CH352 Assignment 3: Due Thursday, 27 April 2017

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Q1 Adiabatic quasi-static volume and temperature changes in ideal gases

In the last assignment you showed that the internal energy of a mono-atomic ideal gas sample containing N particles was proportional to the temperature, T and N, so that $U = \frac{3}{2}Nk_BT$. Since the heat capacity at constant volume is $C_V = (\partial U/\partial T)_{V,N}$, $C_V = \frac{3}{2}Nk_B$ for an ideal gas. Thus, in this system, we find $\mathrm{d}U = C_V\,\mathrm{d}T$.

(i) Use the above result and the differential form of the fundamental energy equation, $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$, (assuming fixed N) to obtain an expression for the differential entropy change $\mathrm{d}S$ in a general, constant-N, ideal gas process.

Solution:

$$\begin{aligned}\mathrm{d}S &= \frac{1}{T}\,\mathrm{d}U + \frac{p}{T}\,\mathrm{d}V \\ &= \frac{C_V}{T}\,\mathrm{d}T + \frac{p}{T}\,\mathrm{d}V \\ &= \frac{3}{2}\frac{Nk_B}{T}\,\mathrm{d}T + \frac{p}{T}\,\mathrm{d}V\end{aligned}$$

(ii) Consider a quasi-static transformation of an N-particle sample of ideal gas, and re-express your result for $\mathrm{d}S$ from (i) for this special case ideal gas process.

Solution:

For a quasi-static process, $p_{\text{int}} = p_{\text{ext}} = Nk_BT/V$, so

$$\begin{aligned}\mathrm{d}S &= \frac{C_V}{T}\,\mathrm{d}T + \frac{Nk_B}{V}\,\mathrm{d}V \\ &= Nk_B\left(\frac{3}{2}\frac{1}{T}\,\mathrm{d}T + \frac{1}{V}\,\mathrm{d}V\right)\end{aligned}$$

(iii) Integrate your result from (ii) to obtain a general expression for the entropy change $\Delta S = S_2 - S_1$ accompanying the quasi-static, fixed-N transformation from (T_1, V_1), to (T_2, V_2).

Solution:

$$\begin{aligned}\Delta S &= \int_1^2 \mathrm{d}S \\ &= Nk_B \left(\frac{3}{2} \ln\left(\frac{T_2}{T_1}\right) + \ln\left(\frac{V_2}{V_1}\right) \right)\end{aligned}$$

(iv) In an adiabatic quasi-static expansion of an ideal gas, how do you reconcile the following two facts: (1) the increase in volume should lead to an increase in entropy, but (2) in an adiabatic process $\delta q = 0$ so there should be no change in entropy (since $\mathrm{d}S = \delta q/T = 0$)?

Solution:

$$\frac{3}{2} \ln\left(\frac{T_2}{T_1}\right) = -\ln\left(\frac{V_2}{V_1}\right)$$

The increase in entropy from an increase in volume is exactly offset by the decrease in entropy from a decrease in temperature.

Q2 The work of compression

One mole of a van der Waals gas is compressed quasi-statically and isothermally from V_1 to V_2. For a van der Waals gas the equation of state is

$$p = \frac{RT}{(V-b)} - \frac{a}{V^2} \tag{Q2.1}$$

where a and b are positive constants of the gas, V is the volume, and RT is the gas constant times temperature. The constant b is related to the excluded volume of each gas molecule, and a is related to the strength of intermolecular attraction between molecules.

(i) Write an expression for the work done.

Solution:

$$
\begin{aligned}
w &= -\int_{V_1}^{V_2} p\,\mathrm{d}V \\
&= -\int_{V_1}^{V_2} \left(\frac{RT}{(V-b)} - \frac{a}{V^2}\right)\mathrm{d}V \\
&= RT\ln\left(\frac{V_1-b}{V_2-b}\right) + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)
\end{aligned}
$$

(ii) Compared to compression of an ideal gas, is more or less work required in the low density limit? What about the high density limit? Why?

Solution:

In the low density limit, the volumes for this mole of gas are large compared to b, and the work required to compress a van der Waals gas is **less** because of the negative attractive (a) term.

In the high density limit, the volumes are relatively similar and the excluded volume (b) term will dominate, increasing the work required for compression compared to an ideal gas. Therefore, the work required to compress a van der Waals gas is **more** than for an ideal gas.

Q3 Ideal efficiency of a car engine

Suppose the compression ratio in your car engine is $V_2/V_1 = 8$. For a diatomic gas, $C_V = (5/2)Nk_B$ and for ethane $C_V \sim 5Nk_B$.

(i) What is the efficiency of your engine if the working fluid is a diatomic gas?

Solution:

Based on the textbook,

$$\eta = 1 - \frac{1}{r^{Nk_B/C_V}}$$

where r is the compression ratio.

$$
\begin{aligned}
&= 1 - \frac{1}{8^{2/5}} \\
&= 0.564725 = 56.4725\%
\end{aligned}
$$

(ii) Which is more efficient: a diatomic gas or ethane?

Solution:

The ideal diatomic gas is more efficient: $0.340246 < 0.564725$.

(iii) Would your engine be more or less efficient with a higher compression ratio?

Solution:

A higher compression ratio would make the engine more efficient: If the compression ratio is $r = 1$, the engine has 0% efficiency for any value of heat capacity. A large compression ratio means you're subtracting a smaller number from 1 to calculate the efficiency.

Q4 Computing enthalpy and entropy with a temperature dependent heat capacity

The heat capacity of liquid n-butane depends on temperature:

$$C_p(T) = a + bT \tag{Q4.1}$$

where $a = 100\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and $b = 0.1067\,\mathrm{J\,K^{-2}\,mol^{-1}}$ from its freezing temperature $T_\mathrm{f} = 140\,\mathrm{K}$ to $T_\mathrm{b} = 270\,\mathrm{K}$, its boiling temperature.

(i) Compute ΔH for heating liquid butane from $T_A = 170\,\mathrm{K}$ to $T_B = 270\,\mathrm{K}$ at constant pressure.

Solution:

$$\begin{aligned}
\left(\frac{\partial H}{\partial T}\right)_p &= C_p \\
\mathrm{d}H &= C_p(T)\,\mathrm{d}T \\
&= (a + bT)\,\mathrm{d}T \\
\Delta H &= \int_{170\,\mathrm{K}}^{270\,\mathrm{K}} (a + bT)\,\mathrm{d}T \\
&= \left(aT + \frac{1}{2}bT^2\right)\Bigg|_{170\,\mathrm{K}}^{270\,\mathrm{K}} \\
&= 100\,\mathrm{K}\,a + \frac{1}{2}b\left(270^2 - 170^2\right)\mathrm{K}^2 \\
\Delta H &= 12.3474\,\mathrm{kJ\,mol^{-1}}
\end{aligned}$$

(ii) Compute ΔS for the same process.

Solution:

$$\begin{aligned}
\mathrm{d}S &= \frac{C_p}{T}\,\mathrm{d}T \\
\Delta S &= \int_{170\,\mathrm{K}}^{270\,\mathrm{K}} \left(\frac{a}{T} + b\right) \mathrm{d}T \\
&= (a \ln T + bT)\Big|_{170\,\mathrm{K}}^{270\,\mathrm{K}} \\
&= a \ln\left(\frac{270}{170}\right) + b100\,\mathrm{K} \\
\Delta S &= 56.9324\,\mathrm{J\,K^{-1}\,mol^{-1}}
\end{aligned}$$

Q5 Objects in thermal contact and enthalpy of vaporization of water at $T = 473\,\mathrm{K}$

(i) Suppose two objects A and B with heat capacities C_A and C_B and initial temperatures T_A and T_B, are brought into thermal contact. If $C_A \gg C_B$ is the equilibrium temperature closer to T_A or T_B or is not enough information given? What about if $c_A \gg c_B$? Show some math to support your argument.

Solution:

The equilibrium temperature of the system, as derived in class will be

$$T = \frac{C_A T_A + C_B T_B}{C_A + C_B}.$$

Then, if $C_A \gg C_B$,

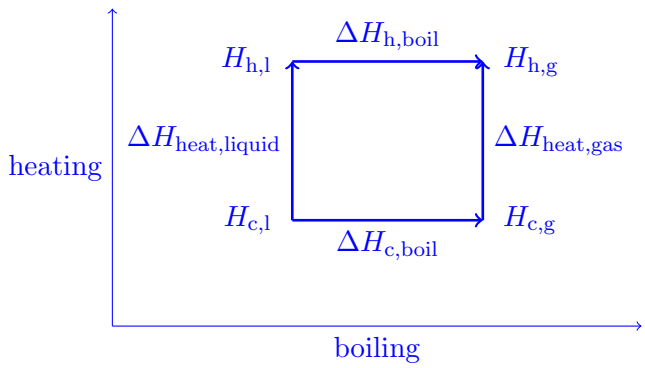
$$\begin{aligned}
T &\approx \frac{C_A T_A}{C_A} \\
&= T_A
\end{aligned}$$

For $c_A \gg c_B$: To give an answer, the relative sizes of the two objects need to be known, so not enough information is given. c_A is a specific heat, and it is an intensive property of an object or material.

(ii) Suppose you want to know how much heat it would take to boil water at $p = 1\,\mathrm{atm}$ and $T = 473\,\mathrm{K}$, rather than at $T = 373\,\mathrm{K}$. At $T = 373\,\mathrm{K}$ the enthalpy of vaporization is $\Delta H_{\mathrm{boil}}(T = 373\,\mathrm{K}) = 40.7\,\mathrm{kJ\,mol^{-1}}$. Assuming that the heat capacities of the liquid ($C_{p,\mathrm{liquid}} = 75\,\mathrm{J\,K^{-1}\,mol^{-1}}$)

and the vapor ($C_{p,\text{vapor}} = 3.5\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$) are constant over this temperature range, calculate the enthalpy of vaporization at $T = 473\,\text{K}$, $\Delta H_{\text{boil}}(T = 473\,\text{K})$.

Solution:



$$
\begin{aligned}
\Delta H_{\text{c,boil}} &= 40.7\,\text{kJ}\,\text{mol}^{-1} \\
\Delta H_{\text{heat,liquid}} &= \int_{373\,\text{K}}^{473\,\text{K}} C_{p,\text{liquid}}\,\text{d}T \\
&= 7500\,\text{J}\,\text{mol}^{-1} \\
\Delta H_{\text{heat,gas}} &= \int_{373\,\text{K}}^{473\,\text{K}} C_{p,\text{vapor}}\,\text{d}T \\
&= 350\,\text{J}\,\text{mol}^{-1} \\
\Delta H_{\text{h,boil}} &= -\Delta H_{\text{heat,liquid}} + \Delta H_{\text{c,boil}} + \Delta H_{\text{heat,gas}} \\
&= (-7.5 + 40.7 + 0.35)\,\text{kJ}\,\text{mol}^{-1} \\
\boxed{\Delta H_{\text{h,boil}} = 33.6\,\text{kJ}\,\text{mol}^{-1}}
\end{aligned}
$$

Q6 Oxygen gas at room temperature

Consider a gas phase system of N identical, indistinguishable, independent oxygen atoms, with partition function Q. Suppose the single particle partition function is the product of a translational partition function q_{t} and an electronic partition function q_{e}, so

$$q = q_{\text{t}} q_{\text{e}}. \tag{Q6.1}$$

The nine electronic states of the lowest energy ^3P electronic level are split due to spin-orbit coupling. Table 1 lists various characteristics of these states as well as some of the higher energy levels. Data are reported for $T = 300\,\text{K}$, and for convenience energies are given in Kelvin units.

Table 1: Atomic oxygen electronic energy level characteristics

$^{2S+1}L_J$	$g = 2J+1$	$(\Delta\epsilon_n/k_B)/\mathrm{K}$	$\beta\Delta\epsilon_n$	$(\beta\Delta\epsilon_n)^2$
$^3P_2$	5	0	0	0
$^3P_1$	3	232	0.7733	0.5980
$^3P_0$	1	348	1.16	1.3456
$^1D_2$	5	22 860	76.2	
$^1S_0$	1	48 621	162.1	

(i) Use the fact that the internal energy is

$$U = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} \tag{Q6.2}$$

to show that

$$U = -N\left(\frac{1}{q_\mathrm{t}}\frac{\partial q_\mathrm{t}}{\partial \beta} + \frac{1}{q_\mathrm{e}}\frac{\partial q_\mathrm{e}}{\partial \beta}\right) = U_\mathrm{t} + U_\mathrm{e} \tag{Q6.3}$$

Solution:

$$\begin{aligned}
Q &= \frac{q^N}{N!} = \frac{q_\mathrm{t}^N q_\mathrm{e}^N}{N!} \\
U &= -\frac{1}{Q}\frac{\partial Q}{\partial \beta} \\
&= -\frac{\partial \ln Q}{\partial \beta} \\
&= -N\frac{\partial}{\partial \beta}\ln\left(q_\mathrm{e} q_\mathrm{t}\right) \\
&= -N\left(\frac{\partial \ln q_\mathrm{t}}{\partial \beta} + \frac{\partial \ln q_\mathrm{e}}{\partial q_\mathrm{e}}\right) \\
&= -N\left(\frac{1}{q_\mathrm{t}}\frac{\partial q_\mathrm{t}}{\partial \beta} + \frac{1}{q_\mathrm{e}}\frac{\partial q_\mathrm{e}}{\partial \beta}\right) \\
&= U_\mathrm{t} + U_\mathrm{e}
\end{aligned}$$

where $U_i = -N\frac{1}{q_i}\frac{\partial q_i}{\partial \beta}$.

(ii) Calculate (a) the translational component of the internal energy U_t and (b) the translational component of the constant volume heat capacity:

$$C_V^\mathrm{t} = \left(\frac{\partial U_\mathrm{t}}{\partial T}\right)_{N,V}. \tag{Q6.4}$$

Solution: As derived in the last homework, the internal energy for a structureless ideal gas

$$\boxed{U_{\mathrm{t}} = \frac{3}{2} N k_B T}$$

$$\boxed{C_V^{\mathrm{t}} = \frac{3}{2} N k_B}$$

(iii) (a) Comment on why we can neglect the contributions from the states $^1D_2$ and $^1S_0$ at room temperature and calculate the general expression in this case for (b) the electronic component of the internal energy U_{e} and (c) the electronic heat capacity

$$C_V^{\mathrm{e}} = \left(\frac{\partial U_{\mathrm{e}}}{\partial T}\right)_{N,V} = -k_B \beta^2 \left(\frac{\partial U_{\mathrm{e}}}{\partial \beta}\right)_{N,V}. \tag{Q6.5}$$

Solution: The $^1D_2$ and $^1S_0$ states can be ignored because they are so high in energy that at room temperature, they are not populated and therefore do not contribute to the energy or the heat capacity.

$$\begin{aligned}
q_{\mathrm{e}} &= \sum_{i=1}^{3} g_i \mathrm{e}^{-\epsilon_i \beta} \\
U_{\mathrm{e}} &= -N \frac{1}{q_{\mathrm{e}}} \frac{\partial q_{\mathrm{e}}}{\partial \beta} \\
&= N \frac{1}{q_{\mathrm{e}}} \left(0 + g_2 \epsilon_2 \mathrm{e}^{-\epsilon_2 \beta} + g_3 \epsilon_3 \mathrm{e}^{-\epsilon_3 \beta}\right) \\
&\boxed{U_{\mathrm{e}} = \frac{N}{q_{\mathrm{e}}} \sum_{i=2}^{3} g_i \epsilon_i \mathrm{e}^{-\epsilon_i \beta}}
\end{aligned}$$

$$\begin{aligned}
C_V^{\mathrm{e}} &= -k_B \beta^2 \left(\frac{\partial U_{\mathrm{e}}}{\partial \beta}\right)_{N,V} \\
&= N k_B \beta^2 \left[\frac{1}{q_{\mathrm{e}}} \frac{\partial^2 q_{\mathrm{e}}}{\partial \beta^2} - \frac{1}{q_{\mathrm{e}}^2} \left(\frac{\partial q_{\mathrm{e}}}{\partial \beta}\right)^2\right] \\
&= N k_B \beta^2 \frac{1}{q_{\mathrm{e}}^2} \left[q_{\mathrm{e}} \sum_{i=2}^{3} g_i \epsilon_i^2 \mathrm{e}^{-\epsilon_i \beta} - \left(\sum_{i=2}^{3} g_i \epsilon_i \mathrm{e}^{-\epsilon_i \beta}\right)^2\right]
\end{aligned}$$

(iv) You should be able to write your results from (ii) and (iii) in the form $C_V = Nk_B \times x$ where x is some dimensionless number. Compute these dimensionless numbers for C_V^{t} and, using the data in Table 1 for $T = 300\,\mathrm{K}$, C_V^{e} at this temperature. From this, you can get an idea of how big the spin-orbit contribution to the heat capacity is compared to the translational heat capacity for atomic oxygen at room temperature.

Solution:

$$C_V^{\mathrm{t}} = \frac{3}{2} N k_B$$
$$C_V^{\mathrm{e}}(300\,\mathrm{K}) = 0.1407 N k_B$$

At this temperature, the translation heat capacity is only about 10 times larger than the electronic heat capacity.