Thermodynamics and Statistical Physics

## Part 1– Thermodynamics

## Intermediate Exam 3

Tuesday, October 31 2017, 9:00-12:00, Aletta Jacobshal 01

The total number of points that can be reached in this exam is 90.

Final grade = (points/10) + 1.

1) Short questions (**30 pt**)

a) Describe the second law of thermodynamics in your own words. (**2 pt**)
b) Describe the third law of thermodynamics in your own words. (**2 pt**)
c) Explain the concept of *reversible changes/processes* in thermodynamics. Why are reversible processes conceptually important? (**3 pt**)
d) Derive the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$. (**3 pt**)
e) Consider a heat engine working between two reservoirs with temperatures $T_1 = 1200\text{K}$ and $T_2 = 300\text{K}$. Show that the maximum work the machine can deliver per 2 kJ of heat extracted from reservoir 1, amounts to 1.5 kJ. (**3 pt**)
f) A photon of visible light with energy 2 eV is absorbed by a macroscopic body held at 300 K. By what factor does the number of microstates of the body change? What is the change for a 800 MHz photon used in mobile phones (photon energy is about 3.3 x $10^{-6}$ eV)? (**3 pt**)
g) The number of ideal gas molecules per unit volume having speeds between $v$ and $v + dv$ and traveling at angles between $\theta$ and $\theta + d\theta$ is given by $nf(v)dv\frac{1}{2}sin\theta d\theta$ with $f(v)$ being the Maxwell Boltzmann distribution. Show that the number of these particles that hit a unit area of wall per unit time is proportional to $vf(v)$. What does this tell you about the mean kinetic energy of ideal gas particles effusing out of a large vessel through a small hole? (**5 pt**)
h) Describe the concept of thermal conductivity within the kinetic theory of gases (use a sketch). What is the role of the mean free path? (**4 pt**)
i) An ideal mono-atomic gas has initial volume $V_i$= 1 l, temperature $T_i$= 373 K and pressure $p_i$= 6.258 $10^4$ Pa. The gas is reversibly cooled and compressed to $T_f$= 298 K and $V_i$= 0.5 l. What is the entropy change of the surroundings? (**5 pt**)

2) Two compartments (**30 pt**)

Consider an ideal gas in a container. The container is separated into two compartments A and B, separated by a wall that moves without friction. Also, the wall thermally isolates compartments A and B from each other. Compartment B is in contact with an infinite heat bath and stays at constant temperature $T_B$. The starting conditions are $T_A = T_B = 300$ K, $V_A = V_B$ =2 l and $n_A = n_B = 2$ mol. Now compartment A is heated and the frictionless wall moves reversibly, until $V_B$ is reduced to 1 l. The molar heat capacity at constant volume is $C_{V,m} = 20$ JK$^{-1}$mol$^{-1}$.

a) Show that the work done by the gas in compartment A is $\Delta W_A = -3.458$ kJ. (**8 pt**)
b) Determine the change in internal energy $\Delta U_B$ of the ideal gas in compartment B. (**6 pt**)
c) Calculate the amount of heat that went into compartment B during the process. (**4 pt**)
d) Determine the change in internal energy $\Delta U_A$ of the ideal gas in compartment A (**8 pt**)
e) Calculate the heat that went into compartment A. (**4 pt**)

## 3) A thermodynamic cycle (**30 pt**)

Consider one mol of ideal gas (the system) in a state $A$ with volume $V_A$, pressure $p_A$ and temperature $T_A = 300$K. Consider the following thermodynamic cycle:

$$A \rightarrow B \rightarrow C \rightarrow A$$

Step 1: reversible adiabatic expansion from *A* to *B*.
Step 2: reversible compression at constant volume from *B* to *C*.
Step 3: reversible compression at constant pressure from *C* to *A*.

In state *B*, the gas has a pressure $p_B$ and a volume $2V_A$. In state *C*, the gas has a pressure $p_A$ and a volume $2V_A$. The heat capacities are given by $C_{p,m} = \frac{7}{2}R$ and $C_{p,m} - C_{V,m} = R$.

a) Sketch this thermodynamic cycle in a $p - V$ diagram. Indicate in which steps heat flows and in which direction (into the system and out of the system). (**5 pt**)

b) For the reversible adiabatic expansion/compression of an ideal gas, show that $T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1}$ with $\gamma = 1 + \frac{R}{C_{V,m}}$ and determine $T_B$ and $p_B$. (**5 pt**)

c) Determine $T_C$. (**5 pt**)

d) Determine $\Delta Q$ and $\Delta W$ for each of the three steps. Hint: For step 3 (constant pressure), it is handy to calculate the enthalpy change of an ideal gas. (**10 pt**)

e) To let this thermodynamic cycle do work, do we have to run it in the direction $A \rightarrow B \rightarrow C \rightarrow A$ or do we have to reverse the process? Give a motivation! (**5 pt**)

**Physical constants**:

| | |
|---|---|
| Avogadro's number: | $N_0$= 6.02 x $10^{23}$ $mol^{-1}$ |
| Planck's constant: | $h$ = 6.626 x $10^{-34}$ Js |
| | $\hbar = \frac{h}{2\pi}$ = 1.055 x $10^{-34}$ Js |
| Boltzmann's constant: | $k$ = 1.381 x $10^{-23}$ J $K^{-1}$ |
| Gas constant: | $R$ = 8.31 J $mol^{-1}$ $K^{-1}$ |
| Speed of light: | $c$ = 3 x $10^8$ m $s^{-1}$ |
| Electron rest mass: | $m_e$ = 9.11 x $10^{-31}$ kg |
| Proton rest mass: | $m_p$ = 1.67 x $10^{-27}$ kg |
| Charge of the electron: | $e$ = 1.60 x $10^{-19}$ C |
| Bohr magneton: | $\mu_B = \frac{e\hbar}{2m_e}$ = 9.27 x $10^{-24}$ A $m^2$ |
| Permeability of vacuum: | $\mu_0$ = $4\pi$ x $10^{-7}$ N $A^{-2}$ |
| Molar volume at STP: | 22.4 litre |

**Formula Sheet:**

Mean of a probability distribution: $\langle x\rangle = \int xP(x)dx$

Boltzmann distribution: $P \propto e^{-E/(k_BT)}$

*Ideal gas properties (note these are NOT universal relationships – always check if the required assumptions are valid for a given problem!):*

Maxwell Boltzmann distribution: $f(v)dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 dv\, e^{-mv^2/(2k_BT)}$, $\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}}$, $\langle v^2\rangle = \frac{3k_BT}{m}$

Molecular flux per area per second: $\Phi = \frac{1}{4}n\langle v\rangle$

Mean free path: $\lambda \approx \frac{1}{\sqrt{2}n\sigma}$

Viscosity: $\eta = \frac{1}{3}nm\lambda\langle v\rangle$ and momentum flux: $\Pi_z = -\eta\frac{\partial\langle u_x\rangle}{\partial z}$

Thermal conductivity: $\kappa = \frac{1}{3}C_V\lambda\langle v\rangle$ and heat flux: $J_z = -\kappa\frac{\partial T}{\partial z}$

Diffusion coefficient: $D = \frac{1}{3}\lambda\langle v\rangle$ and heat flux: $\Phi_z = -D\frac{\partial n^*}{\partial z}$

Thermal diffusion equation: $\frac{\partial T}{\partial t} = D\nabla^2 T$ with $D = \frac{\kappa}{C}$

Heat capacity at constant volume: $C_V = \left(\frac{\partial Q}{\partial T}\right)_V$

Heat capacity at constant pressure: $C_p = \left(\frac{\partial Q}{\partial T}\right)_p$

For an ideal gas: $C_p - C_V = R$

Adiabatic index: $\gamma = \frac{C_p}{C_V}$

Efficiency of a Carnot engine: $\eta = (T_h - T_l)/T_h$

Definition of entropy: $dS = \frac{dQ_{rev}}{T}$

Statistical def. Boltzmann entropy: $S = k_B ln\Omega$

Statistical def. Gibbs entropy: $S = -k_B \sum_i P_i lnP_i$

Fundamental equation: $dU = TdS - pdV$

Enthalpy: $H = U + pV$

Helmholtz energy: $F = U - TS$

Gibbs energy: $G = H - TS$