

# **CHEM2011 – INTRODUCTION TO THERMODYNAMICS**

## **TEST 1**

February 27, 2022

### **INSTRUCTIONS**

- **Duration: 90 minutes**
- The test is out of **50 marks**.
- The test is **11 pages long (SINGLE SIDED)** and contains **4 questions**.
- You may write in pen OR pencil
- Only allowable aid is a **non-programmable calculator**
- If you need extra space, you can write at the back of a page, but please indicate so, otherwise it won't be marked
- Constants, equation sheet and periodic table are provided at the back
- **Pages 9-11** can be detached and discarded after the test

**Question source:**

General chapter 1 background (book, notes, Jeopardy CH1/2 Q1 (200))

General chapter 2 background (Jeopardy CH2-2 Q1(200))

**QUESTION 1 [12 pts]**

a) Briefly answer the following questions.

- i) [2] Does Charles' Law hold during a reversible adiabatic expansion or compression of an ideal gas? Briefly explain your answer.

No, Charles' law is  $V_1/T_1 = V_2/T_2$  but for a reversible adiabatic process  $T_1V_1^{(\gamma-1)} = T_2V_2^{(\gamma-1)}$

Or for Charles' law to hold, P is kept constant, whereas in the adiabatic expansion/compression P will change.

- ii) [1] Dalton's Law of partial pressure states that for unreactive gases, behaving ideally, the pressure exerted by one gas in a mixture is independent of the other gases in the mixture.

TRUE FALSE

- iii) [1] For real gases the ratio  $PV/RT$  can be greater or smaller than one.

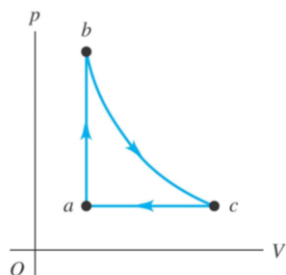
TRUE FALSE

A positive deviation (meaning  $PV/RT > 1$ ) is due to the molecules having intermolecular forces and is quantified by the "a" factor.

- iv) [1] Non-ideal behavior in gases is more important at high temperature and low pressure

TRUE FALSE

- v) [3 pts] An ideal gas is taken around the cycle (a-b-c-a) shown in this pV-diagram. Process  $b \rightarrow c$  is isothermal. For the complete cycle, what are the signs of q, w and  $\Delta U$  - positive, negative or zero? Circle the right answers.



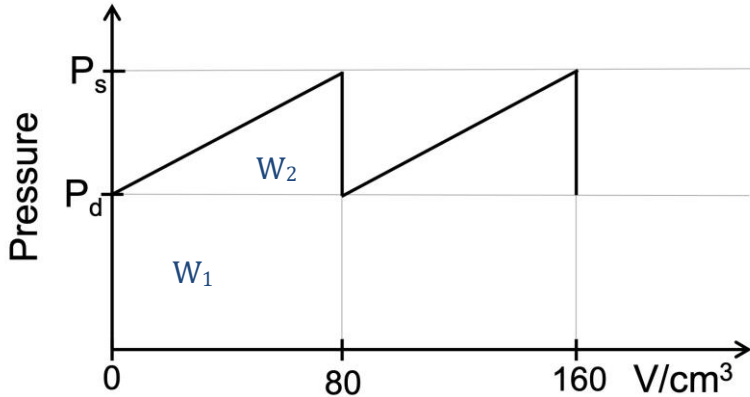
$\Delta U$	positive	negative	<u>zero</u>
q	<u>positive</u>	negative	zero
w	positive	<u>negative</u>	zero

**Question source:**

Question similar to the assigned homework question 2.7, or Jeopardy – column 3, Q4(800)

**QUESTION 1 [12 pts] cont'd**

- b) [4 pts] The P – V diagram below can be used to represent the pressure dependence in a ventricle of the human heart as a function of the volume of blood pumped. The systolic pressure,  $P_s$ , is 137 mmHg, and the diastolic pressure  $P_d$ , is 81 mmHg. If the volume of blood pumped in one heartbeat is  $80 \text{ cm}^3$ , calculate the work done in one heartbeat.



$$w = - \int_{V_1}^{V_2} P_{ex} dV$$

$$V = 80 \text{ cm}^3 \times 10^{-6} \text{ m}^3/\text{cm}^3 = 80 \times 10^{-6} \text{ m}^3$$

$$W_1 = P_d (V_f - V_i) = (81 \text{ mmHg}/760 \text{ mmHg}) 101325 \text{ Pa} (80 \times 10^{-6} \text{ m}^3 - 0 \text{ m}^3) = 0.8639 \text{ J}$$

$$W_2 = [(P_s - P_d) (V_f - V_i)] / 2 = (56 \text{ mmHg}/760 \text{ mmHg}) 101325 \text{ Pa} (80 \times 10^{-6} \text{ m}^3 - 0) / 2 = 0.2986 \text{ J}$$

$$W = 0.2986 \text{ J} + 0.8639 \text{ J} = 1.163 \text{ J} = 1.2 \text{ J per heartbeat}$$

**Question source:**

Question similar to example problem on slide 64 in CH 2

Question similar to example problem on slide 29 in CH 3

Homework questions 2.23, 3.36

Question similar to Jeopardy question – column 3, Q5(1000)

**QUESTION 2 [13 pts]**

- (a) [6 pts] A 243.0 g sample of Silicon (Si) in the crystalline solid form is heated from 300 K to 425 K at constant pressure. Over this temperature range,  $C_{p,m}$  is given by the expression:

$$\frac{C_{P,m}}{JK^{-1}mol^{-1}} = -6.25 + 0.1681 \frac{T}{K} - 3.437 \times 10^{-4} \frac{T^2}{K^2}$$

Calculate  $\Delta H$  and  $q_p$ .

For an ideal gas,  $\Delta H$  is given by:

$$\Delta H = n \int_{T_i}^{T_f} C_{P,m} dT = n \int_{300K}^{425K} \left( -6.25 + 0.1681 \frac{T}{K} - 3.437 \times 10^{-4} \frac{T^2}{K^2} \right) dT$$

$$\Delta H = \frac{243.0 g}{28.0855 g mol^{-1}} \left( -6.25 T + \frac{0.1681}{2} T^2 - \frac{3.437 \times 10^{-4}}{3} T^3 \right)$$

$$\Delta H = \frac{243.0 g}{28.0855 g mol^{-1}} \left( -6.25 (425 - 300) + \frac{0.1681}{2} (425^2 - 300^2) - \frac{3.437 \times 10^{-4}}{3} (425^3 - 300^3) \right)$$

$$\Delta H = 8.652 mol (-781.25 + 7617 - 5701.5) = 9814 J = 9.81 kJ$$

**At constant pressure  $\Delta H = q_p$**

## QUESTION 2 [13 pts] cont'd

- (b)[5 pts] How large is the relative error in  $\Delta H$  if we assume that  $C_{P,m}$  is a constant at 300 K and that  $C_{P,m}$  remains constant for temperature interval considered in part (a).

$$\frac{C_{P,m}}{JK^{-1}mol^{-1}} = -6.25 + 0.1681 \frac{T}{K} - 3.437 \times 10^{-4} \frac{T^2}{K^2}$$

$$\frac{C_{P,m}}{JK^{-1}mol^{-1}} = -6.25 + 0.1681 \frac{300K}{K} - 3.437 \times 10^{-4} \frac{(300K)^2}{K^2} = 13.247 JK^{-1}mol^{-1}$$

$$\Delta H = n C_{P,m} \int_{T_i}^{T_f} dT = \frac{243.0 g}{28.0855 g mol^{-1}} 13.247 JK^{-1}mol^{-1} (425 K - 300 K) = 14.3 kJ$$

The relative error is:  $100 \times |(9.81 kJ - 14.3 kJ) / 9.81| kJ = 46 \%$  or **-46% if sign is needed**

- (c) [2 pts] For the process described in part (a) calculate  $\Delta U$ .

For solids:  $\Delta U \approx \Delta H$

**Question source:**

CH 2 notes – example on slide 78, example on slide 80

CH 2 Tutorial – 2d and 2e

Homework questions: 2.38, 2.41a, 2.44b, 2.48, 2.52, 2.53

Concepts reviewed in: Jeopardy question – column 1-Q2(400), column 2-Q3(600), column 2-Q4(800),

**QUESTION 3 [13 pts]**A sample of **two moles** of an ideal diatomic gas is initially at **T = 290 K** and at a pressure of **10.0 bar**.(a) [6 pts] The gas then undergoes a reversible adiabatic expansion to a final pressure of **1.50 bar**.Calculate the **final temperature, q, w, ΔU, and ΔH**.

$$C_{P,m} = 7/2R \quad C_{V,m} = 5/2R \quad \gamma = 7/5 = 1.4 \quad T_1 P_1^{[(1-\gamma)/\gamma]} = T_2 P_2^{[(1-\gamma)/\gamma]}$$

$$T_2 = \frac{T_1 P_1^{[(1-\gamma)/\gamma]}}{P_2^{[(1-\gamma)/\gamma]}} = T_1 \left( \frac{P_1}{P_2} \right)^{[(1-\gamma)/\gamma]} = 290 \left( \frac{10}{1.5} \right)^{[(1-\frac{7}{5})/\frac{7}{5}]} = 169 \text{ K}$$

$$q = 0$$

$$\Delta U = w = C_V(T_2 - T_1) = \left( \frac{5}{2} \right) (8.314 \frac{\text{J}}{\text{Kmol}}) (2 \text{ mol}) (169 \text{ K} - 290 \text{ K}) = -5.03 \text{ kJ}$$

$$\Delta H = C_P(T_2 - T_1) = \left( \frac{7}{2} \right) (8.314 \frac{\text{J}}{\text{Kmol}}) (2 \text{ mol}) (169 \text{ K} - 290 \text{ K}) = -7.04 \text{ kJ}$$

(b) [4 pts] In a second experiment, the gas sample is found at the same initial conditions, but it expands to a **final pressure of 1.50 bar** during an irreversible adiabatic expansion against a **constant pressure of 1.50 bar**, calculate the **final temperature** and the **work** done in that process.

$$n C_{V,m}(T_2 - T_1) = -p_{\text{ext}}(V_2 - V_1) \quad n C_{V,m}(T_2 - T_1) = -p_{\text{ext}} \left( \frac{n R T_2}{p_2} - \frac{n R T_1}{p_1} \right)$$

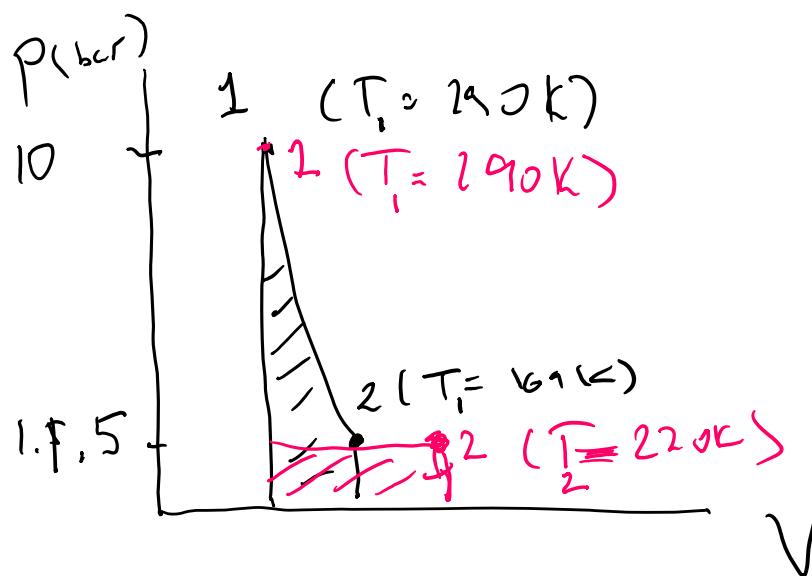
$$\left( C_{V,m} + \frac{R p_{\text{ext}}}{p_2} \right) T_2 = \left( C_{V,m} + \frac{R p_{\text{ext}}}{p_1} \right) T_1 \quad \left( 5R/2 + \frac{R p_{\text{ext}}}{p_2} \right) T_2 = \left( 5R/2 + \frac{R p_{\text{ext}}}{p_1} \right) T_1$$

$$T_2 = \frac{\left( 5/2 + \frac{p_{\text{ext}}}{p_1} \right)}{\left( 5/2 + \frac{p_{\text{ext}}}{p_2} \right)} T_1 = \frac{\left( 5/2 + \frac{1.5 \text{ bar}}{10.0 \text{ bar}} \right)}{\left( 5/2 + \frac{1.5 \text{ bar}}{1.5 \text{ bar}} \right)} (290 \text{ K}) = 220 \text{ K}$$

$$\Delta U = w = C_V(T_2 - T_1) = \left( \frac{5}{2} \right) (8.314 \frac{\text{J}}{\text{Kmol}}) (2 \text{ mol}) (220 \text{ K} - 290 \text{ K}) = -2.91 \text{ kJ}$$

QUESTION 3 [13 pts] cont'd

- (c) [3 pts] On the same PV diagram, sketch the work that was done in a) as well as in b). Clearly label the area that corresponds to each of the processes. Who did the work in a) and b) – the system or the surroundings?



— a) rev.

— b) irrev.

**Question source:**

CH 3 – book, notes (slide 7, 10, 27, 39)

Concepts reviewed in: Jeopardy question –column 4-Q2(400), column 5-Q1(200), column 5-Q2(400), column 6-Q3(600), column 6-Q4(800)

**QUESTION 4 [12 pts]**

(a) [2 pts] Enthalpy (H) is a state function and dH is an exact differential. Write an expression for the full differential expression of dH illustrating the dependence of enthalpy on P and T.

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

(b) [2 pts] Write the cyclic rule expression for H(T, P).

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

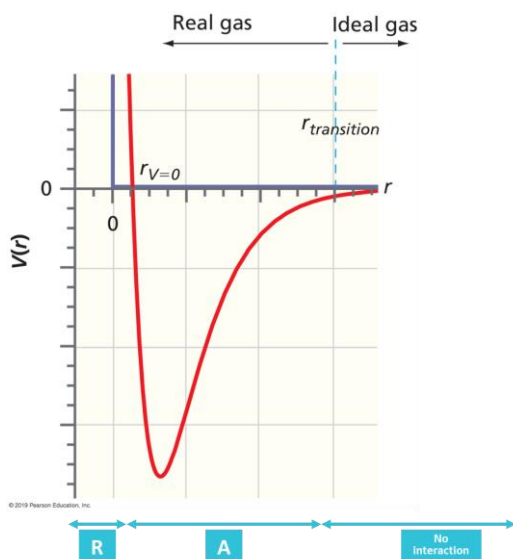
(c) [4 pts] Using the equation given below demonstrate that for an ideal gas  $\left(\frac{\partial H}{\partial P}\right)_T = 0$ .

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T + V$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial \left(\frac{nRT}{V}\right)}{\partial T}\right)_V = \frac{nR}{V} \quad \left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial \left(\frac{nRT}{P}\right)}{\partial P}\right)_T = -\frac{nRT}{P^2}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T + V = T \frac{nR}{V} \left(-\frac{nRT}{P^2}\right) + V = 0$$

(d) [4 pts] The potential energy of interaction of two molecules or atoms is shown in the figure below (as a function of their separation, r). On the diagram, indicate where there is i) no interaction, ii) attraction, iii) repulsion between gas molecules.



iv) For real gases  $\left(\frac{\partial H}{\partial P}\right)_T = -C_P \mu_{J-T}$ .

In which region is  $\left(\frac{\partial H}{\partial P}\right)_T > 0$  for real gases?

Circle the correct answer.

ATTRACTIVE      OR      **REPULSIVE**