

Problem Set 1  
3.20 MIT  
Professor Gerbrand Ceder  
Fall 2003

LEVEL 1 PROBLEMS

**Problem 1.1**

The internal energy per kg for a certain gas is given by

$$\underline{U} = 0.17T + C$$

where  $\underline{U}$  is in kJ/kg, T is in Kelvin, and C is a constant.

- a) If the gas is heated in a rigid container (constant volume) from a temperature of 40°C to 315°C, compute the amount of work and heat flow into the system (per kg of gas).
- b) Compute the entropy change (per kg of gas) for the above change of state, under the assumption that the gas is ideal.

DATA:

molecular weight of the gas: 120 g/mol

**Problem 1.2**

Two moles of an ideal gas undergo an equation of state that brings them from 20°C and 5 atm to 110°C and 45 atm.

Calculate the entropy change of this gas.

DATA:

$$C_p = 7/2 R$$

$$C_v = 5/2 R$$

Molar mass of the gas: 32g/mol

**Problem 1.3**

One hundred gram of iron is quenched from a temperature of 1100°C to 0°C by throwing it in a bucket of ice water (water + ice).

- a) What is the enthalpy change of the iron sample when it cools from 1100 °C to 0°C ?
- b) What is the minimal amount of ice (in grams) that has to be present to keep the bucket at 0 °C after it has equilibrated with the iron ? You may assume that the bucket does not exchange heat with the environment (only with the iron).

DATA:

Above 912°C Fe is  $\gamma$ -Fe (fcc) ; below 912° C it is  $\alpha$ -Fe (bcc).

$$H(\gamma\text{-Fe}) - H(\alpha\text{-Fe}) = 900 \text{ J/mole}$$

Heat capacity for  $\gamma$ -Fe: 34J/mol-K

Heat capacity for  $\alpha$ -Fe: 38J/mol-K

Enthalpy of melting for ice: 6.048 kJ/mol

Molar mass for Fe: 56g/mole

Molar mass for H<sub>2</sub>O: 18g/mol

**Problem 1.4**

One m<sup>3</sup> of diatomic ideal gas is first expanded from an initial state at 298K and 15 atm pressure to a final state at 1atm. During this expansion the gas is thermally insulated from the environment. After this expansion the insulation is removed and the gas is allowed to cool (or heat) back to 298K, while keeping the pressure constant at 1atm. What is the amount of work done on the gas in these two processes. It might be helpful if you draw the processes on an appropriate state diagram.

**Problem 1.5**

Consider the two differentials:

$$df_1 = y(3x^2 + y^2)dx + x(x^2 + 2y^2)dy$$

$$df_2 = y(3x^2 + y)dx + x(x^2 + 2y)dy$$

Integrate them between the points  $x = 0, y=0$  and  $x=1, y=1$ , along the path  $y=x$  and along  $y=x^2$ . Which of the two differentials is an exact differential?

In thermodynamics exact differentials correspond to properties of materials (statefunctions) such as internal energy and volume. Energy exchanges (flows) on the other hand are inexact differentials. They are path dependent.

**Problem 1.6**

One mole of air is compressed isothermally at 300K from one atmosphere to fifteen atmospheres.

- Calculate the amount of work required in the compression.
- How much heat must be added or removed from the gas to maintain its temperature at 300K.
- Does the enthalpy of the gas change? If so, how much?
- Does the entropy of the gas change? If so, how much?

DATA:

You may assume that air is an ideal gas with a constant volume heat capacity of  $\frac{5}{2}R$

**Problem 1.7**

The heat of evaporation of water at 100°C and 1 atm is 2261 J/g. (The density of water vapor at 100°C and 1 atm pressure is 0.597 kg/m<sup>3</sup>.)

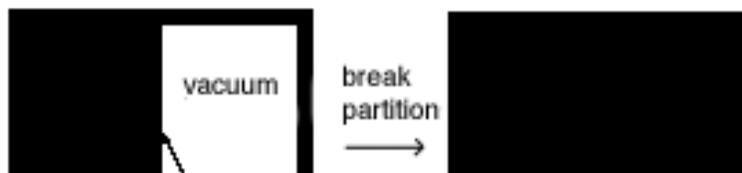
- What percentage of that energy is used as work done by the vapor?
- What is the internal energy change for the evaporation of water?

**Problem 1.8**

The initial state of a quantity of monoatomic ideal gas is  $P=1$  atm and  $V=1$  liter and  $T=373$  K. The gas is isothermally expanded to a volume of 2 liters and then is cooled at constant pressure to the volume  $V$ . This volume is such that a reversible adiabatic compression to a pressure of 1 atm returns the system to its initial state. All of the changes of state are conducted reversibly. Calculate the value of  $V$  and the total workdone on or by the gas.

**Problem 1.9**

Free expansion: Consider a chamber with a partition (see figure). One side of the chamber is filled with a gas and the other side is vacuum. Assume that both sides of the partition have a volume  $V$  (the chamber then has a volume  $2V$ ). Suddenly, the partition is broken and the gas expands to fill the whole chamber having final volume  $2V$ .



- What is the work performed by gas?

Assume that the walls of the chamber are insulating (adiabatic).

(ii) What is then the change in internal energy of the gas after once it has equilibrated after the free expansion?

(iii) If the gas is an ideal gas, does the temperature of the gas change?

(iv) Does the temperature change if the gas is not ideal (i.e.  $U=U(T,V)$ )

Assume that the walls of the chamber conduct heat.

(v) If the gas is ideal, does the internal energy of the gas change?

(vi) If the gas is not ideal (i.e.  $U=U(T,V)$ ) does the internal energy of the gas change after the expansion? Is any heat exchanged with the environment and if so how much.

## LEVEL 2 PROBLEMS

### **Problem 2.1**

Carefully consider the following situations and answer whether the entropy of the universe increases, decreases, or remains constant.

a) ideal (frictionless) electrical motor pulling a weight.

$$\Delta S > 0 \quad \Delta S < 0 \quad \Delta S = 0$$

b) ideal electrical heater

$$\Delta S > 0 \quad \Delta S < 0 \quad \Delta S = 0$$

### **Problem 2.2**

One  $\text{m}^3$  of diatomic ideal gas is expanded from an initial state at 298K and 15atm pressure to a final state at 2 atm and 298K.

a) What is the volume of the gas after the expansion ?

b) What is the amount of work done by the gas if the temperature remained constant during the expansion.

c) What is the amount of work done if the gas is thermally insulated from its environment during the expansion to 2atm and then allowed to cool (or warm) back to 298K, keeping the pressure constant at 2atm. ? It might be helpful if you draw the processes on an appropriate state diagram.

### **Problem 2.3**

The energy of a system of one mole, is given by  $U = AP^2V$  where  $A$  is a positive constant of dimension  $[\text{P}]^{-1}$ . Find the equation of the reversible adiabats in the P-V plane (Callen: problem 1.8-5).

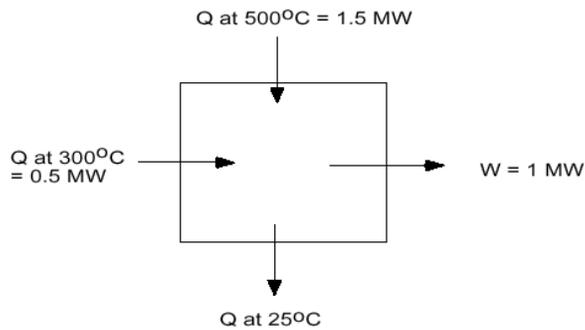
### **Problem 2.4**

You are the head of a venture-capital firm that is trying to evaluate whether to put money into the commercial development of a new power generation device developed by Power&Heat Associates. The machine needs to generate electrical power at the rate of

1 MW. The engineers suggest a machine with the heat flows shown on the figure below: At  $500^\circ\text{C}$  1.5MW of heat is delivered from a burner to a high temperature boiler. The machine also absorbs 0.5 MW as heat from the burning of a low-grade fuel at  $300^\circ\text{C}$ . Cooling of the machine occurs in the environment at  $25^\circ\text{C}$ .

a) Calculate the amount of heat that needs to be absorbed from the system at  $25^\circ\text{C}$  (cooling requirement)

b) Can this machine operate as planned ? Prove your answer!



**Problem 2.5**

Ten (10) moles of ideal gas at 500 °C are adiabatically expanded in a turbine from a pressure of 100 atm to a pressure of 2 atm. Because you are the King (or Queen) of Thermo you can compute that a reversible adiabatic expansion between these pressure can produce 108kJ of work.

Unfortunately, the mechanical engineers that built the turbine mess up, and the expansion only produces 80kJ of work (but is still adiabatic).

- a) What is the final temperature of the gas coming out of the turbine?
- b) If the expansion were reversible the entropy change of the gas would be zero. What is the entropy change of the gas due to the mechanical engineer's mess up?

DATA:  
 $C_p = 7/2 R$   
 $C_v = 5/2 R$

**Problem 2.6**

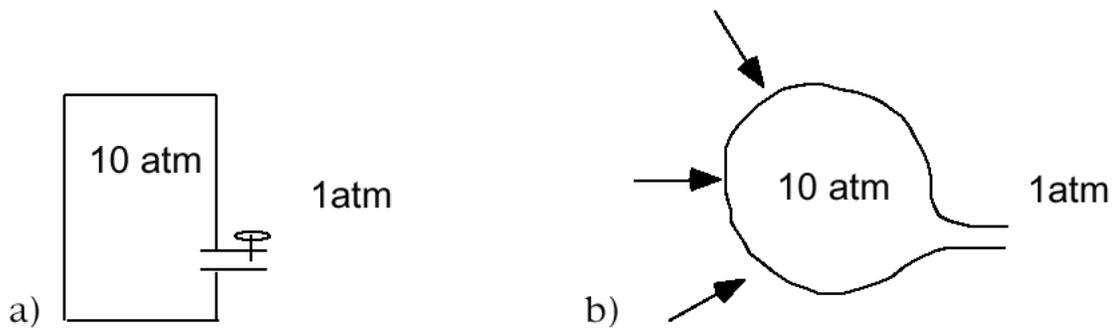
An insulated tank contains a gas at 10atm pressure (fig a). When the valve on the tank is opened, air flows out of the tank while the air remaining in the tank cools down.  $T_a$  is the temperature of the last air coming out of the tank (when the pressure inside has become equal to 1atm).

Compare this now to the situation in figure b. A balloon originally filled so that the pressure inside is 10 atm is drained by slowly letting air out (similar to the flow through the valve in figure a). As the air flows out the balloon shrinks.  $T_b$  is the temperature of the air in the balloon when it is deflated (when the pressure inside is 1 atm).

What is the relation between  $T_a$  and  $T_b$  ? Chose one of the options below and briefly explain ! You do not need to calculate the temperatures  $T_a$  or  $T_b$  You may assume that there are no heat flows through the balloon (process is adiabatic).

Mark the correct result below and EXPLAIN BRIEFLY !

$T_a = T_b$  \_\_\_\_\_     $T_a < T_b$  \_\_\_\_\_     $T_a > T_b$  \_\_\_\_\_



**Problem 2.7**

A tank contains 50 liters of water at  $80^{\circ}\text{C}$ . An additional 10 liters needs to be added to this tank, keeping the total contents of the tank at  $80^{\circ}\text{C}$ . For this I have water available at  $5^{\circ}\text{C}$  and an electrical heater.

Two different procedures for accomplishing this are suggested.

I) The 10 liters at  $5^{\circ}\text{C}$  is first mixed with the 50 liters at  $80^{\circ}\text{C}$  and then the mixture is heated up to  $80^{\circ}\text{C}$ .

II) The 10 liters is first heated from  $5^{\circ}\text{C}$  to  $80^{\circ}\text{C}$  and then mixed with the 50 liters at  $80^{\circ}\text{C}$ .

Calculate for both scenarios

- a) the total amount of electrical energy required (in kWh)
- b) the total entropy change of the universe (system + surroundings).

DATA:

heat capacity for  $\text{H}_2\text{O}$ :  $1\text{cal/g}\cdot\text{K}$

$M_{\text{H}_2\text{O}}=18\text{g/mole}$

1 liter of water = 1 kg

All mixing and heating is done under constant atmospheric pressure.

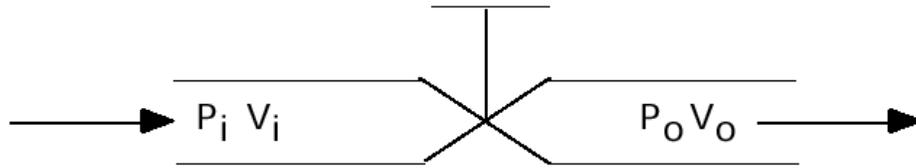
**Problem 2.8**

Consider a system at  $T_1, P_1, V_1$  which is composed of one mole of a classical ideal gas for which  $PV=RT$  and  $U=A+BT$ . Let the system change in four steps. The first step is a very slow compression to  $P_2, V_2$  at a constant temperature of  $T_1$ . The second step is a quick compression to  $T_3, P_3, V_3$ . The third step is a very slow expansion to  $P_4, V_4$  at a constant temperature  $T_3$ . The fourth step is a very quick expansion back to  $T_1, P_1, V_1$ . The second and fourth steps are so quick that there is no heat exchange. Calculate the relations between the total work, heat of the first step and the heat of the third step, expressing the results in terms of  $T_1$  and  $T_3$ .

(Hillert: problem 1.3.3)

**Problem 2.9**

When an ideal gas undergoes a Joule-Thompson expansion its temperature remains constant. Show that this expansion is irreversible by showing that entropy of the universe (system + environment) increases. The Joule-Thompson expansion is an adiabatic flow through an insulated valve, i.e. the gas comes out a lower pressure than it goes in. For an ideal gas the temperature of the gas going out is identical to the temperature of the incoming gas, i.e.  $T_i = T_o$



### Problem 2.10

For a particular system it is found that if the volume is kept constant at the value  $V_o$  and the pressure is changed from  $P_o$  to an arbitrary pressure  $P'$ , the heat transfer to the system is

$$Q' = A(P' - P_o) \quad (A > 0)$$

In addition it is known that the reversible adiabats of the system are of the form

$$PV^\gamma = \text{constant} \quad (\gamma > 0)$$

Find the internal energy  $U(P,V)$  for an arbitrary point in the  $P$ - $V$  plane, expressing  $U(P,V)$  in terms of  $P_o, V_o, A$  and  $\gamma$  (as well as  $P$  and  $V$ )

(Callen: problem 1.8-6)

### LEVEL 3 PROBLEMS

#### Problem 3.1

Ammonia gas ( $\text{NH}_3$ ) in a pressure cylinder is quickly brought to a temperature of 1200K by rapidly compressing it to 10 atm. At the end of the compression the piston is fixed so that the system remains at constant volume.

At 1200K  $\text{NH}_3$  will start to decompose according to the reaction:



Assume that no  $\text{NH}_3$  has decomposed during the rapid compression.

- What is the pressure inside the system when all the  $\text{NH}_3$  has decomposed at a constant temperature of 1200K?
- Compute the heat one needs to supply/extract from the cylinder to keep the temperature at 1200K during the decomposition of the ammonia in the cylinder?
- If the decomposition reaction occurred adiabatically, what would be the temperature of the system after complete decomposition

DATA:

$\Delta H$  for reaction (1) at 1200K: 87kJ/mol (per mole of  $\text{N}_2$  formed)

$C_p, \text{N}_2 = 33\text{J/mol-k}$

$C_p, \text{H}_2 = 33\text{J/mol-k}$

$C_p, \text{NH}_3 = 36\text{J/mol-k}$

Assume that all gasses behave ideal.

Some properties of ideal gasses:

$$C_p - C_v = R$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial H}{\partial p}\right)_T = 0$$

**Problem 3.2**

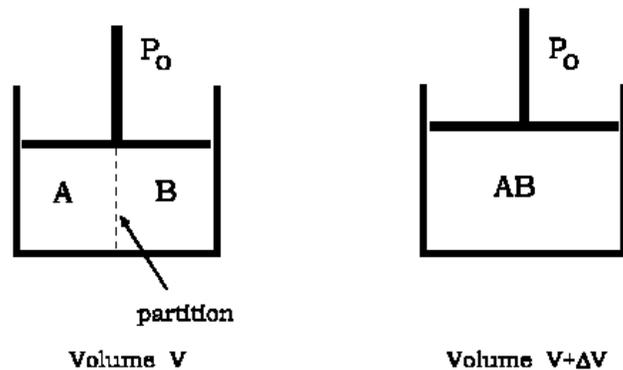
An insulated tank contains air at 0.5 atm pressure and 298K. The outside pressure is at 1atm pressure and 298K. A valve is opened and air is allowed to flow into the tank. What is the temperature of the gas in the tank after it is filled?

**Problem 3.3**

In class, it was shown that  $(\partial Q)_P = (dH)_P$  is valid. This equality was derived only for infinitesimal and reversible processes. In general though,

$$\Delta H = Q$$

holds for any irreversible process between an initial equilibrium state and a final equilibrium state that occurs in an environment with constant pressure.  $Q$  is the heat exchanged between the system and the environment during the irreversible process and  $\Delta H$  is the enthalpy difference between the initial and final equilibrium states. The only requirement is that the process occurs at constant pressure.



Consider a chamber with a moveable frictionless piston and diathermal walls. The chamber is divided by a partition as illustrated in the figure. On one side of the partition is a gas A and on the other side of the partition is a gas B. When the partition is removed, the two components react to form AB. This reaction proceeds under explosive conditions that is so far from equilibrium that the pressure in the chamber during the process cannot be defined. Furthermore, the piston moves up and down violently during the reaction.

Show that the heat  $Q$  exchanged between the gas in the chamber and the environment is equal to the change in enthalpy of the gas (i.e.  $Q = \Delta H = H_{AB} - H_A - H_B$ ). Assume that the change in volume during the reaction is  $\Delta V$ .

**Problem 3.4**

An evacuated ( $P=0$ ), insulated tank is surrounded by a very large volume (assume infinite volume) of an ideal gas at a temperature  $T_o$ . The valve on the tank is opened and the surrounding gas is allowed to flow quickly into the tank until the pressure inside the tank equals the pressure outside. Assume that no heat flow takes place. What is the final temperature of the gas in the tank?

The heat capacities of the gas,  $C_p$  and  $C_v$ , each may be assumed to be constant over the temperature range spanned by the experiment. Your answer may be left in terms of  $C_p$  and  $C_v$ .

Hint: One way to approach the problem is to define the system as the gas that ends up in the tank.

(Ragone: problem 1.5)

**Problem 3.5**

Two tanks with equal volume are connected with a Joule-Thompson valve. Tank I contains an ideal gas at 10 atm pressure and 300K while tank II is empty ( $P = 0$ ). The valve is opened slowly so that gas can flow from tank I into tank II. The valve is closed once the pressure in tank I has reached 5 atm.

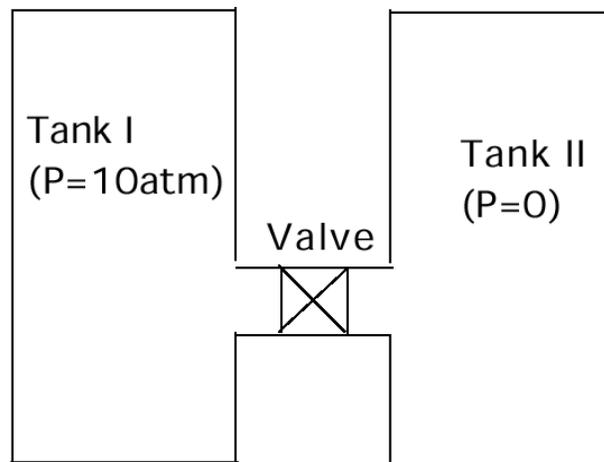
- What is the temperature of the gas in tank I when the pressure there is 5atm ?
- What is the temperature of the gas in tank II when the pressure in tank I has reached 5 atm ?
- Prove that this process is irreversible by calculating the total entropy change of the system.

DATA:

$C_p$  for the ideal gas is  $7/2 R$

$C_v$  for the ideal gas is  $5/2 R$

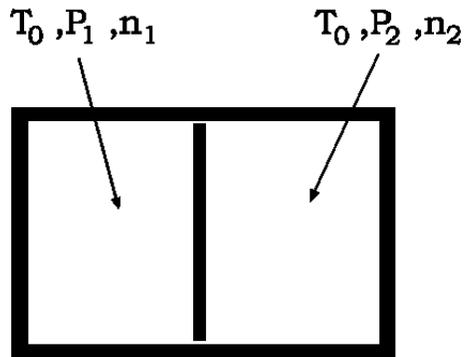
Note that pressure changes in the tank may be considered to be reversible processes. The expansion across the Joule-Thompson valve is irreversible but conserves enthalpy, as discussed in class. The complete enclosure of the tank is insulated so that no heat exchange with the environment occurs.



## LEVEL 4 PROBLEMS

**Problem 4.1**

NOTE: this problem is extremely tricky



The above picture shows two identical ideal gasses separated by a movable insulated piston. The two gasses are at the same temperature but different pressure. The compartments are fully insulated from the environment. In the initial state, the volumes of the two compartments are both equal to  $V_0$ .

What is the final temperature and pressure after the piston is slowly allowed to equilibrate? (so that process is reversible)?

What will happen if the process is irreversible?