

# Final exam Thermodynamics

Thursday, January 29<sup>th</sup>, 2014; 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 average homework grade divided by 10)

Constants:

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$N_A = 6.022 \times 10^{23}$$

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**Problem 1(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? (2 pt)
- d) Derive the Maxwell relation  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$  from  $dA = -pdV - SdT$ . (2 pt)
- e) Consider a gas of molecular nitrogen ( $N_2$ ). We can assume it behaves as a perfect gas. Explain why the molar heat capacity equals to  $C_{V,m} = 5/2R$ . Why can molar heat capacities of perfect gases be dependent on  $T$ ? (4 pt)
- f) A volume of  $5.0 \text{ dm}^3$  contains  $4.0 \times 10^{23}$   $N_2$  molecules ( $M=28 \text{ g/mol}$ ). The pressure exerted by the  $N_2$  gas equals 200 kPa. We can assume it behaves as a perfect gas. Determine the temperature of the gas. What would be the temperature, if the mass of  $N_2$  molecules was replaced by the same mass of  $H_2$  molecules ( $M=2 \text{ g/mol}$ )? (4 pt)
- g) A gas obeys the van der Waals equation with  $a=0.76 \text{ m}^6\text{Pa mol}^{-2}$ . Its volume is found to be  $4.0 \times 10^{-4} \text{ m}^3\text{mol}^{-1}$  at 288 K and 4.0 MPa. Calculate the van der Waals constant  $b$  and the compression factor under these conditions. Discuss. (4 pt)

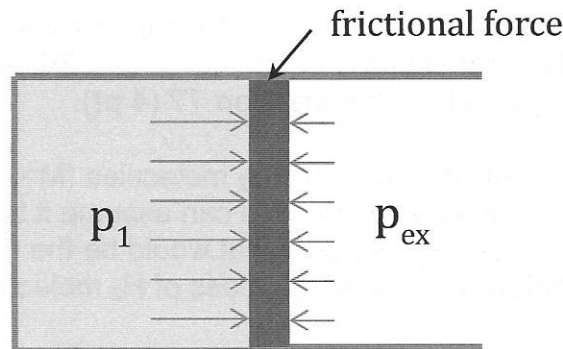
Consider two solid solid-state blocks of gold with the same constant molar heat capacity  $C_{v,m}$ . Their initial temperatures are  $T_1=300 \text{ K}$  and  $T_2=900 \text{ K}$ , respectively. The second block has only half the mass of the first block.

- h) Show, that the final temperature of the objects when they are brought in thermal contact, is  $T_f=500 \text{ K}$ . (4 pt)
- i) Determine the change in entropy of each of the objects in the previous problem. How large is the total change in entropy? (4 pt)
- j) Could you have predicted the sign of the total entropy change? (give arguments) (2 pt)

**Problem 2 (25 pt)**

One mole of perfect gas in a cylinder expands *isothermally* from volume  $V_1$  to volume  $V_2$ . During the expansion, the gas pressure in the cylinder decreases from  $p_1=200$  kPa to  $p_{ex}=100$  kPa.  $p_{ex}$  is the external pressure (pressure of the surroundings), i.e. the standard atmospheric pressure outside the cylinder. The system is always in thermal equilibrium with the surroundings at  $T=300$  K.

The expansion proceeds by movement of a piston (see figure). A frictional force between the piston and the cylinder almost compensates the force due to the (decreasing) pressure in the cylinder. The piston thus moves slowly, without acceleration. Cylinder and piston are perfect heat conductors.



- In this expansion process, due to the frictional force, the net force that acts on the piston is very small throughout the entire process. However, because the additional force is a friction force, the expansion is NOT reversible. Explain. **(3 pt)**
- Calculate the expansion work of the gas in the cylinder against the constant atmospheric pressure of the surroundings. **(7 pt)**
- What is the total change in internal energy ( $\Delta U$ ) of the (perfect!) gas in the cylinder during this isothermal process. Explain! **(3 pt)**
- Use the results from a) and b) together with the thermodynamic definition of entropy, to calculate the entropy change of the surroundings. **(6 pt)**
- Calculate the total entropy change of the system and the surroundings. **(6 pt)**

**Problem 3 (20 pt)**

Assume the reaction:  $\text{O}_2(\text{gas}) + \frac{1}{2} \text{N}_2(\text{gas}) \rightarrow \text{NO}_2(\text{gas})$

- a) What is the standard molar entropy of gas phase  $\text{N}_2$ ? **(4 pt)**

Consider the reaction:  $\text{S}(\text{solid}) + \frac{3}{2} \text{O}_2(\text{gas}) \rightarrow \text{SO}_3(\text{gas})$

- b) Calculate the standard molar Gibbs energy of formation for gaseous  $\text{SO}_3$  at 300 K. **(3 pt)**

Consider the reaction:  $\text{NO}_2(\text{gas}) + \text{SO}_2(\text{gas}) \rightarrow \text{NO}(\text{gas}) + \text{SO}_3(\text{gas})$

- c) Calculate the standard reaction enthalpy  $\Delta_r H$  of this process at 300 K. **(3 pt)**
- d) Repeat the calculation at 380 K assuming constant  $C_{p,m}$ . **(3pt)**
- e) Calculate the molar internal energy  $\Delta_r U_m$  of this reaction at 300 K. **(3 pt)**
- f) Is the reaction spontaneous? Discuss and answer with a calculation. **(4 pt)**

Data table. All data for 300 K.

	$\Delta_f H_m$ (kJ mol <sup>-1</sup> )	$\Delta_f G_m$ (kJ mol <sup>-1</sup> )	$S_m$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$C_{p,m}$ (J K <sup>-1</sup> mol <sup>-1</sup> )
$\text{N}_2(\text{gas})$	0	0	?	29.1
$\text{NO}(\text{gas})$	90.2	86.6	210.8	29.8
$\text{NO}_2(\text{gas})$	33.2	51.3	240.1	37.2
$\text{O}_2(\text{gas})$	0	0	205.1	29.4
$\text{S}(\text{solid})$	0	0	31.8	22.6
$\text{SO}_2(\text{gas})$	-296.8	-300.2	248.2	39.9
$\text{SO}_3(\text{gas})$	-395.7	?	256.8	50.7

**Problem 4 (15 pt)**

The working principle of combustion engines in many cars is called the Otto cycle. A mixture of air with fuel is assumed to be the working substance. As a simplification, this mixture is assumed to be a perfect gas. The thermodynamic cycle consists of the following steps:

- 1) reversible adiabatic compression from A to B.
- 2) reversible pressure increase at constant-volume from B to C due to combustion of a small amount of fuel.
- 3) reversible adiabatic expansion from C to D.
- 4) reversible pressure decrease at constant volume from D to A.

The perfect gas can has molar heat capacities  $C_{p,m}=7/2 R$  and  $C_{p,m}-C_{v,m}=R$ . The state A is described by:  $V_A=6 \text{ dm}^3$ ,  $p_A=100 \text{ kPa}$ ,  $T_A=300 \text{ K}$ . The compression ratio is  $V_A/V_B=12$  and the pressure increase is  $p_C/p_B=2$ .

Hint: For adiabatic changes in a perfect gas:  $\frac{V_i}{V_f} = \left(\frac{T_f}{T_i}\right)^c$ ,  $c = C_{v,m}/R$

- a) Sketch this thermodynamic cycle in a p-V diagram. Indicate, where heat flows and the direction of heat flow. **(3pt)**
- b) Show, that  $T_B=810.6 \text{ K}$ ,  $T_C=1621.2 \text{ K}$  and  $T_D=600 \text{ K}$ . **(4pt)**
- c) Determine  $\Delta U$ ,  $q$ ,  $w$  and  $\Delta S_{\text{sys}}$  for every step. **(4pt)**
- d) Calculate the efficiency of the cycle. **(4pt)**