Chemistry 410B Exam 5 Fall 2016
Solutions

1. **40 points.**

   (a) Fill in the appropriate symbol: =, >, or <:

   i. $\Delta S_T \boxed{>} 0$

   ii. $\Delta G \boxed{<} 0$ for a spontaneous process at constant T and P

   iii. $S_T \boxed{>} 0$

   iv. $\mu_\mathrm{A} \boxed{=} \mu_\mathrm{B}$ when A and B are in equilibrium

   v. $S(T = 0\,\mathrm{K}) \boxed{=} 0$

   (b) Draw the periodic boundary conditions in the grid below, and calculate the total interaction energy (in terms of D) for the boxed spin.

$$\begin{array}{c|cccc|c} - & + & - & - & - & + \\ \hline + & + & + & + & \boxed{+} & + \\ + & + & - & + & + & + \\ - & - & + & + & - & - \\ - & + & - & - & - & + \\ \hline + & + & + & + & + & + \end{array} \Rightarrow \begin{array}{c|cccc|c} & & & & & \\ \hline & -2 & -2 & 0 & \boxed{\text{-4D}} & \\ & -2 & 6 & -4 & -4 & \\ & 0 & 0 & 2 & 0 & \\ & 0 & 4 & 2 & 2 & \\ \hline & & & & & \end{array}$$

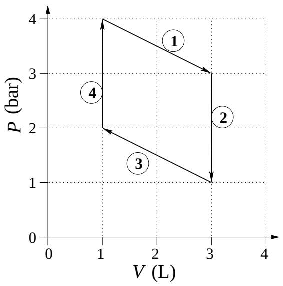
   (c) Find the heat needed to raise the temperature of 2.50 mol graphite from 298 K to 323 K, if $C_{Pm} = 8.23\,\mathrm{J\,K^{-1}\,mol^{-1}}$. **Solution:**

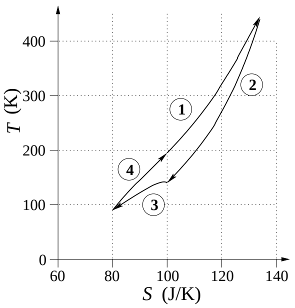
$$q = nC_{Pm}\Delta T = (2.50\,\mathrm{mol})(8.23\,\mathrm{J\,K^{-1}\,mol^{-1}})(323\,\mathrm{K} - 298\,\mathrm{K}) = \boxed{514\,\mathrm{J}.}$$

   (d) The $\Delta_\mathrm{vap}H^\circ$ of water at 373 K is $40.65\,\mathrm{kJ\,mol^{-1}}$. Find $\Delta_\mathrm{vap}S^\circ$. **Solution:**

$$\Delta_\mathrm{vap}S^\circ = \frac{\Delta_\mathrm{vap}H^\circ}{T_b} = \frac{(40.65\,\mathrm{kJ\,mol^{-1}})(10^3\,\mathrm{J/\,kJ})}{373\,\mathrm{K}} = \boxed{109\,\mathrm{J\,K^{-1}\,mol^{-1}}.}$$

2. An imaginary engine operates on a cycle with the PV and TS graphs shown below. (This is **not** a Carnot cycle.) Calculate the efficiency of the engine.





Solution: The efficiency is the net work done divided by the heat input, which in this case is

$$\epsilon = -\frac{w_1 + w_2 + w_3 + w_4}{q_1 + q_4}.$$

We include both q_1 and q_4 because the heat is being added to the system during these steps, and we don't count the heat that's released in in steps 2 and 3 because that heat is just released into the surroundings. The net work can be calculated from the area of the parallelogram described by the cycle in the PV graph, which is $(2.0\,\text{bar})(2.0\,\text{L}) = 4.0\,\text{bar}\,\text{L} = 400\,\text{J}$.

The heat input can be estimated (more approximately) by the area under a line from roughly $(S,T) = (80, 95)$ to (130,430) in the TS graph, which is the sum of the areas of a rectangle and a triangle:

$$q_1 + q_4 \approx \left[(95)(130-80) + \tfrac{1}{2}(430-95)(130-80)\right]\,\text{J} = 13125\,\text{J}.$$

So we get an efficiency of

$$\epsilon = \frac{400\,\text{J}}{13125\,\text{J}} = \boxed{0.030.}$$

Why is this engine so inefficient? It's partly because the straight lines in the PV curve deviate substantially from the curve for the reversible isothermal and adiabatic expansions, so the work is not being maximized, and also because the low temeprature is a significant fraction of the high temperature.

3. Calculate the absolute molar entropy of CO at 498 K, assuming that only translations and rotations contribute. The rotational constant is $1.93\,\text{cm}^{-1}$. **Solution:** We use the Sackur-Tetrode equation for the translational contribution, and Eq. 9.43 for the rotational contribution:

$$S_{m,\text{trans}} = R\left\{\frac{5}{2} + \ln\left[\left(\frac{2\pi m k_\text{B} T}{h^2}\right)^{3/2}\frac{RT}{\mathcal{N}_A P}\right]\right\}$$

$$\left(\frac{2\pi m k_\text{B} T}{h^2}\right)^{3/2} = \left(\frac{2\pi(28.0\,\text{amu})(1.661\cdot 10^{-27}\,\text{kg}\,\text{amu}^{-1})(1.381\cdot 10^{-23}\,\text{J}\,\text{K}^{-1})(498\,\text{K})}{(6.626\cdot 10^{-34}\,\text{J}\,\text{s})^2}\right)^{3/2} = 3.097\cdot 10^{32}\,\text{m}^3$$

$$\frac{RT}{\mathcal{N}_A P} = \frac{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(498\,\text{K})}{(6.022\cdot 10^{23}\,\text{mol}^{-1})(1.00\cdot 10^5\,\text{Pa})} = 6.876\cdot 10^{-26}\,\text{m}^{-3}$$

$$S_{m,\text{trans}} = R\left\{\frac{5}{2} + \ln\left[(3.097\cdot 10^{32})(6.876\cdot 10^{-26}\,\text{m}^{-3})\right]\right\} = 19.374R$$

$$S_{m,\text{rot}} = R\left(\ln\frac{k_\text{B}T}{B} + 1\right) = R\left(\ln\frac{(0.6950\,\text{cm}^{-1}\,\text{K}^{-1})(498\,\text{K})}{1.93\,\text{cm}^{-1}} + 1\right) = 6.189R$$

$$S_m = S_{m,\text{trans}} + S_{m,\text{rot}} = 19.374R + 6.189R = 25.563 = \boxed{212.5\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}.}$$

4. The vapor pressure of acetone is 0.0526 bar at 263.8 K and 0.526 bar at 312.7 K. Find the latent enthalpy of vaporization. **Solution:** The pressures and temperatures are related by the Clausius-Clapeyron equation. If we go back to how that equation was derived, recall that it connects any two sets of P and T. We chose to integrate from the reference pressure at 1.00 bar and the normal boiling point T_b, but we could also have integrated from any P_1, T_1 and gotten essentially the same equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_\text{vap}H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\Delta_\text{vap}H = R\ln\left(\frac{P_2}{P_1}\right)\left[\frac{1}{T_1} - \frac{1}{T_2}\right]^{-1}$$

$$= (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\ln\left(\frac{0.526}{0.0526}\right)\left[\frac{1}{263.8\,\text{K}} - \frac{1}{312.7\,\text{K}}\right]^{-1}$$

$$= 32295\,\text{J}\,\text{mol}^{-1} = \boxed{32.3\,\text{kJ}\,\text{mol}^{-1}.}$$