4.3

$$đQ = c\,dT + \bar{p}\,dV \qquad \text{by the first law}$$
$$= c\,dT + \frac{RT}{V}\,dV \qquad \text{since } pV = RT$$
$$\Delta S = \int_i^f \frac{đQ}{T} = \int_{T_i}^{T_f} c\frac{dT}{T} + \int_{V_i}^{V_f} R\frac{dV}{V}$$
$$= c\ln\frac{T_f}{T_i} + R\ln\frac{V_f}{V_i} \qquad \text{independent of process}$$

5.1

(a) $pV^\gamma =$ constant for an adiabatic quasistatic process. Substituting $pV = \nu RT$ we have

$$\frac{\nu RT_i V_i^\gamma}{V_i} = \frac{\nu RT_f V_f^\gamma}{V_f} \quad \text{or} \quad T_f = T_i\left(\frac{V_f}{V_i}\right)^{1-\gamma}$$

(b) The entropy change of an ideal gas in a process taking it from T_i, V_i to T_f, V_f was found in problem 4.3 $\quad \Delta S = \nu C_V \ln\frac{T_f}{T_i} + \nu R\ln\frac{V_f}{V_i}$

$\Delta S = 0$ for an adiabatic quasistatic process. Hence

$$0 = \ln\frac{T_f}{T_i}\left(\frac{V_f}{V_i}\right)^{\frac{R}{C_V}}$$

Since $\frac{R}{C_V} = \frac{C_p - C_V}{C_V} = \gamma - 1$, and since $\ln 1 = 0$, it follows that

$$T_f = T_i\left(\frac{V_f}{V_i}\right)^{1-\gamma}$$

5.3

(a) $\quad C_V = \frac{\partial E}{\partial T} = \frac{5}{2}R$

(b) $\quad W = \int p\,dV =$ area under curve $= 1300$ Joules

(c) To find the heat, Q, we first find the energy change in going from A to C. This, of course, is independent of the path.

$$\Delta E = C_V\Delta T = \frac{5}{2}R(T_C - T_A) = \frac{5}{2}(P_C V_C - P_A V_A) = 1500 \text{ joules}$$

Then since $Q = \Delta E + W$

$$= 1500 + 1300 = 2800 \text{ Joules}$$

(d) From problem 4.3 $\quad \Delta S = C_V \ln\frac{T_C}{T_A} + R\ln\frac{V_C}{V_A}$

$$= \frac{5}{2}R\ln\frac{12\times10^2/R}{6\times10^2/R} + R\ln\frac{3\times10^3}{10^3}$$
$$= 2.83R = 23.5 \text{ joules/K}$$

6.1

(a) The probability that the system is in a state with energy E is proportional to the Boltzman factor $e^{-E/kT}$. Hence the ratio of the probability of being in the first excited state to the probability of being in the ground state is

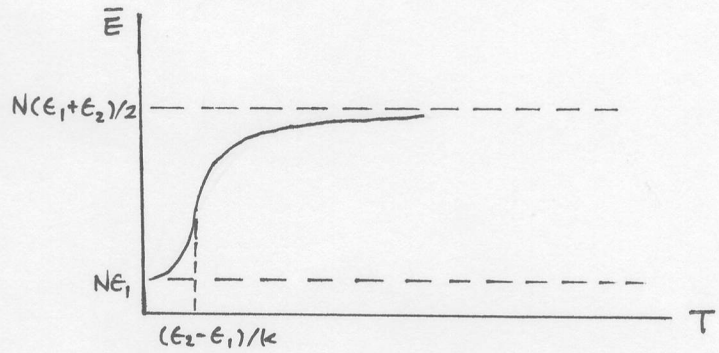
$$\frac{e^{-3\hbar\omega/2kT}}{e^{-\hbar\omega/2kT}} = e^{-\hbar\omega/kT}$$

(b) By the definition of mean value

$$\bar{E} = \frac{\frac{1}{2}\hbar\omega\, e^{-\hbar\omega/2kT} + \frac{3}{2}\hbar\omega\, e^{-3\hbar\omega/2kT}}{e^{-\hbar\omega/2kT} + e^{-3\hbar\omega/2kT}} = \frac{\hbar\omega}{2}\,\frac{1 + 3e^{-\hbar\omega/kT}}{1 + e^{-\hbar\omega/kT}}$$

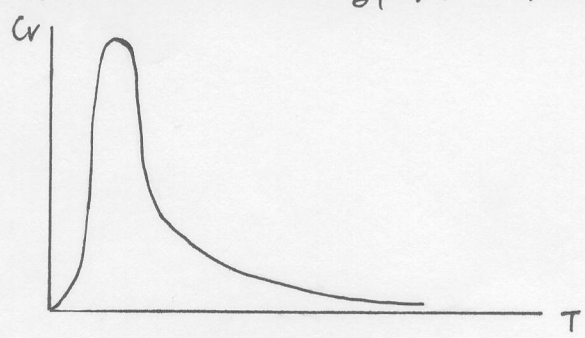
6.6

(a)



As T approaches 0 the system tends to the low energy state, while in the limit of high temperatures all states become equally probable. The energy goes from the low to the high temperature limit when $\epsilon_2 - \epsilon_1 \approx kT$.

(b). The specific heat is, $C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V$, i.e., the slope of $\bar{E}$.



(c) $$\bar{E} = N\left[\frac{\epsilon_1 e^{-\epsilon_1/kT} + \epsilon_2 e^{-\epsilon_2/kT}}{e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT}}\right] = N\left[\frac{\epsilon_1 + \epsilon_2 e^{-(\epsilon_2-\epsilon_1)/kT}}{1 + e^{-(\epsilon_2-\epsilon_1)/kT}}\right]$$

$T \to 0$, $\bar{E} \to N\epsilon_1$, and $T \to \infty$, $\bar{E} \to N\left(\frac{\epsilon_1+\epsilon_2}{2}\right)$

To find the temperature at which $\bar{E}$ changes from the low to the high temperature limit, we evaluate T where

$$\bar{E} = N\epsilon_1 + \frac{N}{2}\left[\frac{\epsilon_1+\epsilon_2}{2} - \epsilon_1\right] = N\left[\frac{\epsilon_1 + \epsilon_2 e^{-(\epsilon_2-\epsilon_1)/kT}}{1+e^{-(\epsilon_2-\epsilon_1)/kT}}\right]$$

which yields $\frac{\epsilon_2-\epsilon_1}{kT} = \ln 3 \approx 1$ or $(\epsilon_2-\epsilon_1) \approx kT$

The heat capacity is $C_V = \frac{\partial \bar{E}}{\partial T} = \frac{N(\epsilon_2-\epsilon_1)^2 e^{-(\epsilon_2-\epsilon_1)/kT}}{kT^2\left[1+e^{-(\epsilon_2-\epsilon_1)/kT}\right]^2}$

and $C_V \to 0$ as $T \to 0$, $T \to \infty$.

6.7

(a) The mean energy per mole is

$$\bar{E} = N_A \frac{0\, e^{-0/kT} + 2\epsilon e^{-\epsilon/kT}}{1+2e^{-\epsilon/kT}} = \frac{2N_A\epsilon e^{-\epsilon/kT}}{1+2e^{-\epsilon/kT}} \quad (1)$$

where N_A is Avogadro's number.

(b) We find the molar entropy from the partition function Z. Clearly, $Z = \zeta^{N_A}$ where $\zeta = \sum_i e^{-\epsilon_i/kT}$, the sum being over states of a single nucleus.

Thus $\zeta = 1 + e^{-\epsilon/kT} + e^{-\epsilon/kT}$

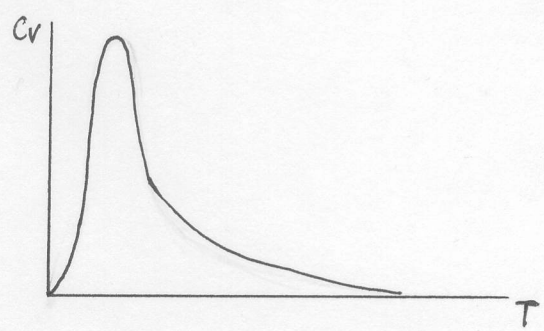
and $S = k(\ln Z + \beta\bar{E}) = N_A k \ln(1+2e^{-\epsilon/kT}) + \frac{N_A\epsilon e^{-\epsilon/kT}}{T(1+2e^{-\epsilon/kT})}$ (2)

(c) As $T \to 0$, the nucleii go to the ground state, and by the general definition of entropy $S = N_A k \ln \Omega = N_A k \ln 1 = 0$

As $T \to \infty$, all states become equally probable, $\Omega \to 3$ and $S = N_A k \ln 3$

It is easily verified that expression (2) approaches these limits by the fact that: $e^{-\epsilon/kT} \to 1$ $(T \to \infty)$, $e^{-\epsilon/kT} \to 0$ $(T \to 0)$

(d) From (1) we have

$$c = \frac{\partial \bar{E}}{\partial T} = \frac{2N_A\epsilon^2 e^{-\epsilon/kT}}{kT^2(1+2e^{-\epsilon/kT})^2}$$

For large T, $e^{-\epsilon/kT} \approx 1$ and $c \propto T^{-2}$.