Chemistry 231 **Assignment #6** (due Tuesday, 01 November, in class)

1. **a)** Calculate the efficiency (ε) of a steam engine operating between temperatures $T_H = 373$ K (100 °C, the boiling temperature of water at 1 atm) and $T_C = 300$ K. If 100 kJ of heat is absorbed at T_H, calculate the maximum amount of work the engine can do on the surroundings.

[3]

b) Modern steam engines operate at high pressures, up to 200 atm. These engines are considerably more expensive to build than atmospheric steam engines. Why are they used?

2. **a)** 1.00 mole of an ideal gas at 10.0 bar and 300 K expands isothermally with $p = p_{ext}$ to a final pressure of 1.00 bar. Calculate ΔU, ΔS, q and w for this process.

[4]

b) The Second Law gives $(\Delta S = 0)_{\text{isolated system}}$ as the fundamental criterion for a reversible process. Use this result to prove that the gas expansion described in part **a** is reversible. (*Hint*: The gas is not an isolated system, but the gas + surroundings together form an isolated system.)

3. **a)** 1.00 mole of an ideal gas at 10.0 bar and 300 K expands isothermally against a constant 1.00 bar external pressure ($p > p_{ext}$) to a final pressure of 1.00 bar. Calculate ΔU, ΔS, q and w.

[4]

b) Use the criterion $(\Delta S > 0)_{\text{isolated system}}$ for an irreversible processes to prove that the gas expansion described in part **a** is irreversible.

4. **a)** 1.00 mole of helium ($C_{Vm} = 3R/2$) initially at 1.00 bar and 300 K is compressed adiabatically and reversibly to a final pressure of 5.00 bar. Explain, in words, why ΔS is zero for this process.

[3]

b) Calculate the increase in entropy of the helium caused by the temperature increase and the decrease in the entropy of the helium caused by the volume decrease. Show that the two contributions to the entropy change cancel to give $\Delta S = 0$ for the reversible adiabatic expansion.

5. **a)** Show that ΔH_m° and ΔS_m° for the reversible freezing of one mole of liquid water at 0 °C and 1 bar are -6010 J mol^{-1} and -22.00 J K^{-1} mol^{-1}, respectively. *Data*: $\Delta H^\circ_{\text{fus,m}}(H_2O) = 6010$ J mol^{-1}.

[6]

b) Calculate ΔH_m° and ΔS_m° for freezing one mole of liquid water at -10 °C and 1 bar. *Hint*: H and S are state functions, so take a convenient reversible path ($T_2 = 263.15$ K, $T_1 = 273.15$ K):

$$\Delta H^\circ_m(T_2) = \int_{T_2}^{T_1} C^o_{pm}(l)\,dT + \Delta H^\circ_m(T_1) + \int_{T_1}^{T_2} C^o_{pm}(s)\,dT \qquad \Delta S^\circ_m(T_2) = \int_{T_2}^{T_1} \frac{C^o_{pm}(l)}{T}\,dT + \frac{\Delta H^\circ_m(T_1)}{T_1} + \int_{T_1}^{T_2} \frac{C^o_{pm}(s)}{T}\,dT$$

Data: the molar heat capacities of $H_2O(s)$ and $H_2O(l)$ are 36.9 and 75.5 J K^{-1} mol^{-1}, respectively.

c) Prove that freezing liquid water at -10 °C and 1 bar is an irreversible process.

d) The molar entropy change for freezing water at $T_1 = 273.15$ K is $\Delta H_m^\circ(T_1)/T_1$. Why can't the entropy change for freezing water at $T_2 = 263.15$ K be calculated using $\Delta H_m^\circ(T_2)/T_2$?

Chem 231 $\boxed{\text{Assignment \#6}}$ (2016)

① a) heat engine operating with $T_H = 373\,K$, $T_C = 300\,K$

$$\varepsilon = \text{efficiency} = \frac{\text{work done on surroundings}}{\text{heat absorbed at } T_H} = \frac{-w}{q_H} = 1 - \frac{T_C}{T_H}$$

$$\varepsilon = 1 - \frac{300\,K}{373\,K} = 1 - 0.804 = \boxed{0.196} \quad (19.6\%)$$

b) max. work done on the surroundings (for a reversible heat engine) $-w = \varepsilon q_H$

$$-w = 0.196\,(100.0\text{ kJ}) = \boxed{19.6\text{ kJ}}$$

c) high-pressure steam engines: $T_H > T_H$ (for atmospheric engines)

$\boxed{\text{higher } T_H}$

higher efficiency $\varepsilon = 1 - \frac{T_C}{T_H}$ if T_H is raised above 373 K for an atmospheric steam engine ($T_H = 373\,K$ at 1 atm)

boi

$\boxed{\text{boiling temp. increases with pressure}}$

(system (gas) absorbs 5740 J heat, surroundings loses 5740 J heat)

Q2 a) isothermal ideal gas: $\boxed{\Delta U = 0} = q + w$

reversible ($P_{ext} = P$)

$$w = -\int P_{ext}\,dV = -\int \frac{nRT}{V}\,dV = -nRT\int\frac{dV}{V} = -nRT\ln\left(\frac{V_f}{V_i}\right)$$

$$\Downarrow$$

$$\left(\text{isothermal: } P_iV_i = P_fV_f = nRT \Rightarrow \frac{V_f}{V_i} = \frac{P_i}{P_f}\right) \Rightarrow \quad w = -nRT\ln\left(\frac{P_i}{P_f}\right)$$

$$w = (-1.00\text{ mol})(8.314\text{ J K}^{-1}\text{mol}^{-1})(300\,K)\ln\left(\frac{10.0\text{ bar}}{1.00\text{ bar}}\right) = -5740\text{ J}$$

$$\boxed{q = -w = 5740\text{ J}} = q_{rev}$$

$$\Delta S = \int\frac{dq_{rev}}{T} = \frac{1}{T}\int dq_{rev} = \frac{q_{rev}}{T} = \frac{+5740\,J}{300\,K}$$

$$\boxed{\Delta S = 19.1\text{ J K}^{-1}}$$

$q_{system} = -q_{surroundings}$

b) $(\Delta S_{system} + \Delta S_{surroundings}) = \Delta S_{total}$ for an isolated system (the "universe"!)

$$\Delta S_{total} = \frac{q_{system}}{T} + \frac{q_{surroundings}}{T} = \frac{5740\,J}{300\,K} + \frac{-5740\,J}{300\,K} = 0$$

for both Q2 and Q2: $\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = nR \ln \frac{p_i}{p_f} = 19.\frac{J}{K}$ S is a state function

(Q3) 1.00 mol ideal gas at 10.0 bar and 300 K expands against constant external pressure $p_{ext} = 1.00$ bar to a final 1.00 bar isothermally.

a)

isothermal ideal gas $\boxed{\Delta U = 0}$ (so $q + w = 0$)

$$w = -\int \overset{const.}{p_{ext}}\, dV = -p_{ext}\int dV = -p_{ext}(V_f - V_i)$$

$p_{ext} = p_f$

$$w = -p_{ext}\left(\frac{nRT}{p_f} - \frac{nRT}{p_i}\right) = -p_f\, nRT\left(\frac{1}{p_f} - \frac{1}{p_i}\right)$$

$$w = -nRT\left(1 - \frac{p_f}{p_i}\right) = -(1.00\,\text{mol})(8.314\,\text{J K}^{-1}\text{mol}^{-1})(300\,\text{K})\left(1 - \frac{1.00}{10.0}\right)$$

$$w = -2240\ \text{J} \qquad \boxed{q = -w = 2240\ \text{J}}$$

$\boxed{\Delta S = 19.1\ \text{J K}^{-1}}$ same initial, final states as in Q2, so same ΔS ⇒ S is a state function

[or /// integrate $dS = \frac{C_V}{T}\underset{0}{dT} + nR\frac{dV}{V}$ to calculate ΔS]

$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = nR \ln\left(\frac{p_i}{p_f}\right)$.

(important! can't use $\int \frac{dq}{T} = \frac{q}{T}$ to calculate ΔS here — the process is not reversible)

b) system: 1 mol ideal gas at 300 K, $\Delta S = 19.1\ \text{J K}^{-1}$, $q = 2240\ \text{J}$

surroundings at 300 K: $q_{surr} = -2240\ \text{J}$

system + surroundings = isolated system

system absorbs 2240 J heat from surroundings

∴ $q_{surroundings} = -q_{system} = -2240\ \text{J}$

$$\Delta S_{surroundings} = \frac{q_{surr}}{T_{surr}} = \frac{-2240\ \text{J}}{300\ \text{K}} = -7.47\ \frac{\text{J}}{\text{K}}$$

>0 ∴ irreversible

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr.} = 19.1\frac{\text{J}}{\text{K}} - 7.47\frac{\text{J}}{\text{K}} = \boxed{+11.6\frac{\text{J}}{\text{K}}}$$

$$\left(dS \equiv \frac{dq_{rev}}{T} \right)$$

Ⓠ4 a) reversible adiabatic process $\Delta S = \int \frac{\cancel{dq_{rev}}^{\,0}}{\cancel{T}} = 0$
$(q = q_{rev})$ $(q = 0)$

b) $$dS = \frac{C_V}{T}dT + \frac{nR}{V}dV = \underbrace{\frac{C_p}{T}dT - \frac{nR}{p}dp}_{\text{(more convenient here)}} = 0$$

$p_i = 1.00$ bar $T_i = 300K$
$p_f = 5.00$ bar $T_f = ?$

$$C_p = nC_{pm} = n(C_{vm} + R)$$

$$\Delta S = \int dS = \int \frac{C}{T}dT - \int \frac{nR}{p}dp = 0 \qquad C_p \int_{T_i}^{T_f} \frac{dT}{T} = nR \int_{p_i}^{p_f} \frac{dp}{p}$$

$$n(\overset{\frac{3}{2}R}{C_{vm}} + R)\ln\left(\frac{T_f}{T_i}\right) = nR\, d\ln\left(\frac{p_f}{p_i}\right) \qquad \frac{5}{2}R\ln\left(\frac{T_f}{T_i}\right) = R\ln\left(\frac{p_f}{p_i}\right)$$

$$\ln\left(\frac{T_f}{T_i}\right) = \frac{2}{5}\ln\left(\frac{p_f}{p_i}\right) \qquad \frac{T_f}{T_i} = \left(\frac{p_f}{p_i}\right)^{2/5} = \left(\frac{5.00\text{bar}}{1.00\text{bar}}\right)^{2/5} = 1.904$$

$$T_f = 1.904\,T_i = 1.904(300\,K) = 571\,K$$

$$V_f = \frac{nRT_f}{p_f} = \frac{(1.00\text{ mol})(0.08314\text{ L bar K}^{-1}\text{mol}^{-1})(571K)}{5.00\text{ bar}} = 9.494L$$

$$V_i = \frac{nRT_i}{p_i} = \frac{1.00(0.08314)300}{1.00} = 24.94\,L$$

$$dS = \frac{C_v}{T}dT + \frac{nR}{V}dV = \frac{nC_{vm}}{T}d + \frac{nR}{V}dV$$

$n = 1.00$ mol

$$\Delta S = \int \frac{C_v}{T}dT + nR\int\frac{dV}{V} = nC_{vm}\int\frac{dT}{T} + nR\int\frac{dV}{V} = nC_{vm}\ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right)$$

$$= n\frac{3}{2}R\ln\left(\frac{571\,K}{300\,K}\right) + nR\ln\left(\frac{9.494}{24.94}\right) = nR\,0.965 + nR(-0.965)$$

$$= 0$$

ⓆⓈ Q5

$$H_2O(\ell) \xrightarrow[\Delta H_m^\circ,\ \Delta S_m^\circ]{\text{freezing}\ 0^\circ C} H_2O(s) \qquad \left(\text{opposite of melting}\right)$$

a) $\Delta H_m^\circ = -\Delta H_{m,fus}^\circ = -6010\ J\ mol^{-1}$

$H_2O(\ell)$ and $H_2O(s)$ are in equilibrium at 0°C, 1bar $\Longrightarrow$ reversible freezing

$$\Delta H_m^\circ = q = q_{rev} \qquad \Delta S_m^\circ = \frac{-6010\ J\ mol^{-1}}{273.15\ K} = -22.00\ \frac{J}{mol\ K}$$

b)

$$\begin{tikzcd}
H_2O(\ell) \arrow[r, "\text{freeze reversibly}", "0^\circ C\ \text{(II)}"'] & H_2O(s) \arrow[d, "\text{(III) cool solid reversibly}"] \\
H_2O(\ell) \arrow[u, "\text{heat liquid reversibly (I)}"] \arrow[r, "\text{freeze}", "-10^\circ C"'] & H_2O(s)
\end{tikzcd}$$

See Q8, tutorial #3 for more details

$$\Delta H_{-10C}^\circ = \underbrace{\int_{263.15}^{273.15K} C_{p,m}^\circ(\ell)\,dT}_{\text{(I)}} + \underbrace{\Delta H_{0C}^\circ}_{\text{(II)}} + \underbrace{\int_{273.15}^{263.15K} C_{p,m}^\circ(s)\,dT}_{\text{(III)}}$$

$$= C_{p,m}^\circ(\ell)(10K) - 6010 + C_{p,m}^\circ(s)(-10K)$$

$$= (755 - 6010 - 369)\ J\ mol^{-1}$$

$$\boxed{\Delta H_{-10C}^\circ = -5624\ J\ mol^{-1}}$$

$$\Delta S_{-10C}^\circ = \int_{263.15}^{273.15K} \frac{C_{p,m}^\circ(\ell)\,dT}{T} + \Delta S_{0C}^\circ + \int_{273.15}^{263.15} \frac{C_{p,m}^\circ(s)\,dT}{T}$$

$$= 75.5 \ln\left(\frac{273.15}{263.15}\right) - 22.00 + 36.9 \ln\left(\frac{263.15}{273.15}\right)$$

$$\boxed{\Delta S_{-10C}^\circ = -20.56\ J\ K^{-1}\ mol^{-1}}$$

(Q5 cont.)

c) at $-10\,^\circ C$ $\quad q = \Delta H^\circ_{-10C} = -5624\ J\ mol^{-1}$

notice $\frac{q}{T} = \frac{-5624\ J\ mol^{-1}}{263.15\ K} = -21.37\ J\ K^{-1} mol^{-1}$

$\neq \Delta S^\circ_{-10C} \left(= -20.56 \frac{J}{K\ mol}\right)$

$\therefore \frac{q}{T} \neq \frac{q_{rev}}{T} \Rightarrow$ irreversible freezing

or $(\Delta S_{freezn} + \Delta S_{surr})_{isolated} = -20.56 \frac{J}{K} + \frac{5624\ J}{263.15\ K}$

$= (-20.56 + 21.37) \frac{J}{K}$

$= +0.81 \frac{J}{K} > 0$

$\therefore$ irreversible

or $q = -5624\ J\ mol^{-1}$

$T\Delta S = (263.15\ K)(20.56\ J\ K^{-1})$
$= -5410\ J$

$q < T\Delta S$ $\therefore$ irreversible

d) at $-10\,^\circ C$ can't use $\frac{q}{T} = \frac{\Delta H_{10C}}{T}$

to calculate ΔS°_{-10C} because

$q \neq q_{rev}$ at $-10\,^\circ C$ (spontaneous freezing)