10.40 Thermodynamics **Fall 2003**
Problem Set 6

Problem 3

For the same lattice in number 2., but now with only 2 non-interacting particles, each of which can exist in only two states, such that E_1 = 3 kcal/mol and E_2 = 5 kcal/mol, calculate $\underline{U}$, $\underline{S}$, $\underline{G}$, and $\underline{C}_v$. (Note that this is a simple model of a two-state equilibrium, such as a protein which can exist in either a folded or unfolded state, in solution.)

Solution:

The system is a canonical ensemble since it has constant N, $\underline{V}$, and T. In order to evaluate the thermodynamic properties like we did in problem 2, we need to determine our new partition function, Q.

Q = (configuration contribution)(energetic contribution)

There are two ways to interpret this problem. When the question was written, it was assumed that you could only measure the total energy of the system, hence you would be unable to differentiate between a particle in one lattice point and a particle in another lattice point. Therefore, the particles would be indistinguishable regardless of their positions in the lattice. We will call this Method 1: Indistinguishable Particles. The other method assumes that you can measure the energy of an individual lattice point and thus the particles become distinguishable when they occupy different lattice points. We will call this Method 2: Distinguishable Particles. The methods give different answers. We will start with Method 1.

Method 1: Indistinguishable Particles

The energetic contribution to $Q = \sum_j^3 e^{-\beta E_j}$ where $\beta = 1/kT$ and E_j is the energy state

There are three possible energy states (3+3=6), (3+5=8), (5+5=10). There is only one energy state equal to 8 since it is impossible to distinguish between 3+5 and 5+3.

The configuration contribution is due to the fact that there are Ω ways to arrange the two particles in order to get each of the possible energy states.

$$\Omega = \frac{(M+N-1)!}{N!(M-1)!} = \frac{1001!}{100!999!} = 500,500$$ where M = # of sites = 1000, N = # of particles = 2

the particles are non-interacting and indistinguishable

$$Q = \Omega\left(e^{-6\beta} + e^{-8\beta} e^{-10\beta}\right) \qquad \beta = 0.592\ kcal/mol \tag{1}$$

Using similar reasoning to problem 2, the thermodynamic variables in terms of the partition function are:

$$\begin{aligned}
\underline{A} &= -kT\ln\Omega = \underline{G} \\
\underline{S} &= kT\left(\frac{\partial \ln Q}{\partial T}\right)_{\underline{V},N} + k\ln Q \\
\underline{U} &= kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{\underline{V},N} \\
\underline{C}_v &= \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}}
\end{aligned} \tag{2}$$

Using the MATLAB code that is attached to the end of the program to evaluate the functions:

$$\begin{aligned}
\underline{G} &= -1.24\times10^{-20}\ \text{J} \\
\underline{S} &= 1.83\times10^{-22}\ \text{J/K} \\
\underline{U} &= 4.22\times10^{-20}\ \text{J} \\
\underline{C}_v &= 5.70\times10^{-24}\ \text{J/K}
\end{aligned}$$

Method 2: Distinguishable Particles

The energetic contribution to $Q = \sum_j e^{-\beta E_j}$ where β=1/kT and E_j is the energy state

There are four possible energy states (3+3=6), (3+5=8), (5+3=8), (5+5=10) when the particles are **not** on the same lattice point. There are two energy states equal to 8 since it is possible to distinguish between 3+5 and 5+3 (particle with energy 3 kcal/mol on site *i* and particle with energy 5 kcal/mol on site *j* versus 3 kcal/mol on site *j* and 5 kcal/mol on site *i*). When the particles are on the same lattice point there are only three possible energy states since it is impossible to distinguish among the particles on the same lattice point, regardless of their individual energies.

The configurational contribution, Ω, is the same for the 6 and 10 kcal/mol energy states as the indistinguishable case (500,500). However, for the 8 kcal/mol energy level, the configuration contribution, Ω', is different. It is equal to the distinguishable, non-interacting case minus the number of lattice sites (we must subtract the number of lattice sites to avoid double counting the indistinguishable cases where the particles occupy the same site).

$$\Omega' = M^N - M = 999{,}000$$

Thus, the partition function is:

$$Q = \Omega\left(e^{-6\beta} + e^{-10\beta}\right) + \Omega'\left(e^{-8\beta}\right) \tag{3}$$

We now evaluate equation (2) using equation (3) with the MATLAB code that is attached at the end to yield the following results.

$\underline{G} = -1.26\times10^{-20}$ J

$\underline{S} = 1.85\times10^{-22}$ J/K

$\underline{U} = 4.26\times10^{-20}$ J

$\underline{C}_v = 1.00\times10^{-23}$ J/K

MATLAB Codes

Method 1: Indistinguishable Particles

```
% Declare variables symbolically
syms Cv Q E0 E1 E2 q N k T R Nav A S U G dlnQ_dT d2lnQ_dT2;

% We can divide the partition function into two parts,
% a configurational part and an energetic part, so
% Q = q(config) + q(energetic)
% First define energetic partition function for system of 2 particles in
% which the particles can exist in three states:
% [3 3], [3 5] or [5 3],  [5 5]
% The [3 5] and [5 3] states are indistinguishable since we can
% only measure the total energy of the lattice.  Therefore, they
% state where E1 = 8 kcal/mol only appears once in q(energetic)
% q(config) comes directly from Problem 2, so Q = ...
Q = 500500 * (exp(-E0/(R*T)) + exp(-E1/(R*T)) + exp(-E2/(R*T)));

% Determine what the derivative lnQ wrt T is
dlnQ_dT = diff(log(Q), 'T');

% Now we define our variables of interest
A = -k * T * log(Q);
S = k * T * dlnQ_dT + k * log(Q);
U = k * T^2 * dlnQ_dT;
Cv = diff(U, 'T');
G = U - T*S;

% Now start plugging in values for variables,
% paying special attention to units
E0 = 6;     % kcal/mol
E1 = 8;     % kcal/mol
E2 = 10;    % kcal/mol
E0 = E0 * 1000 * 4.186;  % convert to J/mol
E1 = E1 * 1000 * 4.186;  % convert to J/mol
E2 = E2 * 1000 * 4.186;  % convert to J/mol
N = 2;   % # of particles
k = 1.3806503E-23;  % J/K
R = 8.31451; % J/molK
T = 298;  % K
Nav = 6.022137E23; %Avogadro's number, mol^(-1)

% Now we evaluate numbers, working inside out
disp(['A = ', num2str(eval(A)), ' J'])
disp(['S = ', num2str(eval(S)), ' J/K'])
disp(['U = ', num2str(eval(U)), ' J'])
disp(['Cv = ', num2str(eval(Cv)), ' J/K'])
disp(['G = ', num2str(eval(G)), ' J'])

U = eval(U)* Nav / 4186;
disp(['T = ', int2str(T), ' K'])
disp(['U = ', num2str(U), ' kcal/mol'])
```

Method 2: Distinguishable Particles

```
% Declare variables symbolically
syms Cv Q E0 E1 E2 q N k T R Nav A S U G dlnQ_dT d2lnQ_dT2;

% First define partition function for system of 2 particles in
% which the particles can exist in four states:
% (3 3) (3 5) (5 3) (5 5)
% It is assumed that the (35) and (53) states are distinguishable by
% their location in the lattice, except when they occupy the same
% position.  For this case, Q is ...
Q = 500500 * (exp(-E0/(R*T)) + exp(-E2/(R*T))) + 990000*exp(-E1/(R*T));

% Determine what the derivative lnQ wrt T is
dlnQ_dT = diff(log(Q), 'T');

% Now we define our variables of interest
A = -k * T * log(Q);
S = k * T * dlnQ_dT + k * log(Q);
U = k * T^2 * dlnQ_dT;
Cv = diff(U, 'T');
G = U - T*S;

% Now start plugging in values for variables,
% paying special attention to units
E0 = 6;     % kcal/mol
E1 = 8;     % kcal/mol
E2 = 10;    % kcal/mol
E0 = E0 * 1000 * 4.186;  % convert to J/mol
E1 = E1 * 1000 * 4.186;  % convert to J/mol
E2 = E2 * 1000 * 4.186;  % convert to J/mol
N = 2;   % # of particles
k = 1.3806503E-23;  % J/K
R = 8.31451; % J/molK
T = 298;  % K
Nav = 6.022137E23; %Avogadro's number, mol^(-1)

% Now we evaluate numbers, working inside out
disp(['A = ', num2str(eval(A)), ' J'])
disp(['S = ', num2str(eval(S)), ' J/K'])
disp(['U = ', num2str(eval(U)), ' J'])
disp(['Cv = ', num2str(eval(Cv)), ' J/K'])
disp(['G = ', num2str(eval(G)), ' J'])

U = eval(U)* Nav / 4186;
disp(['T = ', int2str(T), ' K'])
disp(['U = ', num2str(U), ' kcal/mol'])
```