Answers D

Problem 3.36

a) For $q \gg 1$ and $N \gg 1$, we have

$$S \simeq kq \ln\left(\frac{q+N}{q}\right) + kN \ln\left(\frac{q+N}{N}\right) = k(q+N)\ln(q+N) - kq\ln(q) - kN\ln(N)$$

so

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} = -kT \ln\left(\frac{q+N}{N}\right).$$

b) For $N \gg q$, we have

$$dS = -\frac{\mu}{T} dN = k\ln(1+q/N) \simeq \frac{kq}{N}.$$

In this case, there are many more oscillators than energy quanta. Most oscillators therefore have no energy quanta and a few have a single energy quantum. Adding one more oscillator therefore only leads to a small increase in the entropy for a given energy.

For $q \gg N$, we have

$$dS = -\frac{\mu}{T} dN = k\ln(1+q/N) \simeq k\ln(q/N).$$

In this case, the oscillators are highly excited. Adding one more oscillator gives more ways to distribute the energy quanta, and it makes sense that the entropy increases more than before.

Problem 6.12

We consider CN molecules. The first excited state has degeneracy 3, and the difference in energy between the first excited state and the ground state is $E_1 = 4.7 \cdot 10^{-4}\,\text{eV}$. We have

$$\frac{\mathcal{P}(\text{excited})}{\mathcal{P}(\text{ground})} = 3e^{-E_1/(kT)} = \frac{3}{10}.$$

Isolating T, we obtain

$$T = \frac{E_1}{k\ln(10)} = 2.4\,\text{K}.$$

Problem 6.13

The temperature is

$$T = 10^{11}\,\text{K}.$$

Let m_N be the mass of the neutron, m_P the mass of the proton, E_N the energy of the neutron, E_P the energy of the proton, and c the speed of light. Then

$$E_\text{N} - E_\text{P} = (m_\text{N} - m_\text{P})c^2 = 2.3 \cdot 10^{-30}\,\text{kg} \cdot (2.998 \cdot 10^8\,\text{m/s})^2 = 2.1 \cdot 10^{-13}\,\text{J}.$$

Let $\mathcal{P}_\mathrm{N}$ be the probability that a nucleon was a neutron, and let $\mathcal{P}_\mathrm{P}$ be the probability that a nucleon was a proton. We have $\mathcal{P}_\mathrm{N} + \mathcal{P}_\mathrm{P} = 1$ and

$$\frac{\mathcal{P}_\mathrm{N}}{\mathcal{P}_\mathrm{P}} = e^{-(E_\mathrm{N}-E_\mathrm{P})/(kT)} = 0.86.$$

Note that

$$\frac{\mathcal{P}_\mathrm{N}}{\mathcal{P}_\mathrm{P}} = \frac{1-\mathcal{P}_\mathrm{P}}{\mathcal{P}_\mathrm{P}} = \frac{1}{\mathcal{P}_\mathrm{P}} - 1 \quad \Leftrightarrow \quad \mathcal{P}_\mathrm{P} = \frac{1}{1+\mathcal{P}_\mathrm{N}/\mathcal{P}_\mathrm{P}} = 0.54.$$

We hence conclude that:
The fraction of the nucleons that were protons was 0.54.
The fraction of the nucleons that were neutrons was 0.46.

Problem 6.16

The partition function is

$$Z = \sum_s e^{-\beta E(s)}.$$

Therefore

$$-\frac{\partial}{\partial \beta}\ln(Z) = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{1}{Z}\sum_s \frac{\partial}{\partial \beta} e^{-\beta E(s)} = \frac{1}{Z}\sum_s E(s) e^{-\beta E(s)} = \bar{E}.$$

Problem 6.20

a)

$$\begin{array}{r|l} & 1 + x + \dots \\ \hline 1-x & 1 \\ & \underline{1-x} \\ & x \\ & \underline{x-x^2} \\ & x^2 \\ & \vdots \end{array}$$

If $|x| < 1$, the remainder goes to zero, when the number of terms approaches infinity.

Another way of showing it:

$$\sum_{n=0}^{N} x^n = \frac{1}{1-x}(1-x)\sum_{n=0}^{N} x^n = \frac{1}{1-x}\left(\sum_{n=0}^{N} x^n - \sum_{n=0}^{N} x^{n+1}\right)$$

$$= \frac{1}{1-x}\left(\sum_{n=0}^{N} x^n - \sum_{n=1}^{N+1} x^n\right) = \frac{1}{1-x}(x^0 - x^{N+1}) = \frac{1-x^{N+1}}{1-x}.$$

Taking the limit $N \to \infty$ gives

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \quad \text{for} \quad |x| < 1.$$

b)

$$Z = \sum_{n=0}^{\infty} e^{-nhf/(kT)} = \frac{1}{1 - e^{-hf/(kT)}}$$

c)

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = (1 - e^{-hf/(kT)})\frac{hf e^{-hf/(kT)}}{(1 - e^{-hf/(kT)})^2} = \frac{hf}{e^{hf/(kT)} - 1}$$

d)

$$U = \frac{Nhf}{e^{hf/(kT)} - 1}$$

e)

$$C_V = \frac{Nh^2f^2}{kT^2}\frac{e^{hf/(kT)}}{(e^{hf/(kT)} - 1)^2}$$

$$\lim_{T\to 0} C_V = \lim_{T\to 0} \frac{Nh^2f^2}{kT^2} e^{-hf/(kT)} = 0$$

$$\lim_{T\to\infty} C_V = \lim_{T\to\infty} \frac{Nh^2f^2}{kT^2}\frac{1}{(1 + hf/(kT) - 1)^2} = Nk$$

The $T \to 0$ limit is zero, as it should be according to the third law of thermodynamics, and the $T \to \infty$ limit fits with the result from the equipartition theorem.

Problem D1

a) Since

$$\sum_{n=0}^{M} x^n = \frac{1}{1-x}\left(\sum_{n=0}^{M} x^n - \sum_{n=0}^{M} x^{n+1}\right) = \frac{1}{1-x}(1 - x^{M+1}),$$

we have

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

for $|x| < 1$. Using this, we obtain

$$Z = \sum_{n=0}^{\infty} e^{-\frac{nhf}{kT}} = \frac{1}{1 - e^{-\frac{hf}{kT}}}.$$

For $kT \gg hf$, this reduces to

$$Z \simeq \frac{kT}{hf}.$$

Hence $\kappa = 1$.

b)

$$Z = \sum_{n=0}^{\infty} \left(e^{-nhf/(kT)} + e^{-nhf/(kT)} e^{-\epsilon_0/(kT)}\right) = \frac{1 + e^{-\epsilon_0/(kT)}}{1 - e^{-hf/(kT)}}$$

$$P_A = \frac{1}{Z}\sum_{n=0}^{\infty} e^{-nhf/(kT)} = \frac{1}{1+e^{-\epsilon_0/(kT)}}$$

c)

$$E(T) = -\frac{\partial \ln(Z)}{\partial \beta} = \frac{\epsilon_0 e^{-\beta\epsilon_0}}{1+e^{-\beta\epsilon_0}} + \frac{hfe^{-\beta hf}}{1-e^{-\beta hf}} = \frac{\epsilon_0}{1+e^{\epsilon_0/(kT)}} + \frac{hf}{e^{hf/(kT)}-1}$$

We have

$$E(T) \approx \frac{\epsilon_0}{2} - \frac{hf}{2} + kT \quad \text{for} \quad kT \gg hf \quad \text{and} \quad kT \gg \epsilon_0,$$

so

$$a = \frac{\epsilon_0}{2} - \frac{hf}{2} \quad \text{and} \quad b = k.$$

Problem D2

a) The partition function is

$$Z = 3e^{-\epsilon_1/(kT)} + 2e^{-\epsilon_2/(kT)} + e^{-\epsilon_3/(kT)}.$$

b) The mean energy is

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{3\epsilon_1 e^{-\epsilon_1/(kT)} + 2\epsilon_2 e^{-\epsilon_2/(kT)} + \epsilon_3 e^{-\epsilon_3/(kT)}}{3e^{-\epsilon_1/(kT)} + 2e^{-\epsilon_2/(kT)} + e^{-\epsilon_3/(kT)}}.$$

c) To find the limits, we first rewrite the expression for the mean energy as follows

$$\bar{E} = \frac{3\epsilon_1 + 2\epsilon_2 e^{-(\epsilon_2-\epsilon_1)/(kT)} + \epsilon_3 e^{-(\epsilon_3-\epsilon_1)/(kT)}}{3 + 2e^{-(\epsilon_2-\epsilon_1)/(kT)} + e^{-(\epsilon_3-\epsilon_1)/(kT)}}.$$

Then

$$\lim_{T\to 0} \bar{E} = \frac{3\epsilon_1 + 0 + 0}{3+0+0} = \epsilon_1$$

and

$$\lim_{T\to \infty} \bar{E} = \frac{3\epsilon_1 + 2\epsilon_2 + \epsilon_3}{3+2+1} = \frac{\epsilon_1}{2} + \frac{\epsilon_2}{3} + \frac{\epsilon_1}{6}.$$

For $T \to 0$, there is little energy available, and the particle is therefore in one of the states with lowest energy. Since all these states have energy ϵ_1, the mean energy is ϵ_1.

For $T \to \infty$, there is plenty of energy available, and the system maximizes its entropy by letting the particle be in any of the six energy levels with the same probability. The mean energy is hence the average over the six states.

Problem Hand-in D

We consider the entropy

$$S = -k\sum_r p_r \ln(p_r).$$

a) For an isolated system in equilibrium, we have $p_r = p_0 = 1/\Omega$, so

$$S = -k\Omega\frac{1}{\Omega}\ln(1/\Omega) = k\ln(\Omega) \equiv S_0.$$

b) We have

$$S_0 - S = -k\sum_r p_0 \ln(p_0) + k\sum_r p_r \ln(p_r) = -k\sum_r p_r \ln(p_0) + k\sum_r p_r \ln(p_r)$$
$$= k\sum_r p_r \ln\left(\frac{p_r}{p_0}\right) = k\sum_r p_0 \frac{p_r}{p_0} \ln\left(\frac{p_r}{p_0}\right)$$

c) Let $f(x) = x\ln(x) - x + 1$. Then

$$S_0 - S = k\sum_r p_0 \frac{p_r}{p_0} \ln\left(\frac{p_r}{p_0}\right) - kp_0\sum_r \frac{p_r}{p_0} + k\sum_r p_r$$
$$= kp_0\sum_r \frac{p_r}{p_0} \ln\left(\frac{p_r}{p_0}\right) - kp_0\sum_r \frac{p_r}{p_0} + k\sum_r p_0 = kp_0\sum_r f\left(\frac{p_r}{p_0}\right)$$

d) We have

$$f'(x) = \ln(x) + 1 - 1 = \ln(x)$$

and

$$\begin{aligned}
&\ln(x) > 0 \quad \text{for} \quad 1 < x,\\
&\ln(x) < 0 \quad \text{for} \quad 0 < x < 1,\\
&f(1) = 1 \cdot \ln(1) - 1 + 1 = 0,\\
&\lim_{x\to 0} f(x) = 1,
\end{aligned}$$

so $f(x) > 0$ for all $x \geq 0$, except for $x = 1$ where $f(1) = 0$.

e) Since $f(x) \geq 0$ for all $x \geq 0$, we have $S_0 - S \geq 0$, and hence $S \leq S_0$. The equality sign only holds when $\sum_r f\left(p_r/p_0\right) = 0$. Since $f(p_r/p_0)$ is nonnegative, however, the sum can only be zero if $f\left(p_r/p_0\right) = 0$ for all r. This in turn means that $p_r = p_0$ for all r.