

10.40 Thermodynamics

Fall 2003

Problem Set 6

Problem 4

For 0.5 mol of O₂ at 0.1 atm., and 1000 K, compute \underline{U} , \underline{S} , \underline{G} , and \underline{C}_v . You may treat O₂ as an ideal gas at these T and P conditions. Note that both O₂ and the O atom have a net spin of 1 in their ground states. Also the first excited electronic state of O₂ occurs at a thermal energy of 11,300 K and has a net spin of 1/2. The bond dissociation energy of O₂, D_o , is 117.1 kcal/mol and the thermal vibrational and rotational energies are 2230 K and 2.07 K respectively.

Solution:

Since O₂ for this problem is a diatomic, ideal gas, we can use the equations given at the end of the Lecture 23 notes in the *Statistical Thermodynamics: Fundamentals* handout from class. The equations calculate A , U , C_v , and S using expressions derived from the canonical partition function for an ideal gas. The equations are shown below.

$$-\frac{A}{kT} = \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e \right] + \ln \left[\frac{8\pi^2 I kT}{\sigma h^2} \right] - \sum_{i=1}^{3N_{\text{atoms}}-5} \left[\frac{\Theta_{i,v}}{2T} + \ln \left(1 - e^{-\Theta_{i,v}/T} \right) \right] + \frac{D_e}{kT} + \ln \omega_e;$$

$$\frac{U}{kT} = \frac{3}{2} + \frac{2}{2} + \sum_{i=1}^{3N_{\text{atoms}}-5} \left[\frac{\Theta_{i,v}}{2T} + \frac{\Theta_{i,v}/T}{e^{\Theta_{i,v}/T} - 1} \right] - \frac{D_e}{kT};$$

$$\frac{C_V}{k} = \frac{3}{2} + \frac{2}{2} + \sum_{i=1}^{3N_{\text{atoms}}-5} \left[\left(\frac{\Theta_{i,v}}{T} \right)^2 \frac{e^{\Theta_{i,v}/T}}{(e^{\Theta_{i,v}/T} - 1)^2} \right];$$

$$\frac{S}{k} = \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} e^{5/2} \right] + \ln \left[\frac{8\pi^2 I kT e}{\sigma h^2} \right] + \sum_{i=1}^{3N_{\text{atoms}}-5} \left[\frac{\Theta_{i,v}/T}{e^{\Theta_{i,v}/T} - 1} - \ln \left(1 - e^{-\Theta_{i,v}/T} \right) \right] + \ln \omega_e.$$

\underline{G} could also be found by noting that

$$\underline{G} = \underline{U} + NkT - T\underline{S}$$

Thereby eliminating the need to calculate \underline{A} as done in the notes. However, we will calculate A for completeness here. The calculations are straightforward, but tedious. It was recommended that they be performed using Matlab, Maple, Excel, or some other type of software. Some points do need to be clarified to resolve the information given in the problem statement with the form of the equations in the notes.

First, since O₂ has two atoms, there are 2 rotational degrees of freedom and $3N-5 = 1$ vibrational degrees of freedom. The vibrational and rotational energies are given in terms of temperature in the problem statement, where:

$$\theta_v = \frac{h\nu}{k}$$

$$\theta_r = \frac{h^2}{8\pi I k}$$

These expressions could then be inserted directly into the equations. Giving the vibrational and rotational energies in this form saved students the trouble of calculating I and ν in the problem statement. Also, it can be deduced from the reading that for O₂, $\sigma = 2$.

The only other modification that needed to be made to the equations given in the Lecture 23 notes was that the equations assume that only the ground electronic state of the diatomic molecule is occupied, whereas for O₂ at 1000 K we must account for the 1st excited electronic state also being occupied as well. From class notes, we have that the electronic partition function in this case is:

$$q_e = e^{D_e/kT} \left(\omega_{e1} + \omega_{e2} e^{-(\epsilon_2 - \epsilon_1)/kT} \right)$$

$$\ln q_e = \frac{D_e}{kT} + \ln \left(\omega_{e1} + \omega_{e2} e^{-(\epsilon_2 - \epsilon_1)/kT} \right)$$

where $\omega_{e1} = 3$, the degeneracy of the ground state of O₂, $\omega_{e2} = 2$, the degeneracy of the 1st excited electronic state of O₂, $\theta_e = (\epsilon_2 - \epsilon_1)/k = 11,300$ K is the energy of the first excited state, and $D_e = D_o + (1/2)h\nu$. We must replace the contribution from the electronic partition function in each of the equations above with the contribution from this new partition function that takes into account the 1st excited electronic state. Specifically:

$$-\frac{A_e}{kT} = \ln q_e = \frac{D_e}{kT} + \ln \left(\omega_{e1} + \omega_{e2} e^{-\theta_e/T} \right)$$

$$\begin{aligned} \frac{U_e}{kT} &= T \left(\frac{\partial \ln q_e}{\partial T} \right)_{V,N} = T \left(-\frac{D_e}{kT^2} + \frac{\left(\frac{\omega_{e2} \theta_e}{T^2} \right) e^{-\theta_e/T}}{\omega_{e1} + \omega_{e2} e^{-\theta_e/T}} \right) \\ &= -\frac{D_e}{kT} + \frac{\omega_{e2} \theta_e}{T} \frac{e^{-\theta_e/T}}{\left(\omega_{e1} + \omega_{e2} e^{-\theta_e/T} \right)} \end{aligned}$$

$$\begin{aligned} \frac{C_{Ve}}{k} &= \frac{1}{k} \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial}{\partial T} \left(T^2 \left(\frac{\partial \ln q_e}{\partial T} \right)_{V,N} \right) \right)_V = \frac{\partial}{\partial T} \left(-\frac{D_e}{k} + \left(\frac{\omega_{e2} \theta_e e^{-\theta_e/T}}{\omega_{e1} + \omega_{e2} e^{-\theta_e/T}} \right) \right) \\ &= \omega_{e1} \omega_{e2} \left(\frac{\theta_e}{T} \right)^2 \frac{e^{-\theta_e/T}}{\left(\omega_{e1} + \omega_{e2} e^{-\theta_e/T} \right)^2} \\ \frac{S_e}{k} &= T \left(\frac{\partial \ln q_e}{\partial T} \right)_{V,N} + \ln q_e = T \left(-\frac{D_e/k}{kT^2} + \frac{\left(\frac{\omega_{e2} \theta_e}{T^2} \right) e^{-\theta_e/T}}{\omega_{e1} + \omega_{e2} e^{-\theta_e/T}} \right) + \frac{D_e/k}{kT} + \ln \left(\omega_{e1} + \omega_{e2} e^{-(\epsilon_2 - \epsilon_1)/kT} \right) \\ &= \ln \left(\omega_{e1} + \omega_{e2} e^{-(\epsilon_2 - \epsilon_1)/kT} \right) + \frac{\omega_{e2} \theta_e}{T} \frac{e^{-\theta_e/T}}{\left(\omega_{e1} + \omega_{e2} e^{-\theta_e/T} \right)} \end{aligned}$$

We are now ready to go ahead with our calculations. As shown from the contribution of the electronic partition function to the thermodynamic properties, these calculations are very tedious. The results are shown in the table below. The contribution from each of the translational, rotational, vibrational, and electronic partition functions were calculated to facilitate the comparison of intermediate calculations while searching for coding bugs. Note that all properties are extensive.

	<u>A</u> (J)	<u>S</u> (J/K)	<u>U</u> (J)	<u>G</u> (J)	<u>C_V</u> (J/K)
q_t	-91899	98.14	6236	-87742	6.236
q_r	-22811	26.97	4157	-18654	4.157
q_v	4162	1.59	5752	8320	2.791
q_e	-254293	4.57	-249725	-250136	0.004
Q	-364841	131.2	-233580	-360684	13.188

From these calculations, one can see that while the electronic partition function contributed greatly to U and G, it had little affect on C_V. The translational partition function contributed the most to the entropy. Similar conclusions can be drawn about the contributions from other partition functions as well.

Rather than typing in all the equations at the end of Lecture 23, one could derive these using the natural log of each of the translational, vibrational, etc. partition functions, the equations that relate the canonical partition function to the thermodynamic properties from Section 22.4 of the handout, and the symbolic differentiation tool in Matlab. Two sets of code for Matlab, one that used all the equations given in Lecture 23, and the other that uses the shortcut described above, are shown below.

Method 1: Equations from Lecture 23

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% To determine the thermodynamic properties for an ideal, diatomic gas, we will
% use the equations listed at the end of the handout notes for Lecture 23
% We will break up these up into their contributions from the translational
% rotational, vibrational, and electronic degrees of freedom
% First we identify our constants and input values for them
% paying special attention to units
T = 1000;           %K
Nav = 6.022137E23;  % Avogadro's Number, mol^-1
N = 0.5 * Nav;      % number of particles
h = 6.62608E-34;    % Js
k = 1.38066E-23;    % J/K
m = 2*16*1.66054E-27; % mass of O2, kg
theta_r = 2.07;     % K
theta_v = 2230;     % K
theta_e = 11300;    % K
De = 117.1 * 4186 / Nav + (1/2) * theta_v * k; % De = Do (kcal/mol --> J) + (1/2)hv
we1 = 3; we2 = 2;
sigma = 2;
e = exp(1);
P = 0.1*10^5/0.986923; % Pa

% Next we define V using the Ideal Gas EOS
V = N*k*T/P;

% Next, we calculate A, the Helmholtz Free Energy:
At = -k*T*N*log((2*pi*m*k*T/h^2)^(3/2)*V*e/N);
Ar = -k*T*N*log(T/(sigma*theta_r));
Av = k*T*N*((theta_v/(2*T)) + log((1-exp(-theta_v/T))));
Ae = -k*T*N*(De/(k*T) + log((we1 + we2*exp(-theta_e/T))));
A = At + Ar + Av + Ae;

% Calculate S, the Entropy
St = k*N*log((2*pi*m*k*T/h^2)^(3/2)*V*e^(5/2)/N);
Sr = k*N*log(T*e/(sigma*theta_r));
Sv = k*N*log(((theta_v/T)/(exp(theta_v/T)-1) - log((1-exp(-theta_v/T))));
Se = k*N*log((we1 + we2*exp(-theta_e/T)) + (we2*theta_e*exp(-theta_e/T))/T/(we1 + we2*exp(-theta_e/T)));
S = St + Sr + Sv + Se;

% Calculate U, the Internal Energy
Ut = N*k*T*(3/2);
Ur = N*k*T*(2/2);
Uv = N*k*T*(theta_v/(2*T) + (theta_v/T)/(exp(theta_v/T)-1));
Ue = N*k*T^2*(-De/(k*T^2) + (we2*theta_e*exp(-theta_e/T))/T^2/(we1 + we2*exp(-theta_e/T)));
U = Ut + Ur + Uv + Ue;

% Calculate G, the Gibbs Energy
Gt = At + P*V;
Gr = Ar + P*V;
Gv = Av + P*V;
Ge = Ae + P*V;
G = A + P*V;

% Calculate Cv, the Gibbs Energy
Cv_t = (3/2)*k*N;
Cv_r = (2/2)*k*N;
Cv_v = k*N*((theta_v/T)^2 * exp(theta_v/T)/((exp(theta_v/T)-1)^2));
Cv_e = k*N*((we1*we2*(theta_e/T)^2*(exp(-theta_e/T))/(we1 + we2*exp(-theta_e/T))^2));
Cv = Cv_t + Cv_r + Cv_v + Cv_e;

s = [St; Sr; Sv; Se; S];
u = [Ut; Ur; Uv; Ue; U];
g = [Gt; Gr; Gv; Ge; G];
cv = [Cv_t; Cv_r; Cv_v; Cv_e; Cv];

format short e
disp([' S (J/K)   U (J)   G (J)   Cv (J/K) ']);
disp([' ===== ===== ===== =====']);
disp(['s u g cv']);

```

Method 2: Using ln(Q)

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% To determine the partition function for an ideal, diatomic gas, we will look at the
% individual partition functions for the translational, vibrational, etc. contributions
% We will evaluate the natural log of these partition functions

% First we declare all our variables
syms ln_Q ln_qt ln_qv ln_qr ln_qe V;

% Now we identify our constants. We will have to give values for all these constants
% before calculating our final solutions. This serves as a checklist
syms T N Nav h k m theta_r theta_v theta_e De we1 we2 sigma e P;

% Next, we start with the translational partition function, and include in it the
% 1/N! term. This gives us
ln_qt = log((2*pi*m*k*T/h^2)^(3/2)*V*e/N);

% Next, we define ln_qr
% Here, we can substitute theta_r = h^2/(8*pi^2*I*k)
ln_qr = log(T/(sigma*theta_r));

% Now we define ln_qv
% Here, we note that theta_v = h*v/k, where v is the vibrational freq.
% Since we have only one vibrational d.o.f.:
ln_qv = -(theta_v/(2*T)) - log((1-exp(-theta_v/T)));

% And finally, we define ln_qe
% at this temp for O2, we must consider the first electronic state
ln_qe = (De/(k*T)) + log(we1 + we2*exp(-(theta_e/T)));

% Next we calculate Q as the product of all contributing q_i's for N particles
ln_Q = N*(ln_qt + ln_qr + ln_qv + ln_qe);

% Now we're ready to input thermodynamic variables of interest
% These are all extensive variables
syms A U S G Cv P_calc;

% We can determine the contribution of each of the partition functions to the
% overall value of the thermodynamic property of interest
% First, we create a vector of partition functions
ln_q = [N*ln_qt N*ln_qr N*ln_qv N*ln_qe ln_Q];
% Next, we create vectors for our thermodynamic properties of interest
s = zeros(length(ln_q), 1);
u = zeros(length(ln_q), 1);
g = zeros(length(ln_q), 1);
cv = zeros(length(ln_q), 1);

% Now we loop it and print it
for i=1:length(ln_q)
    A(i) = -k * T * ln_q(i);
    U(i) = k * T^2 * diff(ln_q(i), 'T');
    S(i) = k * T * diff(ln_q(i), 'T') + k * ln_q(i);
    G(i) = U(i) + P*V - T*S(i);
    Cv(i) = diff(U(i), 'T');
end

% Check the calculated P with the real value
P_calc = k*T*diff(ln_Q, 'V')

% Now we must input values for our constants, paying special attention to units
T = 1000; % K
Nav = 6.022137E23; % Avogadro's Number, mol^-1
N = 0.5 * Nav; % number of particles
h = 6.62608E-34; % Js
k = 1.38066E-23; % J/K
m = 2*16*1.66054E-27; % mass of O2, kg
theta_r = 2.07; % K
theta_v = 2230; % K
theta_e = 11300; % K
De = 117.1 * 4186 / Nav + (1/2) * theta_v * k; % De = Do (kcal/mol --> J) + (1/2)hv

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```

we1 = 3;
we2 = 2;
sigma = 2;
e = exp(1);
P = 0.1*10^5/0.986923; % Pa
V = (N*k*T/P);      % m^3

% We should check for consistency:
disp('All the numbers below should be zero');
disp('G - (A + PV) = 0');
eval(G(length(ln_q)) - eval(A(length(ln_q)) + P*V))
disp('A - (U - TS) = 0');
eval(A(length(ln_q)) - eval(U(length(ln_q)) - T*S(length(ln_q))))
disp('G - (U + PV - TS) = 0');
eval(G(length(ln_q)) - eval(U(length(ln_q)) - T*S(length(ln_q)) + P*V))
disp('P_calc = NkT/R (it`s an ideal gas)');
P_calc

% Finally, output the results
for i=1:length(ln_q)
    s(i) = eval(S(i));
    u(i) = eval(U(i));
    g(i) = eval(G(i));
    cv(i) = eval(Cv(i));
end

format short e
disp([' S (J/K)    U (J)    G (J)    Cv (J/K) ']);
disp([' =====  =====  =====  =====']);
disp([s u g cv]);

```