

Chem 531: First Exam (95 points total)**SOLUTIONS**

Thursday, September 28, 2023

Please budget your time carefully and show all work.

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ Torr} = 1.01325 \text{ bar} \quad (1 \text{ bar} = 10^5 \text{ Pa}); \quad 1 \text{ L} = 1 \text{ dm}^3$$

(1) 1.5 moles of an ideal gas, for which $\bar{C}_v = 3R/2$, is initially at 20.0°C and 10.0 bar and undergoes a 2-stage transformation. For each stage described below, calculate q , w , ΔU , and ΔH . (20 pts)

a) The gas is expanded isothermally and reversibly until the volume doubles.

isothermal, ideal gas: $\Delta U = \Delta H = 0$

$$\begin{aligned} w &= -q = -\int P dV = -\int nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} = -nRT \ln 2 \\ &= -(1.5)(8.3145)(293.15) \ln 2 \\ &= -2534 \text{ J} = -2.5 \text{ kJ} \end{aligned}$$

b) Beginning at the end of the 1st stage, the temperature is raised to 80.0°C at constant volume.

constant V , so $w = 0$

$$\begin{aligned} \Delta U &= q = n \int \bar{C}_v dT = (1.5)(1.5)(8.3145)(80 - 20) \\ &= 1122 \text{ J} = 1.1 \text{ kJ} \end{aligned}$$

$$\Delta H = \Delta U + \Delta(PV)$$

$$= \Delta U + nR\Delta T$$

$$= 1122 + (1.5)(8.3145)(60) = 1870 \text{ J} = 1.9 \text{ kJ}$$

(2) Two moles of an ideal monatomic gas initially at a pressure of 1.00 bar and 25°C is compressed adiabatically by application of a constant external pressure of 15.00 bar until the final pressure of the gas reaches 10.00 bar. Assume the gas has molar heat capacity $\bar{C}_v = 3R/2$ and is independent of temperature. (15 pts)

a) What is the heat absorbed by the gas?

adiabatic, so $q = 0$

b) What is the final temperature of the gas?

since $q = 0$, $\Delta U = w = -\int P_{ext} dV$

ideal gas, so $\Delta U = \int \bar{C}_v dT$

$$\therefore n\bar{C}_v (T_f - T_i) = -(15.00)(V_f - V_i)$$

$$n \frac{3}{2} R (T_f - T_i) = -(15.00) \left[\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right]$$

$$\frac{3}{2} (T_f - T_i) = -(15.00) \left(\frac{T_f}{P_f} - \frac{T_i}{P_i} \right)$$

$$1.5 (T_f - 298) = -(15.00) \left(\frac{T_f}{10.00} - \frac{298}{1.00} \right)$$

$$0.1 T_f - 29.8 = -\frac{T_f}{10} + 298$$

$$0.2 T_f = 327.8$$

$$T_f = 1639 \text{ K}$$

(3) The normal melting point of tin is 231.9°C , with an enthalpy of fusion ΔH_{fus}° of 7.07 kJ/mol .

The heat capacities (\bar{C}_p) are $28.1 \text{ J K}^{-1} \text{ mol}^{-1}$ for the solid and $30.2 \text{ J K}^{-1} \text{ mol}^{-1}$ for the liquid.

Assume these latter values are temperature independent. (20 pts)

a) Calculate the entropy change of the system when one mole of liquid tin, supercooled 55°C below its normal melting temperature, is frozen.

$$\begin{array}{ccc}
 \text{Sn}(l) & \xrightarrow{\Delta S (176.9^{\circ}\text{C})} & \text{Sn}(s) & T = 450.05 \text{ K} \\
 \downarrow \Delta S_1 & & \uparrow \Delta S_3 & \\
 \text{Sn}(l) & \xrightarrow[\Delta S_2]{\Delta S (231.9^{\circ}\text{C})} & \text{Sn}(s) & T = 505.05 \text{ K}
 \end{array}$$

$$\Delta S_1 = \int_{450.05}^{505.05} C_{p,l} \frac{dT}{T} = (30.2) \ln \frac{505.05}{450.05} = 3.48 \text{ J/K}$$

$$\Delta S_2 = \frac{-\Delta H_f}{T} = \frac{-7.07 \times 10^3}{505.05} = -14.00 \text{ J/K}$$

$$\Delta S_3 = \int_{505.05}^{450.05} C_{p,s} \frac{dT}{T} = (28.1) \ln \frac{450.05}{505.05} = -3.24 \text{ J/K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -13.8 \text{ J/K}$$

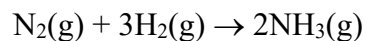
b) The standard enthalpy of fusion at the temperature of part (a) is 6.95 kJ/mol . Determine ΔS_{surr} and ΔS_{univ} for the process of part (a) and confirm that it is spontaneous.

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irrev}}}{T_{\text{surr}}} = \frac{-(-\Delta H_{\text{fus}}(450.05))}{450.05} = \frac{+6.95 \times 10^3}{450.05}$$

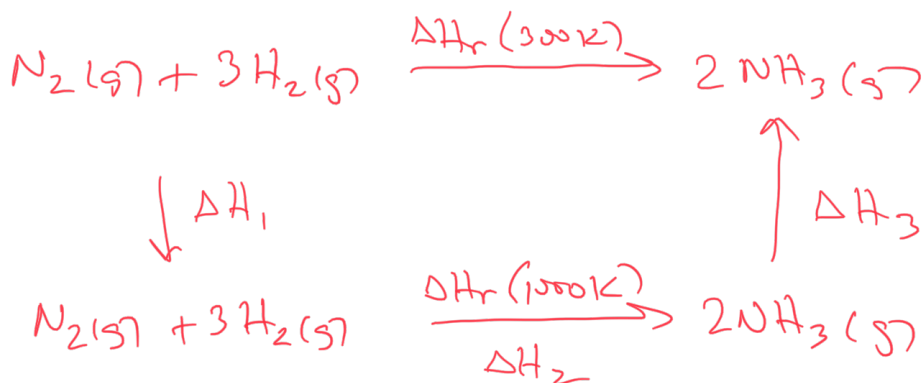
$$= 15.44 \text{ J/K}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -13.8 + 15.4 = 1.6 \text{ J/K}$$

(4) At 1000 K, $\Delta H_r^\circ = -123.77$ kJ for the reaction (15 pts)



with $\bar{C}_p(\text{N}_2) = 3.052R$, $\bar{C}_p(\text{H}_2) = 3.466R$, and $\bar{C}_p(\text{NH}_3) = 4.217R$. Calculate ΔH_f° of $\text{NH}_3(\text{g})$ at 300 K from this information. Assume the heat capacities are independent of temperature.



$$\Delta H_1 = \int_{300}^{1000} C_{p,\text{N}_2} dT + 3 \int_{300}^{1000} C_{p,\text{H}_2} dT$$

$$\Delta H_2 = \Delta H_r(1000\text{K})$$

$$\Delta H_3 = 2 \int_{1000}^{300} C_{p,\text{NH}_3} dT$$

$$\Delta H_r(300\text{K}) = \Delta H_r(1000\text{K}) + \int_{1000}^{300} [2C_{p,\text{NH}_3} - C_{p,\text{N}_2} - 3C_{p,\text{H}_2}] dT$$

$$= -123.77 \times 10^3 + [2R(4.217) - R(3.052) - 3R(3.466)](-700)$$

$$= -123.77 \times 10^3 + (29194)$$

$$= -94,576\text{J} = -94.58 \text{ kJ}$$

$$\Delta H_f^\circ(\text{NH}_3) = \frac{1}{2} \Delta H_r = -47.29 \text{ kJ/mol}$$

(5) At 25°C, a given reaction has a standard reaction enthalpy ΔH_r° of -6.5 kJ/mol and standard reaction entropy ΔS_r° of $-20 \text{ J K}^{-1} \text{ mol}^{-1}$. Determine if this reaction is spontaneous at this temperature by calculating ΔS_{univ} . (10 pts)

$$\Delta S_{\text{sys}} = \Delta S_r^\circ = -20 \text{ J/K}$$

$$\Delta S_{\text{sur}} = \frac{-\Delta H_r}{T_{\text{sur}}} = \frac{+6.5 \times 10^3}{298} = 21.8 \text{ J/K}$$

$$\Delta S_{\text{univ}} = +1.8 \text{ J/K}$$

spontaneous

(6) Short answers (be as specific/accurate as possible): (15 pts)

(a) Give one accurate statement of the 2nd law of thermodynamics

possibilities :

- 1) In a cyclic process you can't extract heat from a hot reservoir & perform an equivalent amt. of work
- 2) $\oint \frac{dq}{T} \leq 0$
- 3) $\Delta S_{\text{univ}} \geq 0$

(b) Under what general conditions is $\Delta S_{\text{sys}} < 0$ for a spontaneous process?

$$\Delta S_{\text{sur}} > 0 \quad \text{and} \quad \Delta S_{\text{sur}} > |\Delta S_{\text{sys}}|$$

(c) The spontaneous mixing of two ideal gases at constant T and P is entirely due to what?

the entropy of the system increases

(d) What is the thermodynamic reference state for enthalpy and how does this differ from that of the entropy?

enthalpy : most stable phase of the element at $P = 1 \text{ bar}$

entropy : perfect crystalline substance at 0 K

(e) If only pressure-volume work is considered, when is heat a state function? (explain your answer)

When constant volume, since $\Delta U = q_v$

When constant pressure, since $\Delta H = q_p$