ChemE 2200 – Physical Chemistry II – Spring 2025 Solution to Homework Assignment 8

- 1. On homework 5, exercise 3 we calculated that compartment A is heated to 900 K.
- (A) For section A, use two successive reversible paths to get from the initial state to the final state: (1) isochoric heating, and then (2) isothermal expansion.

$$\Delta S_{\rm A} = n\overline{C}_{\rm V} \ln \frac{T_{\rm A,2}}{T_{\rm A,1}} + nR \ln \frac{V_{\rm A,2}}{V_{\rm A,1}}$$

= (2 mol)(20 J/(K · mol)) ln $\frac{900 \text{ K}}{300 \text{ K}}$ + (2 mol)(8.314 J/(K · mol)) ln $\frac{3.0 \text{ L}}{2.0 \text{ L}}$
= 50.7 J/K

For section B, the process is reversible isothermal compression.

$$\Delta S_{\rm B} = nR \ln \frac{V_{\rm A,2}}{V_{\rm A,1}} = (2 \text{ mol})(8.314 \text{ J/(K} \cdot \text{mol})) \ln \frac{1.0 \text{ L}}{2.0 \text{ L}} = -11.5 \text{ J/K}$$

(B) On homework 5 we calculated the reversible work for sections A and B: $w_A = -3.46 \times 10^3 \text{ J}$ and $w_B = +3.46 \times 10^3 \text{ J}$. Recall $w_{\text{max}} = w_{\text{rev}} = \Delta A$. This relation is valid only for constant temperature, so we can calculate $\Delta A_B = w_B = +3.46 \times 10^3 \text{ J}$. However, $\Delta A_A \neq w_A$ because the temperature in section A was not constant. We would guess that ΔA_A is negative because w_A is negative, but this is only a guess. ΔA_A is indeterminate.

Or we can use the definition of Helmholtz energy, A = U - TS, and take the difference at constant temperature.

$$\Delta A = \Delta U - T\Delta S$$

Because section B is an ideal gas at constant temperature, we have $\Delta U_{\rm B} = 0$. From part (A), $\Delta S_{\rm B} = -11.5$ J/K.

 $\Delta A_{\rm B} \; = \; \Delta U_{\rm B} \; - \; T_{\rm B} \Delta S_{\rm B} \; = \; 0 \; - \; (300 \; {\rm K}) (-11.5 \; {\rm J/K}) \; = \; +3.46 \times 10^3 \; {\rm J}.$

We obtain the same result as above. The temperature is not constant in section A, so the change in Helmholtz energy is

$$\Delta A_{\rm A} = \Delta U_{\rm A} - \Delta (TS)_{\rm A} = \Delta U_{\rm A} - ((TS)_{\rm A, final} - (TS)_{\rm A, initial})$$

We calculated ΔU_A for homework 5 ($\Delta U_A = +2.4 \times 10^4$ J). Although we calculated the *change* in entropy, ΔS_A , in part (A), we do not know the *absolute values* of $S_{A,initial}$ and $S_{A,final}$. Again we find that ΔA_A is indeterminate.

Again, we can estimate whether ΔA_A is positive or negative. The absolute entropy of an ideal gas depends on the molecular mass and the number of atoms in the molecule. The absolute entropy ranges from about 200 J/K to 1500 J/K. (See "*Prediction of absolute entropy of ideal gas at 298K of pure chemicals*", A. Fazeli, et al., Energy Conversion and Management, **52**, pp 630-4, 2011.) Thus $\Delta(TS)_A$ ranges from about -1×10^5 J to about -9×10^5 J. Again, we estimate ΔA_A is negative.

(C) Because section B was constant temperature, we have $\Delta G = \Delta H - T \Delta S$. $\Delta H_{\rm B} = 0$ because the gas is ideal and $\Delta T = 0$.

$$\Delta G_{\rm B} = \Delta H_{\rm B} - T \Delta S_{\rm B} = 0 - (300 \text{ K})(-11.5 \text{ J/K}) = +3.46 \times 10^3 \text{ J}$$

 ΔG_A is indeterminate because the temperature is not constant.

(D) ΔS_{system} is the sum of the entropy changes for the two sections.

$$\Delta S_{\text{system}} = \Delta S_{\text{A}} + \Delta S_{\text{B}} = +50.7 \text{ J/K} - 11.5 \text{ J/K} = +39.2 \text{ J/K}$$

Because the process was reversible, the process was neither spontaneous in the forward direction nor the reverse direction. That is, the total entropy change for a reversible process, $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$, is zero.

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{surroundings}} = -\Delta S_{\text{system}} = -39.2 \text{ J/K}$$

Adapted from P. Atkins, Physical Chemistry, 6th edition, 1997.

2. This is similar to the example presented in lecture T8. But in this case the surroundings deliver work to the system. So the maximum work done by the system equals the minimum work done by the surroundings. We need to calculate ΔA . We begin with the relation

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Separate and integrate.

dA = -PdV at constant T

$$\int_{A_1}^{A_2} dA = -\int_{V_1}^{V_2} P dV$$

Substitute the ideal gas law.

$$\Delta A = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

Calculate ΔA for the system. Note that $n_A = n_B = 2$ mol and $T_A = T_B = 353$ K.

$$\Delta A = \Delta A_A + \Delta A_B = -n_A R T_A \ln \frac{V_{A,2}}{V_{A,1}} - n_B R T_B \ln \frac{V_{B,2}}{V_{B,1}}$$
$$= -n_A R T_A \left[\ln \frac{V_{A,2}}{V_{A,1}} + \ln \frac{V_{B,2}}{V_{B,1}} \right]$$
$$= -n_A R T_A \ln \frac{V_{A,2} V_{B,2}}{V_{A,1} V_{B,1}}$$
$$= -(2 \text{ mol})(8.314 \text{ J}/(\text{K} \cdot \text{mol}))(353 \text{ K}) \ln \frac{(5 \text{ L})(15 \text{ L})}{(10 \text{ L})(10 \text{ L})} = 1690 \text{ J}$$

The minimum work done by the surroundings on the system is 1690 J. Or, w = +1690 J.

(B) The initial state of the system is

$1 \mod N_2 + 1 \mod H_2$	$1 \mod N_2 + 1 \mod H_2$
10 L, 80°C	10 L, 80°C

As the piston moves infinitesimally to the right, the pressure in the right compartment increases infinitesimally and the pressure in the left compartment decreases infinitesimally. Because the piston is permeable to H_2 , H_2 diffuses from the right compartment to the left compartment such that the chemical potential of H_2 in each compartment is equal. Because H_2 is an ideal gas, equal chemical potentials requires equal partial pressures, and equal partial pressures requires equal partial molar volumes. The ratio of volumes is 15:5 = 3:1, so the H_2 molar ratio is also 3:1. There will be 1.5 moles of H_2 in the 15 L compartment and 0.5 moles of H_2 in the 5 L compartment. Thus the partial molar volume of H_2 will be 15 L / 1.5 mol = 5 L / 0.5 mol = 10 L/mol in both compartments.

The barrier is impermeable to N_2 so the final amounts of N_2 in each compartment is the same as the initial amounts of N_2 in each compartment; 1 mol in each. In the 15 L compartment, the N_2 partial molar volume is 15 L/mol. In the 5 L compartment, the N_2 partial molar volume is 5 L/mol.

$1 \mod N + 15 \mod H$	1 mol N ₂
$1 \text{ mor } N_2 + 1.5 \text{ mor } N_2$	0.5 mol H ₂
15 L, 80 C	5 L, 80°C

(C) Because the partial pressure of H_2 is the same in both compartments throughout the process, H_2 does not oppose the piston movement. The *PV* work due to N_2 is calculated in the same manner as part (A), except now $n_A = n_B = 1$ mol.

$$\Delta A = \Delta A_A + \Delta A_B = -n_A R T_A \ln \frac{V_{A,2}}{V_{A,1}} - n_B R T_B \ln \frac{V_{B,2}}{V_{B,1}}$$
$$= -n_A R T_A \left[\ln \frac{V_{A,2}}{V_{A,1}} + \ln \frac{V_{B,2}}{V_{B,1}} \right]$$
$$= -n_A R T_A \ln \frac{V_{A,2} V_{B,2}}{V_{A,1} V_{B,1}}$$
$$= -(1 \text{ mol})(8.314 \text{ J}/(\text{K} \cdot \text{mol}))(353 \text{ K}) \ln \frac{(15 \text{ L})(5 \text{ L})}{(10 \text{ L})(10 \text{ L})} = 844 \text{ J}$$

Thus w = +844 J. The work is half the work calculated for an impermeable piston.

An alternate way to calculate the work is the relation $w_{max} = \Delta A = -T\Delta S$ for a reversible, isothermal process. Note that ΔA yields the maximum work done *by* a system, or the minimum work that must be done *on* a system. To calculate the entropy change, we need only consider the volume change of H₂ and N₂ in this isothermal, reversible process. The volume of H₂ does not change; H₂ is free to roam the entire 20L throughout the process. For the N₂ in compartment A, the volume increases from 10 L to 15 L. For the N₂ in compartment B, the volume decreases from 10 L to 5 L. First, we need an equation to calculate the entropy change with volume at a constant temperature. Start with a Maxwell relation.

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

Separate and integrate.

$$dS = \left(\frac{\partial P}{\partial T}\right)_{V} dV \qquad \text{at constant } T$$
$$\int_{S_{1}}^{S_{2}} dS = \int_{V_{1}}^{V_{2}} \left(\frac{\partial P}{\partial T}\right)_{V} dV$$

Substitute the ideal gas law.

$$\Delta S = \int_{V_1}^{V_2} \frac{\partial}{\partial T} \left(\frac{nRT}{V} \right) dV = \int_{V_1}^{V_2} \frac{nR}{V} dV = nR \ln \frac{V_2}{V_1}$$

We now use the above equation to calculate ΔS . Again note that $n_A = n_B = 1$ mol for N₂.

$$\Delta S = \Delta S_{N_2,A} + \Delta S_{N_2,B} = n_A R \ln \frac{V_{A,2}}{V_{A,1}} + n_B R \ln \frac{V_{B,2}}{V_{B,1}}$$
$$= n_A R \left[\ln \frac{V_{A,2}}{V_{A,1}} + \ln \frac{V_{B,2}}{V_{B,1}} \right]$$
$$= n_A R \ln \frac{V_{A,2} V_{B,2}}{V_{A,1} V_{B,1}}$$
$$= (1 \text{ mol})(8.314 \text{ J}/(\text{K} \cdot \text{mol})) \ln \frac{(15 \text{ L})(5 \text{ L})}{(10 \text{ L})(10 \text{ L})} = -2.39 \text{ J/K}$$

For an isothermal reversible process,

$$w_{\rm rev} = \Delta A = -T\Delta S = -(353 \text{ K})(-2.39 \text{ J/K}) = +844 \text{ J}$$

This is expected that $-T\Delta S = w_{rev}$ for this system because $\Delta U = 0$ for an ideal gas in an isothermal process, thus

$$\Delta U = 0 = q_{rev} + w_{rev}$$
$$w_{rev} = -q_{rev} = -T\Delta S$$

Adapted from H. B. Callen, Thermodynamics, Wiley, 1960.

3. Start with the hint.

$$dS = \left(\frac{\partial S}{\partial P}\right)_{\rm V} dP + \left(\frac{\partial S}{\partial V}\right)_{\rm P} dV \tag{1}$$

Apply the chain rule to $(\partial S/\partial P)_V$.

$$\left(\frac{\partial S}{\partial P}\right)_{V} = \left(\frac{\partial S}{\partial T}\right)_{V} \left(\frac{\partial T}{\partial P}\right)_{V}$$

From the Useful Equations, $(\partial S/\partial T)_{\rm V} = C_{\rm V}/T$,

$$\left(\frac{\partial S}{\partial P}\right)_{V} = \frac{C_{V}}{T} \left(\frac{\partial T}{\partial P}\right)_{V}$$
(2)

So we have the first term in the target equation.

For the second term, apply the chain rule to $(\partial S/\partial V)_{\rm P}$ and a Useful equation, $(\partial S/\partial T)_{\rm P} = C_{\rm P}/T$,

$$\begin{pmatrix} \frac{\partial S}{\partial V} \end{pmatrix}_{\rm P} = \begin{pmatrix} \frac{\partial S}{\partial T} \end{pmatrix}_{\rm P} \begin{pmatrix} \frac{\partial T}{\partial V} \end{pmatrix}_{\rm P}$$

$$\begin{pmatrix} \frac{\partial S}{\partial V} \end{pmatrix}_{\rm P} = \frac{C_{\rm P}}{T} \begin{pmatrix} \frac{\partial T}{\partial V} \end{pmatrix}_{\rm P}$$
(3)

Substitute equations (2) and (3) into equation (1).

$$dS = \frac{C_{\rm V}}{T} \left(\frac{\partial T}{\partial P}\right)_{\rm V} dP + \frac{C_{\rm P}}{T} \left(\frac{\partial T}{\partial V}\right)_{\rm P} dV$$

4. Take the hint and start with the cyclic rule,

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

to write an expression for $(\partial T/\partial P)_H$.

$$\left(\frac{\partial T}{\partial P}\right)_{H} = -\left(\frac{\partial T}{\partial H}\right)_{P} \left(\frac{\partial H}{\partial P}\right)_{T}$$
(1)

Use the reciprocal rule for $(\partial T/\partial H)_p$.

$$\left(\frac{\partial T}{\partial H}\right)_{P} = \frac{1}{\left(\frac{\partial H}{\partial T}\right)_{P}} = \frac{1}{C_{P}}$$
(2)

For $(\partial H/\partial P)_T$ start with a Practical Equation for dH,

$$dH = C_{\rm P} dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

and assume constant T, which drops the first term on the right-hand side.

$$dH = \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \qquad \text{at constant } T$$
$$\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P \qquad (3)$$

Substitute equations (2) and (3) into equation (1):

$$\left(\frac{\partial T}{\partial P}\right)_{H} = -\left(\frac{\partial T}{\partial H}\right)_{P} \left(\frac{\partial H}{\partial P}\right)_{T} = -\frac{1}{C_{P}} \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P}\right]$$

Here is an alternative method to obtain an equation for $(\partial H/\partial P)_T$. Start with the Fundamental Equation for dH and take the partial derivative with respect to *P* at constant *T*.

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Use a Maxwell relation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ and one arrives at equation (3) above.

Now, substitute equations (2) and (3) into equation (1) to obtain the desired result.

$$\begin{pmatrix} \frac{\partial T}{\partial P} \end{pmatrix}_{H} = -\left(\frac{\partial T}{\partial H}\right)_{P} \left(\frac{\partial H}{\partial P}\right)_{T}$$
$$\begin{pmatrix} \frac{\partial T}{\partial P} \end{pmatrix}_{H} = -\frac{1}{C_{P}} \left[V - T \left(\frac{\partial V}{\partial T}\right)_{P} \right]$$

Here is an alternate method for the entire derivation. Start with a Practical Equation for dH and assume constant H.

$$dH = C_{\rm P}dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P}\right]dP$$
$$0 = C_{\rm P}dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P}\right]dP$$
$$\cdot C_{\rm P}dT = \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P}\right]dP$$

Differentiate both sides with respect to P.

$$-C_{\rm P} \left(\frac{\partial T}{\partial P} \right)_{H} = \left(\left[V - T \left(\frac{\partial V}{\partial T} \right)_{P} \right] \frac{\partial P}{\partial P} \right)_{H} -C_{\rm P} \left(\frac{\partial T}{\partial P} \right)_{H} = \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P} \right] \left(\frac{\partial T}{\partial P} \right)_{H} = -\frac{1}{C_{\rm P}} \left[V - T \left(\frac{\partial V}{\partial T} \right)_{P} \right]$$

5. We seek the temperature and pressure of the triple point. That is, we need to find the point at which any two borders on the phase diagram intersect: the solid-liquid border, the solid-vapor border, or the liquid-vapor border.



Use the Clapeyron equation with the data provided to determine the slope of the solid-liquid border.

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$$\frac{dP}{dT} = \frac{\Delta \overline{H}_{\text{transition}}}{T\Delta \overline{V}_{\text{transition}}}$$
$$= \frac{6.00 \text{ kJ/mol}}{(273 \text{ K})(0.0180 \text{ L/mol} - 0.01964 \text{ L/mol})} = -\frac{13.4 \text{ kJ}}{\text{K} \cdot \text{L}} \frac{1 \text{ L} \cdot \text{atm}}{0.1013 \text{ kJ}} = -132 \text{ atm/K}$$

The slope of the solid-liquid border is -132 atm/K. The border passes through the point T = 0 °C and P = 1 atm. The equation for the border is therefore

$$\frac{\Delta P}{\Delta T} = \frac{rise}{run}$$

$$\frac{1-P}{0-T} = -132 \text{ atm}/\text{K}$$

$$1-P = 132 \times T$$

$$P = -132 \times T + 1 \qquad (1)$$

Note that equation for the border can be expressed in Kelvin or degrees Celsius. Using Kelvin causes the small change in transition temperature to be lost in the (in)significant figures. It is more accurate to derive an equation for the border in units of degrees Celsius.

Use the Clausius-Clapeyron equation to determine the slope of the liquid-vapor border.

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$
$$\frac{dP}{dT} = \frac{P\Delta \overline{H}_{\text{vap}}}{RT^2} = \frac{(0.00861 \text{ atm})(45 \text{ kJ/mol})}{(0.08206 \text{ L} \cdot \text{ atm}/\text{ K} \cdot \text{mol})(278 \text{ K})^2} \frac{1 \text{ L} \cdot \text{ atm}}{0.1013 \text{ kJ}} = 6.03 \times 10^{-4} \text{ atm/K}$$

The slope of the liquid-vapor border is 6.03×10^{-4} atm/K. The border passes through the point $T = 5^{\circ}$ C and P = 0.00861 atm. Again we use degrees Celsius and not Kelvin. This is valid because we are calculating temperature *differences*, not *absolute* temperatures. The equation for the border is therefore

$$\frac{\Delta P}{\Delta T} = \frac{rise}{run}$$

$$\frac{0.00861 - P}{5 - T} = 6.03 \times 10^{-4} \text{ atm} / \text{K}$$

$$0.00861 - P = -6.03 \times 10^{-4} T + 0.00302$$

$$P = 6.03 \times 10^{-4} T + 0.00560 \qquad (2)$$

Find the intersection of the solid-liquid and liquid-vapor borders; find the intersection of equations (1) and (2).

$$-132 \times T + 1 = 6.03 \times 10^{-4} T + 0.00560$$

 $T = 0.00753^{\circ}C$

Calculate P.

$$P = 6.03 \times 10^{-4} (0.00753^{\circ}\text{C}) + 0.00560 = 0.0056 \text{ atm}$$

The triple point for water is at 0.0075°C and 0.0056 atm.

Adapted from B. G. Kyle, Chemical and Process Thermodynamics, 3rd edition, 1999.

- 6.(A) Find the intersection of the line labeled "(4/3)Al₂O₃" and the line labeled "C + O₂ = CO₂" This is the point at which $\Delta G_{rxn}^0 = 0$ for the reaction 2Al₂O₃(s) + 3C(s) \leftrightarrow 4Al(s) + 3CO₂(g). This is at approximately 2740°C.
- (B) Start with the hint and use the Gibbs-Helmholtz equation to derive an expression for $\Delta \overline{G}_{rxn}^0$ as a function of temperature.

$$\left(\frac{\partial(\Delta \overline{G}_{rxn}^{0}/T)}{\partial T}\right)_{P} = -\frac{\Delta \overline{H}_{rxn}^{0}}{T^{2}}$$

Separate and integrate (at constant P).

$$d(\Delta \overline{G}_{rxn}^{0}/T) = -\frac{\Delta \overline{H}_{rxn}^{0}}{T^{2}} dT \qquad \text{at constant } P$$

$$\int_{298}^{T} d(\Delta \overline{G}_{rxn}^{0}/T) = \int_{298}^{T} -\frac{\Delta \overline{H}_{rxn}^{0}}{T^{2}} dT$$

$$\frac{\Delta \overline{G}_{rxn}^{0}(T)}{T} - \frac{\Delta \overline{G}_{rxn}^{0}(298)}{298} = \Delta \overline{H}_{rxn}^{0} \left(\frac{1}{T} - \frac{1}{298}\right)$$

$$\frac{\Delta \overline{G}_{rxn}^{0}(T)}{T} = \frac{\Delta \overline{G}_{rxn}^{0}(298)}{298} + \Delta \overline{H}_{rxn}^{0} \left(\frac{1}{T} - \frac{1}{298}\right)$$

$$\frac{\Delta \overline{G}_{rxn}^{0}(T)}{T} = \frac{\Delta \overline{G}_{rxn}^{0}(298) - \Delta \overline{H}_{rxn}^{0}}{298} + \frac{\Delta \overline{H}_{rxn}^{0}}{T}$$

$$\Delta \overline{G}_{rxn}^{0}(T) = \left(\frac{\Delta \overline{G}_{rxn}^{0}(298) - \Delta \overline{H}_{rxn}^{0}}{298}\right)T + \Delta \overline{H}_{rxn}^{0} \qquad (1)$$

Calculate $\Delta \overline{H}_{rxn}^0$ from the enthalpy data in Table 19.2 (p. 795) of McQuarrie and Simon,

$$\Delta \overline{H}_{rxn}^{0} = \Delta \overline{H}_{f,H_{2}O}^{0} - \Delta \overline{H}_{f,H_{2}}^{0} - \frac{1}{2} \Delta \overline{H}_{f,O_{2}}^{0} = -241.8 - 0 - 0 = -241.8 \text{ kJ/mol}$$

Calculate $\Delta \overline{G}_{rxn}^0$ (298) from the enthalpy data in Table 26.1 (p. 1057) of McQuarrie and Simon,

$$\Delta \overline{G}_{rxn}^{0}(298) = \Delta \overline{G}_{f,H_{2}O}^{0} - \Delta \overline{G}_{f,H_{2}}^{0} - \frac{1}{2} \Delta \overline{G}_{f,O_{2}}^{0} = -228.582 - 0 - 0 = -228.582 \text{ kJ/mol}$$

Substitute into the expression for $\Delta \overline{G}_{rxn}^0(T)$.

$$\Delta \overline{G}_{rxn}^{0}(T) = \left(\frac{-228.582 - (-241.8)}{298}\right)T + -241.8 \text{ kJ/mol}$$
$$\Delta \overline{G}_{rxn}^{0}(T) = 0.04436 T + -241.8 \text{ kJ/mol}$$
(2)

Note that equation (1) is equivalent to

$$\Delta \overline{G}_{rxn}^{0}(T) = \left(\frac{\Delta \overline{G}_{rxn}^{0}(298) - \Delta \overline{H}_{rxn}^{0}}{298}\right) T + \Delta \overline{H}_{rxn}^{0}$$
(1)
$$\Delta \overline{G}_{rxn}^{0}(T) = -\Delta \overline{S}_{rxn}^{0}T + \Delta \overline{H}_{rxn}^{0}$$

From the entropy data in Table 21.2 (p. 864) of McQuarrie and Simon, I calculate $\Delta \overline{S}_{rxn}^0 = 188.8 - \frac{1}{2}(205.2) - 130.7 = 0.0445 \text{ kJ/(K·mol)}$, which is the same as the equation calculated with enthalpies and Gibbs energies, as it should be.

From equation (2) I calculate $\Delta \overline{G}_{rxn}^0$ (773)= -207.5 kJ/mol and $\Delta \overline{G}_{rxn}^0$ (2273) = -141.0 kJ/mol. These points are plotted on the Ellingham diagram and a straight line is drawn.

- (C) The line for the reaction $H_2(g) + \frac{1}{2}O_2(g) \leftrightarrow H_2O(g)$ intersects the line for the reaction (1/3)Al₂O₃(s) \leftrightarrow (2/3)Al(s) + $\frac{1}{2}O_2(g)$ at about 3700°C. The reaction $H_2(g) + \frac{1}{2}O_2(g) \leftrightarrow H_2O(g)$ is not effective because the number of gas molecules decreases, and entropy causes the Gibbs energy to decrease as *T* increases.
- 7. Begin by labeling the lines in the plots. At low temperature (or high pressure) X is a solid. The line at high temperature (or low pressure) corresponds to vapor. The line in the middle is liquid.
- (A) This is the intersection of the solid and liquid lines in the \overline{G} -*T* diagram: 180 K.
- (B) Find the point on the \overline{G} -*P* diagram at 10 atm, the pressure of the data in the \overline{G} -*T* diagram. This is $\overline{G} = 40$ kJ/mol, at the intersection of the vapor and liquid lines. Find the corresponding point on the \overline{G} -*T* diagram. This intersection (which is also $\overline{G} = 40$ kJ/mol) is at T = 380 K.

(C) Use the slope of the liquid line in the \overline{G} -P diagram.

$$\overline{V} = \left(\frac{\partial G}{\partial P}\right)_T = \frac{\text{rise}}{\text{run}} = \frac{41 - 40 \text{ kJ/mol}}{100 - 10 \text{ atm}} \frac{1 \text{ L} \cdot \text{atm}}{0.1013 \text{ kJ}} = 0.11 \text{ L/mol}$$

(D) Use the slopes of the liquid and vapor lines in the \overline{G} -*T* diagram to obtain the molar entropies of the liquid and vapor, respectively.

$$\overline{S}_{\text{liquid}} = -\left(\frac{\partial \overline{G}}{\partial T}\right)_{P} = -\frac{\text{rise}}{\text{run}} = -\frac{40 - 41 \text{ kJ/mol}}{380 - 180 \text{ K}} = 5.0 \text{ J/(K \cdot mol)}$$
$$\overline{S}_{\text{vapor}} = -\left(\frac{\partial \overline{G}}{\partial T}\right)_{P} = -\frac{\text{rise}}{\text{run}} = -\frac{32 - 40 \text{ kJ/mol}}{440 - 380 \text{ K}} = 133 \text{ J/(K \cdot mol)}$$
$$\Delta \overline{S}_{\text{vap}} = \overline{S}_{\text{vapor}} - \overline{S}_{\text{liquid}} = 133 - 5.0 \text{ J/(K \cdot mol)} = 128 \text{ J/(K \cdot mol)}$$

(E) At the liquid-vapor transition, $\Delta \overline{G}_{vap} = 0$

$$\Delta \overline{G}_{vap} = 0 = \Delta \overline{H}_{vap} - T \Delta \overline{S}_{vap}$$
$$\Delta \overline{H}_{vap} = T \Delta \overline{S}_{vap} = (380 \text{ K})(128 \text{ J}/(\text{K} \cdot \text{mol})) = 48.8 \text{ kJ}/\text{ mol}$$

8. From the fundamental equation for Gibbs energy, dG = -SdT + VdP, we have

$$\left(\frac{\partial \overline{G}}{\partial P}\right)_T = \overline{V}$$

So for $\Delta G_{\text{rxn}} = G_{\text{reactants}} - G_{\text{products}}$ and $\Delta V_{\text{rxn}} = V_{\text{reactants}} - V_{\text{products}}$ we have $\left(\frac{\partial \Delta \overline{G}_{\text{rxn}}}{\partial P}\right)_{-} = \Delta \overline{V}_{\text{rxn}}$

The key indicator is ΔV_{rxn} . $\Delta C_{V, rxn}$ should be ignored. Because the volume of solids is negligible, ΔV_{rxn} is proportional to the number of gas moles created in the reaction; $\Delta V_{rxn} = \Delta n_{gas}(RT/P)$.

Consider adding reaction 1 to reaction 2:

net reaction: $P(s) + A(g) + Z(s) \rightarrow Q(s) + K(g)$ $\Delta G^{\circ}(25^{\circ}C) = +57 + -45 = +12 \text{ kJ/mol}$

For reaction 1 + 2, $\Delta V_{rxn} = 0$. So as the pressure increases, ΔG_{rxn} remains approximately +12 kJ/mol. This combination is unlikely to reach $\Delta G_{rxn} = 0$ by increasing the pressure.

Consider adding reaction 1 to reaction 3:

net reaction: $P(s) + 2W(g) \rightarrow Q(s) + B(g) + D(g) \quad \Delta G^{\circ}(25^{\circ}C) = +57 + -51 = +6 \text{ kJ/mol}$

For reaction 1 + 3, $\Delta V_{rxn} = 0$. So as the pressure increases, ΔG_{rxn} remains approximately +6 kJ/mol. This combination is unlikely to reach $\Delta G_{rxn} = 0$ by increasing the pressure.

Consider adding reaction 1 to reaction 4. Note that we need to reverse reaction 4, so we add reaction 1 to the reverse of reaction 4.

net reaction: $P(s) + A(g) + M(s) \rightarrow Q(s) + E(s)$ $\Delta G^{\circ}(25^{\circ}C) = +57 + -23 = +34 \text{ kJ/mol}$

For reaction 1 + (-4), $\Delta V_{rxn} = -1 \times (RT/P)$. So as the pressure increases, ΔG_{rxn} **decreases** from +34 kJ/mol. At a sufficiently high pressure, $\Delta G_{rxn} = 0$.

Summary: add reaction 1 to the reverse of reaction 4.