Final exam Thermodynamics

Monday, January 20th, 2016; 9:00 – 12:00

This exam contains a total of 4 problems.

To allow parallel grading of the problems, use separate sheets of paper for each of the four problems. So, no two problems on the same answer sheet.

Clearly write on each answer sheet your name and student number.

Scoring:

Problem 1: 30 points
Problem 2: 25 points
Problem 3: 20 points
Problem 4: 15 points

Total: 90 points

Final grade = (points/10) + 1 + bonus
(where the bonus is the sum of the grades of your best 5 homeworks divided by 50. If you submitted less than 5 homework assignments, the missing grades are counted as a zero.)

Constants:

R = 8.314 J K^{-1} mol^{-1}
N_A = 6.022 x 10^{23}

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Problem 1 (30 pt)

a) Provide a formulation of the zeroth law of thermodynamics. (**2 pt**)

b) Provide a formulation of the second law of thermodynamics. (**2 pt**)

c) What is a meant by the term "reversible process" in thermodynamics and why is it relevant? (**2 pt**)

d) Consider a gas of molecular hydrogen (H_2). We can assume it behaves as a perfect gas. Explain, under which conditions the molar heat capacity equals to $C_{V,m}=5/2R$. (**3 pt**)

e) A sample consisting of 2 mol H_2 is expanded isothermally at 0 °C from 8 dm^3 to 27 dm^3 i) reversibly, ii) against a constant external pressure (which is equal to the final pressure of the gas) and iii) freely, against zero external pressure. For all processes, calculate $\Delta U, w$ and q. (**4 pt**)

f) A solid rectangular plane of dimension 5 cm x 5 cm is put into a container filled with He gas at 100 Pa and 1000 K. How many He atoms collide with this plane in a single second? (**4 pt**)

g) Explain the concept of viscosity of a gas in terms of kinetic molecular theory. Visualize this with a sketch. (**3 pt**)

A block of silver with $C_{p,m} = 25,351$ JK^{-1}mol^{-1} and $M_{Ag} = 107.87$ g/mol has a mass of 0.5 kg and a temperature of 800 K. It is brought into contact with 1 kg of water with $C_{p,m} = 75,291$ JK^{-1}mol^{-1} and $M_{H2O} = 18.015$ g/mol with a temperature of 298 K. The system is isolated from the rest of the universe. Heat capacities can be assumed as constant for the temperatures under study. Volume effects can be neglected and the pressure is constant.

h) Calculate the heat capacity of the block of silver. (**4 pt**)

i) Show, that the final temperature of a system consisting of two bodies with heat capacities $C_1$and C_2 and with temperatures $T_1$and T_2 is given by the equation
$$T_f = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2}$$
and calculate this temperature for the silver-water system, described above. (**4 pt**)

j) What are the entropy changes of silver, water and the system as a whole? How could you have known the sign of the total entropy changes, without calculating? (**2 pt**)

Problem 2 (25 pt)

Consider a gaseous mixture of A, B, C and D. In the mixture, the following reaction takes place:

$$A + 2B \rightarrow C + D$$
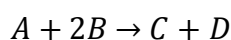
All components exhibit perfect gas behavior. The reaction takes place under standard conditions, i.e. $T = 298$ K and $p = 1$ bar. The table below gives thermodynamic properties of the 4 substances, such as enthalpies of formation $\Delta_f H$ and Gibbs energies of formation $\Delta_f G$.

Substance	$\Delta_f H$(kJ/mol)	$\Delta_f G$ (kJ/mol)	S_m (kJK^{-1}mol^{-1})	$C_{p,m}$ (JK^{-1}mol^{-1})
A	-66	-55	0.2	100
B	0	0	0.05	30
C	-30	-35	0.2	30
D	-20	-15	0.15	75

a) Show that the formation of 1 mole of substance C requires 16 kJ of heat. (**5 pt**)

b) Show with a calculation, if this reaction is spontaneous. (**4 pt**)

c) How much work is done as a consequence of this reaction? (**4 pt**)

d) Assume that there is a temperature T_{eq}, where the 4 substances are in equilibrium, i.e. the reaction is not taking place any more (nor is the reverse reaction). Show, that the equilibrium temperature is given by the following equation: (**4 pt**)

$$T_{eq} = \frac{\Delta_r H(T_{eq})}{\Delta_r S(T_{eq})}$$

e) Show, that the equilibrium temperature is $T_{eq} = 322$ K. Assume that all substances stay in their gaseous state, and that $\frac{|T_{eq}-T|}{T} \ll 1$, so that you can assume: $ln\left(\frac{T_{eq}}{T}\right) \approx \frac{|T_{eq}-T|}{T} \ll 1$. The heat capacity at constant pressure can be considered as constant. (**8 pt**)

Problem 3 (20 pt)

Consider 1 mol of perfect gas (the system) in a state A with volume V_0, pressure p_0 and temperature $T_0 = 300K$. Consider the following thermodynamic cycle:
$$A \rightarrow B \rightarrow C \rightarrow A$$
Step 1: reversible adiabatic expansion from A to B.
Stap 2: reversible compression at constant volume from B to C.
Stap 3: reversible compression at constant pressure from C to A.
In state B, the gas has a pressure p_B and a volume $2V_0$. In state C, the gas has a pressure p_0 and a **volume** $2V_0$. 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). (**3 pt**)

b) For the reversible adiabatic expansion of a perfect gas, initial and final temperature are related by $T_f = T_i \left(\frac{V_i}{V_f}\right)^{1/c}$ with $c = \frac{C_{V,m}}{R}$. Show that $p_f V_f^{C_{p,m}/C_{V,m}} = p_i V_i^{C_{p,m}/C_{V,m}}$. (**3 pt**)

c) Show that the temperatures of the system in states B and C are $T_B = 227.4K$ and $T_C = 600K$. (**3 pt**)

d) Determine the change in internal energy ΔU, the change in enthalpy ΔH, the work w, the heat q and the entropy change ΔS for the system. Give the total values for the entire process. (**6 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! (**3 pt**)

f) Determine the efficiency of the process in the direction, where it does work. (**2 pt**)

Problem 4 (15 pt)

A volume of 1.0 dm^3 contains 1.0 x 10^{23} H$_2$ molecules. The pressure exerted by the H$_2$ gas equals 200 kPa. Consider the system as a perfect gas. Given: M_{H2}=2.0 g/mol, M_{N2}=28.0 g/mol, M_{O2}=32.0 g/mol.

a) Determine the temperature of the gas. (**3 pt**)

b) Determine the root mean square speed of the molecules at a temperature of 100 K. (**4 pt**)

c) Reason whether the temperature would change if the gas would contain O$_2$ molecules instead of H$_2$. Argue whether the root mean square speed would change. (**4 pt**)

d) The Maxwell distribution of speeds is given as: $f(v) = 4\pi \left(\dfrac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$. Draw a sketch of the Maxwell distribution. Approximate what fraction of N$_2$ molecules at a temperature of 500 K have a speed between 290 en 300 m/s. (Hint: "Approximate" means, that you do not have to integrate the Maxwell distribution!) (**4 pt**)