Statistical and Thermal Physics: Class Exam I
3 March 2016

Name: ___________________________ Total: /50

Instructions

- There are 6 questions on 9 pages.
- Show your reasoning and calculations and always justify your answers.

Physical constants and useful formulae

\[ R = 8.31 \text{ J/mol K} \quad N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad k = 1.38 \times 10^{-23} \text{ J/K} \quad 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa} \]

Question 1

An ideal gas undergoes a process in which its volume increases by a factor of 4 and its temperature increases by a factor of 3. By what factor is the final pressure related to the initial pressure?

\[ PV = NkT \implies \frac{P}{V} = \frac{NkT}{V} \]

\[ P_f \cdot \frac{V_f}{V_i} = NkT_f \cdot \frac{V_i}{V_f} \]

\[ = \frac{P_f}{P_i} = \frac{T_f}{T_i} \cdot \frac{V_i}{V_f} = \frac{T_f}{T_i} \cdot \frac{V_i}{V_f} \]

\[ = \frac{P_f}{P_i} = \frac{3}{4} \]

/4
Question 2

Answer either part a) or part b) for full credit for this problem.

a) Determine the isobaric expansion coefficient and the isothermal compressibility for an ideal gas.

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \]

\[ V = \frac{NkT}{P} \]

\[ = 0 \quad \alpha = \frac{1}{V} \frac{Nk}{P} = \frac{Nk}{PV} = \frac{1}{T} = 0 \quad \alpha = \frac{1}{T} \]

iso thermal comp.

\[ k = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \]

\[ \frac{\partial V}{\partial P} = \frac{NkT}{P^2} = 0 \quad k = \frac{NkT}{P^2v} = \frac{PV}{P^2v} \]

\[ = 0 \quad k = \frac{1}{P} \]

As pressure increases, \( k \) decreases.

Question 2 continued ...
b) A monoatomic ideal gas undergoes an adiabatic expansion in which its volume increases by a factor of eight. Determine the work done on the gas in terms of the initial volume and pressure. Note that $\gamma = 5/3$.

\[ W = -\int PdV \]

\[ = -P_i V_i \int_{V_i}^{V_f} \frac{dV}{V_f^{\gamma}} = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} V d\frac{P}{\gamma} = -P_V^x = const. \]

\[ = p \]

\[ PV^\gamma = const. \]

\[ \Rightarrow PV^\gamma = P_i V_i^{\gamma} \]

\[ = -P_i V_i^{\gamma} \left[ \frac{V_f}{(V_f^{\gamma})^{1-\gamma}} - \frac{V_i}{(V_i^{\gamma})^{1-\gamma}} \right] \]

\[ = -P_i V_i^{\gamma} \left[ \left( \frac{V_f}{V_i} \right)^{1-\gamma} - \left( \frac{V_i}{V_i} \right)^{1-\gamma} \right] \]

\[ = -P_i V_i^{\gamma} \left[ \left( \frac{V_f}{V_i} \right)^{1-\gamma} - 1 \right] \]

\[ = -P_i V_i^{\gamma} \left[ \left( 8 \right)^{1-\gamma} - 1 \right] \]

\[ = -P_i V_i^{\gamma} \left[ \left( 8 \right)^{5/3} - 1 \right] \]

\[ = 3 \frac{P_i V_i^{\gamma}}{2} \left[ \left( 8 \right)^{-2/3} - 1 \right] \]

\[ = \frac{3}{2} \frac{P_i V_i^{\gamma}}{2} \left[ \left( \frac{1}{8} \right)^{-1} - 1 \right] = -\frac{9}{8} P_i V_i^{\gamma} \]
Question 3
A heat engine operates by having a monoatomic ideal gas undergo the process indicated on the $PV$ diagram.

a) Determine the work done by the engine in one cycle.

\[
W = - \int P \, dV = - \text{area under } PV
\]

Each block is $100 \text{ J} = 10^5 \text{ Pa} \times 10^{-3} \text{ m}^3$

<table>
<thead>
<tr>
<th>Stage</th>
<th>$dV$</th>
<th>$W$</th>
<th>$W_{\text{total}} = -700 \text{ J}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$dV = 0$</td>
<td>$W_1 = 0$</td>
<td>$W_{\text{done by gas}} = 700 \text{ J}$</td>
</tr>
<tr>
<td>2</td>
<td>area = 4 blocks</td>
<td>$W_2 = -400 \text{ J}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>area = 6 blocks</td>
<td>$W_3 = -600 \text{ J}$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$dV = 0$</td>
<td>$W_4 = 0$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>area = 3 blocks</td>
<td>$W_5 = 300 \text{ J}$</td>
<td></td>
</tr>
</tbody>
</table>

b) Determine the heat that enters the gas during the cycle.

First get $\Delta E$ then use $\Delta E = W + Q$ and $E = \frac{3}{2} N k T = \frac{3}{2} P V$

For stage 1 $\Delta E = \frac{3}{2} \Delta (PV)$

\[= \frac{3}{2} (400 \text{ J} - 100 \text{ J}) = 450 \text{ J} = Q + W = Q - 100 \text{ J} = 0 \Rightarrow Q = 450 \text{ J} \]

$\Delta (PV) = 400 \text{ J}$

\[\Rightarrow \Delta E = 600 \text{ J} \]
c) Determine the efficiency of the engine.

\[ \eta = \frac{W}{Q_{in}} = \frac{450J}{450J + 1000J + 600J} = \frac{450J}{2050J} = 0.22 \]

\[ \text{max when } PV \text{ is max} = 900J \Rightarrow T_h = \frac{900J}{Nk} \]

\[ \min \text{ when } PV \text{ is min} = 100J \Rightarrow T_l = \frac{100J}{Nk} \]

\[ \Rightarrow \eta = 1 - \frac{T_l}{T_h} = 1 - \frac{1}{q} = \frac{8}{q} = 0.89 \]
Question 4
Consider an ideal gas that is thermally isolated from its surroundings. The gas is allowed to expand freely into a region, also isolated thermally from its surroundings, and which was previously a vacuum.

a) Which of the following is true?
   i) The temperature at the end of the expansion is the same as at the beginning.
   ii) The temperature at the end of the expansion is higher than at the beginning.
   iii) The temperature at the end of the expansion is lower than at the beginning.

b) Which of the following is true?
   i) The entropy at the end of the expansion is the same as at the beginning.
   ii) The entropy at the end of the expansion is higher than at the beginning.
   iii) The entropy at the end of the expansion is lower than at the beginning.

Briefly explain your answers.

\[ \Delta E = Q + W \]
\[ Q = 0 \text{ since thermally isolated} \]
\[ W = 0 \text{ since vacuum has } P = 0. \]

\[ \Delta E = 0 \text{ But } E = \frac{3}{2} NkT = 0 \text{ } \Delta E = \frac{3}{2} Nk \Delta T = 0 \text{ } \Delta T = 0 \]

Entropy must increase or stay constant. If it stayed constant the reverse process would be possible. It isn't. So \( \Delta S > 0 \)
Question 5

Answer either part a) or part b) for full credit for this problem.

a) Consider a system with a fixed number of particles. Starting with the fundamental thermodynamic identity, show that

\[
e_V = T \left( \frac{\partial S}{\partial T} \right)_V.
\]

\[
dE = TdS - PdV \quad \text{and} \quad dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV
\]

\[
= T \left( \frac{\partial S}{\partial T} \right)_V dT + \left[ T \left( \frac{\partial S}{\partial V} \right)_T - P \right] dV
\]

Thus \( \left( \frac{\partial E}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V \).

Now \( dE = SdQ + SdW \Rightarrow SdQ = dE - SdW \)

\[
= dE + PdV
\]

\[
= \left( \frac{\partial E}{\partial T} \right)_T dT + \left[ ... \right] dV
\]

Thus \( c_V = T \left( \frac{\partial S}{\partial T} \right)_V \)

Question 5 continued...
b) Using the Gibbs free energy, \( G = E - TS + PV \), show that

\[
\left( \frac{\partial S}{\partial P} \right)_{T,N} = - \left( \frac{\partial V}{\partial T} \right)_{P,N}
\]

\[
dG = dE - TdS - SdT + PdV + VdP + \mu dN
\]

\[
= TdS - PdA - TdS - s dT + PdV + VdP + \mu dN
\]

\[
= -s dT + V dP + \mu dN
\]

\[
= 0
\]

\[
-S = \left( \frac{\partial G}{\partial T} \right)_{P,N}
\]

\[
V = \left( \frac{\partial G}{\partial P} \right)_{T,N}
\]

\[
\frac{\partial S}{\partial P} = - \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial T} \right)_{P,N} = - \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial T} \right)_{P,N} = - \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial P} \right)_{T,N}
\]

\[
= 0
\]

\[
\left( \frac{\partial S}{\partial P} \right)_{T,N} = - \left( \frac{\partial V}{\partial T} \right)_{P,N}
\]
Question 6

A particular chemical reaction takes place in contact with a reservoir at temperature of 298 K and a pressure of 1.00 atm. It is determined that for this reaction $\Delta H = -300 \text{ kJ mol}^{-1}$ and $\Delta S = -800 \text{ J mol}^{-1}$.

a) Determine the change in Gibbs free energy, $\Delta G$, for this reaction.

\[ G = E - TS + PV = H - TS \]

Here $\Delta G = \Delta H - \Delta (TS)$ but $\Delta (TS) = T \Delta S$.

\[ \Rightarrow \Delta G = \Delta H - T \Delta S \]

\[ = -300 \times 10^3 \text{ J mol}^{-1} - 298 (-800 \text{ J mol}^{-1}) \]

\[ = -61.6 \times 10^3 \text{ J mol}^{-1} \]

b) Can this reaction occur without any non-mechanical work done on the system? For your choice describe either how much non-mechanical work the reaction could produce or how much it would require.

In any process $\Delta G \leq W_{\text{non-mech}}$

\[ \Rightarrow -61.6 \times 10^3 \text{ J mol}^{-1} \leq W_{\text{non-mech}} \]

Yes if $W_{\text{non-mech}} = 0$, this is still true.

It could produce $61.6 \times 10^3 \text{ J}$