$$\Delta U = Q_{in} + W_{on} \qquad S = k \ln \Omega \qquad dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{m}{T} dN \qquad dS \geq \frac{Q}{T}$$

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{N,V} \qquad P = T \left(\frac{\partial S}{\partial V} \right)_{U,N} \qquad m = -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \qquad C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

$$e \equiv \frac{Benefit}{Cost} \qquad COP \equiv \frac{Benefit}{Cost} \qquad g = \frac{f+2}{f}$$

$$H \equiv U + PV \qquad\qquad F \equiv U - TS \qquad\qquad G \equiv U - TS + PV = Nm$$

$$dH = TdS + VdP + mdN \qquad dF = SdT - PdV + mdN \qquad dG = -SdT + VdP + mdN$$

$$\Delta F_T \leq W \qquad\qquad \Delta G_{T,P} \leq W_{other}$$

$$pH \equiv -\log_{10} m_{H^+}$$

True under certain conditions

$\Delta U = \frac{f}{2} Nk\Delta T$ where f = # of accessible degrees of freedom.

$$PV = NkT \qquad\qquad P_i V_i^{g} = P_f V_f^{g} \qquad\qquad W_{s\to} = NkT \ln \left(\frac{V_f}{V_i} \right)$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{L/T}{\Delta V}$$

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \qquad\qquad G = -NkT \ln(V - Nb) + \frac{N^2 kTb}{V - Nb} - \frac{2aN^2}{V} + c(T)$$

$$G = m_{solvent}(T,P) N_{solvent} + N_{solute} f(P,T) + N_{solute} kT \ln \left[N_{solute} / N_{solvent} \right] - N_{solute} kT$$

For reaction $n_1 X_1 + n_2 X_2 + ... \leftrightarrow a_1 Y_1 + a_2 Y_2 + ...,$

$$K \equiv e^{-\Delta G^o / RT} = \left(\frac{\left(\frac{P_{Y_1}}{P_o} \right)^{a_1} \left(\frac{P_{Y_2}}{P_o} \right)^{a_2} \cdots}{\left(\frac{P_{X_1}}{P_o} \right)^{n_1} \left(\frac{P_{X_2}}{P_o} \right)^{n_2} \cdots} \right), \qquad \frac{\left(m_{Y_1} \right)^{a_1} \left(m_{Y_2} \right)^{a_2} \cdots}{\left(m_{X_1} \right)^{n_1} \left(m_{X_2} \right)^{n_2} \cdots} = e^{-\Delta G^o / RT} = K$$

k = 1.3×10^{-23} J/K

20 pts 1.   **Quickies**

   5 pts   a.   Qualitatively, what's the origin of the bN term in the Van Der Waals
                   equation? How about the $aN2/V2$ term?

   5 pts   b.   Complete the sentence: In a real steam engine, using the Rankine cycle, liquid
                  water is pumped to high pressure, passed through the boiler where it turns to
                  steam, then it adiabatically drives a turbine, and finally condenses to water
                  again. Complete the sentence: When driving the turbine, the steam's entropy

                  _____.

   5 pts   c.   Complete the sentence: Under just constant *temperature* conditions,
                  maximizing universal entropy is equivalent to minimizing

                  _____.

   5 pts   d.   In terms of cold and hot reservoir temperatures, what's the greatest efficiency
                  a heat engine can have?

26 pts 2.   **Refrigerator.** A refrigerator's cycle is essentially the reverse of a heat-engine's.
                   The cold reservoir (the inside of the fridge T_c) is cooled by heating the coolant Q_c,
                   and the hot reservoir (the kitchen at T_h) is heated by cooling the coolant Q_h. Of
                   course, work, W, must be done on the coolant to make the fridge operate.

   4 pts   a.   Determine the Coefficient of Performance in terms of heat and work.

   20 pts   b.   Use some laws of thermodynamics to set a limit on the CoP strictly in terms
                  of the reservoir temperatures, T_h and T_c.

   2 pt   c.   Say the kitchen is a nice 72°F = 22.22°C=295.4 K, and the fridge is kept at
                  36°F = 2.22°C=275.37 K; what's the limit on the CoP?

28 pts

3.   **Hill.** The 'Hill' cycle is illustrated below. Approximating that it is performed by an ideal gas in a closed chamber (so N doesn't change), derive its efficiency in terms of the three volumes labeled and γ. We'll break this into steps.
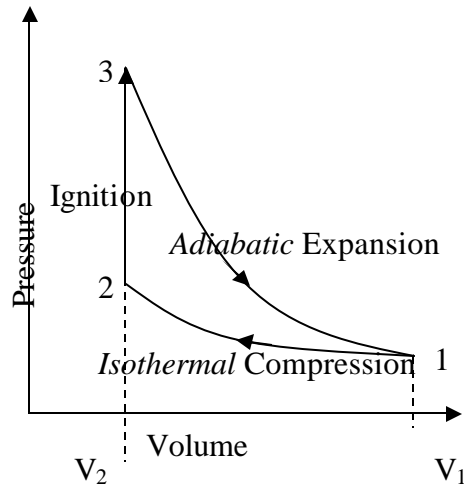
2 pt   a.   For which stroke is $Q = 0$?

6 pts   b.   What's the efficiency in terms of the remaining two Q's?

9 pts   c.   What are these Q's in terms of P's, V's, γ, and f (you may initially have NkT's, but we're imagining we have an *ideal gas*)?

13 pts   d.   Ok, I don't want to take *all* the fun out of it, finish things up on your own.

22 pts

4.   **Phases**. Calcite and aragonite are two phases of $CaCO_3$.   Here are the stats on them, per mole, at 298 K and 1 bar ($1.013 \times 10^5 N/m^2$).

	Calcite	Aragonite
S(J/K)	92.9	88.7
ΔG(kJ)	-1128.8	-1127.8
ΔH(kJ)	-1207.1	-1206.9
V(cm^3)	36.93	34.15

10 pts   a.   Qualitatively Plot G vs. P for the two phases in the vicinity of 1 bar. Indicate values for the *slopes* and *separations* of the curves at 1 bar.

8 pts   b.   Assuming that the values given above hold over a wide enough range of pressure, at what pressure would the two phases be in equilibrium?

4 pts   c.   At that equilibrium point, what would be the slope of the equilibrium curve in a P-T plot?

4 pts   5.   **van der Waals.** What's the chemical potential for a van der Waals gas?

6.   **Chemical Reactions.** In a lead-acid battery, the net chemical reaction is

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$$

   a. Using only the values in the table at the back of the book, what is the energy made available when one mole of Pb is processed at room temperature and atmospheric pressure?

   b. This reaction relies on the fact that, in an aqueous solution, $2SO_4H_2$ dissociates into $2H^+ + SO_4^{2-}$.

   i.   What's the equilibrium constant, K, for this process at this room temperature?

   ii. What is the relationship between the molalities of the two products?

   iii. If the molality of $2SO_4H_2$ is 10^{-5}, what are the molalities of the two products?

7.   **Phases and Domains.** Looking at the T vs. "Weight percent lead" plot in figure 5.34, describe what happens, for a mixture of around .75, as you slowly lower the temperature from above 300°C to 100°C.