-1} \times 30 \text{ K} = -5.2 \text{ kJ mol}^{-1}$$

3. At these pressures, water vapor may be considered a perfect gas; therefore

and $p_i V_i = p_f V_f$ $p_f p_i = V_i / V_f$ $\Delta G_m = RT \ln(p_f / p_i) = RT \ln(V_i / V_f) = 8.315 \text{ J K}^{-1} \text{ mol}^{-1} \times 473 \text{ K} \times \ln(300 \text{ mL}/100 \text{ mL})$ $= +4.3 \text{ kJ mol}^{-1}$

4. Gibbs-Helmholtz equation: $\begin{pmatrix} \frac{\partial}{\partial T} \frac{\Delta_r G}{T} \end{pmatrix}_p = -\frac{\Delta_r H}{T^2}$ $d\left(\frac{\Delta_r G}{T}\right) = -\frac{\Delta_r H}{T^2} dT \qquad \int_{T_1}^{T_2} d\left(\frac{\Delta_r G}{T}\right) = -\Delta_r H \int_{T_1}^{T_2} \frac{dT}{T^2}$ $\frac{\Delta_r G_2}{T_2} - \frac{\Delta_r G_1}{T_1} = \Delta_r H \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ $\Delta_r G_2 = \Delta_r H T_2 \left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \Delta_r G_1 \frac{T_2}{T_1}$ $\Delta_r H = \Delta_r H^{\emptyset}(298 \text{ K}) = 2\Delta_r H (\text{CO}_{2,g}) - 2\Delta_r H (\text{CO}_{,g}) = 2\times(-393.51) - 2\times(-110.53) =$ $-565.96 \text{ kJ mol}^{-1} = \Delta_{r}G^{\emptyset}(298 \text{ K}) = 2\Delta_{f}G(CO_{2},g) - 2\Delta_{f}G(CO,g) = 2\times(-394.36) - 2\times(-137.17) = -514.38 \text{ kJ mol}^{-1} = (-565.96 \text{ kJ mol}^{-1})\times(375 \text{ K})\times\{1/(375 \text{ K}) - 1/(298 \text{ K})\} + (-514.38 \text{ kJ mol}^{-1})\times(375 \text{ K} / 298 \text{ K}) = -501.05 \text{ kJ mol}^{-1}$ 5. Real gas: $G_{m}(\text{real}) = G_{m}^{\emptyset} + RT \ln(f/p^{\emptyset})$ $f = \phi p$ Perfect gas $G_{m}(\text{perfect}) = G_{m}^{\emptyset} + RT \ln(p/p^{\emptyset})$ $G_{m}(\text{real}) - G_{m}(\text{perfect}) = RT\{\ln(f/p^{\emptyset}) - \ln(p/p^{\emptyset})\} = RT \ln(f/p) = RT \ln \phi$ $G_{m}(\text{real}) - G_{m}(\text{perfect}) = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})\times(200 \text{ K})\times\ln(0.72) = -546.3 \text{ J mol}^{-1} \approx$

$$-0.55$$
 kJ mol⁻¹

6. Consider differential d*H*: H = U + pV dH = dU + pdV + Vdp dU = TdS - pdV the fundamental equation dH = TdS - pdV + pdV + Vdp = TdS + Vdp*U* is a state function, so dU is an exact differential. The

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differential: if
$$df = gdx + hdy$$
, then $\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$
Using this, we can conclude that $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
Consider differential dA :

$$A = U - TS$$

$$dA = dU - TdS - SdT = TdS - pdV - TdS - SdT = -pdV - SdT$$

Therefore,

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

7. A Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

For a perfect gas,
$$pV = nRT$$
 $p = nRT/V$ $\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$
 $\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V}$ $dS = nR\frac{dV}{V}$ $\int_{S_0}^{S} dS = nR\int_{V_0}^{V} \frac{dV}{V}$
 $S \propto R \ln V$

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8. (a) The gaseous sample expands. (b) The sample contracts but remains gaseous because 320 K is greater than the critical temperature. (c) The gas contracts and forms a liquid-like

substance without the appearance of a discernible surface. As the temperature lowers further to the solid phase boundary line, solid carbon dioxide forms in equilibrium with liquid. At 210 K the sample has become all solid. (d) The solid expands slightly as the pressure is reduced and sublimes when the pressure reaches about 5 atm. (e) The gas expands as it is heated at constant pressure.

9. $\ln(p^{2}/p) = (\Delta_{vap}H/R)(1/T - 1/T^{2})$ $p^{2} = 1 \text{ atm} = 101.3 \text{ kPa}, p = 50.0 \text{ kPa}, T = 365.7 \text{ K}, \text{ and } T^{2} = 388.4 \text{ K}$ $\ln(101.3/50.0) = (\Delta_{vap}H/8.31451 \text{ J K}^{-1} \text{ mol}^{-1})(1/(365.7 \text{ K}) - 1/(388.4 \text{ K}))$ $0.706 = 1.922 \times 10^{-5} \text{ J}^{-1} \text{ mol} \times \Delta_{vap}H \qquad \Delta_{vap}H = 36.7 \text{ kJ mol}^{-1}$

10.
$$p = p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V} \ln \frac{T}{T^*}$$
 $\ln \frac{T}{T^*} = \frac{\Delta_{fus}V}{\Delta_{fus}H} \left(p - p^*\right)$

$$\Delta_{\rm fus} V = M/\rho(1) - M/\rho(s) = (78.1074 \text{ g mol}^{-1})/(0.879 \text{ g cm}^{-3}) - (78.1074 \text{ g mol}^{-1})/(0.891 \text{ g cm}^{-3}) = 1.197 \text{ cm}^3 \text{ mol}^{-1} = 1.197 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \\ \ln(T/T^*) = (1000 \text{ atm} - 1 \text{ atm}) \times (1.197 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) / (10.59 \text{ kJ mol}^{-1}) \\ \ln(T/T^*) = (000 \times 1.01225 \times 10^5 \text{ Ps}) \times (1.107 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) / (10.59 \times 10^3 \text{ J mol}^{-1}) = 0.000 \text{ mol}^{-1}$$

 $\ln(T/T^*) = (999 \times 1.01325 \times 10^5 \text{ Pa}) \times (1.197 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) / (10.59 \times 10^3 \text{ J mol}^{-1}) = 0.011$ T/T* = 1.0115 T* = 278.65 K T = 281.86 K = 8.7°C