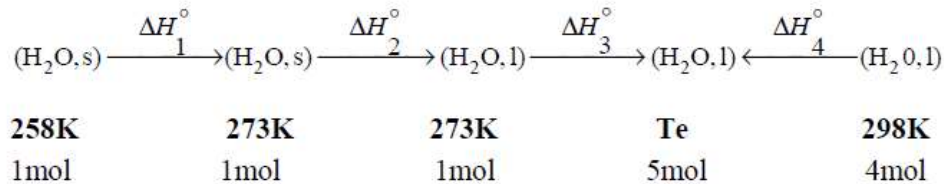


## Chemistry 2: Thermodynamics Exam Solution:

### Exercise 1



The process is adiabatic; we have :  $\sum Q_i = \sum \Delta H_i = 0$

a) The enthalpy of heating one mole of ice from  $-15^\circ\text{C}$  ( $T_1$ ) to  $0^\circ\text{C}$  ( $T_2$ ) is:

$$Q_1 = \Delta H_1^\circ = n_1 \int_{T_1}^{T_2} C_p(\text{H}_2\text{O}, \text{s}) dT$$

$$Q_1 = \Delta H_1^\circ = \int_{258}^{273} 37,62 dT$$

$$Q_1 = 564,3 \text{ J}$$

b) The enthalpy of fusion of ice is:

$$\Delta H_2^\circ = Q_2 = 6,0510^3 \text{ J.}$$

c) The enthalpy of heating one mole of water from  $T_2$  to  $T_{\text{eq}}$  is:

$$Q_3 = \Delta H_3^\circ = n_1 \int_{T_2}^{T_{\text{eq}}} C_p(\text{H}_2\text{O}, \text{l}) dT$$

$$Q_3 = \Delta H_3^\circ = 1 \cdot \int_{273}^{T_{\text{eq}}} 75,24 dT$$

$$Q_3 = 75,24 (T_{\text{eq}} - 273) \text{ J}$$

d) The enthalpy of cooling one mole of water from 298 K to the equilibrium temperature is:

$$\Delta H_4^\circ = Q_4 = 4,75,24 (T_{\text{eq}} - 298)$$

The process is adiabatic; we have :  $\sum Q_i = \sum \Delta H_i = 0$

$$\sum Q_i = Q_1 + Q_2 + Q_3 + Q_4$$

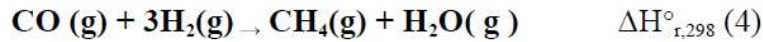
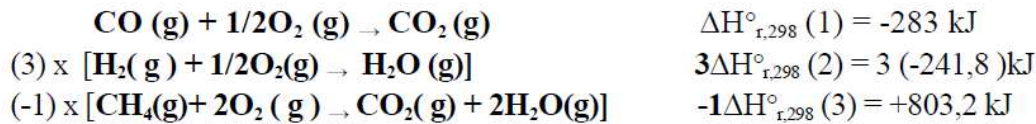
$$\sum Q_i = 564,3 + 6,05 \cdot 10^3 + 75,24 (T_{\text{eq}} - 273) + 4,75,24 (T_{\text{eq}} - 298)$$

$$\Rightarrow T_{\text{eq}} = 275,4\text{K}$$

### Exercise 2

The enthalpy  $\Delta H_{r,298}^\circ$  of the reaction:

Algebraic method: It involves combining these reactions and their respective equations in such a way as to obtain the desired reaction.



$$\Delta H_{r,298}^\circ (4) = \Delta H_{r,298}^\circ (1) + 3\Delta H_{r,298}^\circ (2) - \Delta H_{r,298}^\circ (3)$$

$$\Delta H_{r,298}^\circ (4) = -283 + 3 (-241,8) + 803,2 = -206,23 \text{ kJ}$$

$$\Delta H_{r,298}^\circ (4) = -206,23 \text{ kJ}$$

a) The internal energy  $\Delta H_{r,298}^\circ$  of the reaction:

$$\Delta H_{r,298}^\circ = \Delta U_{r,298}^\circ + RT\Delta n_g;$$

$\Delta n_g$  is the change in stoichiometric coefficients of the gaseous products and reactants.

$$\Delta n_g = \sum n_i (\text{gaseous products}) - \sum n_j (\text{gaseous reactants})$$

$$\Delta n_g = 2 - 4 = -2$$

$$\Delta U_{r,298}^\circ = -206,23 - (8,31/1000) \cdot (298) \cdot (-2) = -201,28 \text{ kJ}$$

$$\Delta U_{r,298}^\circ = -201,28 \text{ kJ}$$

b) The reaction is exothermic because  $\Delta H_{r,298}^\circ < 0$ .

### Exercise 3

1. For the transformation (1 to 2), the pressure increases at constant volume, so it is an isochoric compression.

For the transformation (3 to 4), the volume increases at constant pressure, so it is an isobaric compression.

- Transformation (1 to 2): isochoric compression.
- Transformation (2 to 3): adiabatic compression.
- Transformation (3 to 4): isobaric compression.
- Transformation (4 to 1): adiabatic expansion.

2- Calculate the temperatures  $T_2, T_4$  and the volumes  $V_2, V_3$ , and  $V_4$ .

- (1 to 2): isochoric compression.  $V_1 = V_2$

$$G.P \Rightarrow \frac{P_1 V_1}{T_1} = nRT_1 \Rightarrow \frac{P_2 V_2}{T_2} = nRT_2 \Rightarrow T_2 = \left(\frac{P_2}{P_1}\right) T_1$$

A.N  $T = 2T_1 = 100^\circ C$

- (2 to 3): adiabatic compression  $(P_2, V_2, T_2) \Rightarrow (P_3, V_3, T_3)$

The relation to use is  $(TV^{\gamma-1} = \text{const}) \Rightarrow T_2 V_2^{\gamma-1} = T_3 V_3^{\gamma-1} \Rightarrow V_3 = V_2 \left(\frac{T_2}{T_3}\right)^{\frac{1}{\gamma-1}}$

A.N  $V_2 = V_1$  so  $V_3 = 0.633$  liter

- (3 to 4): isobaric compression  $P_4 = P_3$

$$\frac{P_3 V_3}{T_3} = nRT_3 \Rightarrow \frac{P_4 V_4}{T_4} = nRT_4 \Rightarrow \frac{V_4}{V_3} = \frac{T_4}{T_3} \Rightarrow V_4 = \frac{T_4}{T_3} V_3$$

(1)

- (4 to 1): adiabatic expansion

$$T_4 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}$$

(2)

Multiplying (1) by (2) eliminates  $T_4$  and we get  $V_4 \Rightarrow V_4 = \frac{V_3 T_1 V_1^{\gamma-1}}{T_3} \Rightarrow V_4 = \left(\frac{V_3 T_1}{T_3}\right)^{\frac{1}{\gamma-1}} V_1^{\frac{\gamma}{\gamma-1}}$

A.N  $V_4 = 0.386$  liter and  $T_4 = \frac{V_4 T_3}{V_3} = 73.17^\circ C$

2nd method to calculate  $V_4$

- (2 to 3): adiabatic expansion  $P_2 V_2^\gamma = P_3 V_3^\gamma$

- (4 to 1): adiabatic expansion  $P_4 V_4^\gamma = P_1 V_1^\gamma$

$V_1 = V_2$  and  $P_3 = P_4$

By taking the ratio of the two expressions, we get:

$$\left(\frac{P_2}{P_1}\right) V_1 = 0.386 \text{ liter}$$

3- Provide the expressions for the work  $W_i$  and the heat  $Q_i$  exchanged for each transformation.

Given:  $a = P_2/P_1 = 4$ ;  $V_1 = 1$ ;  $T_1 = 50^\circ\text{C}$ ;  $T_3 = 120^\circ\text{C}$ ;  $\gamma = 1.4$ .

N.B: No numerical calculations for questions 2 and 3.

- (1 to 2): isochoric compression

$$V = \text{const} \quad \text{so} \quad W_1 = 0 \quad \text{and} \quad \Delta U_1 = Q_1 = nC_v \Delta T = nC_v(T_2 - T_1)$$

- (2 to 3): adiabatic compression

$$Q_2 = 0 \quad \text{and} \quad \text{from exercise 1:} \quad W_2 = \frac{(P_3V_3 - P_2V_2)}{(\gamma - 1)} = nC_v(T_3 - T_2)$$

- (3 to 4): isobaric compression

$$P = \text{const} \quad \text{so} \quad W_3 = P_3(V_4 - V_3) = nR(T_4 - T_3) \quad \text{and} \quad Q_3 = nC_p \Delta T = nC_p(T_4 - T_3) \quad (\text{dp} = 0)$$

- (4 to 1): adiabatic expansion

$$Q_4 = 0 \quad W_4 = (P_1V_1 - P_4V_4)/(\gamma - 1) = nC_v(T_1 - T_4)$$

3- Verify that the total energy variation  $\Delta U$  of the cycle is zero.

$$\Delta U = W + Q \Rightarrow nC_v(T_2 - T_1) + nC_v(T_3 - T_2) - nR(T_4 - T_3) + nC_v(T_1 - T_4)$$

By replacing  $nR$  and  $C_p$  in terms of  $C_v$ , we find  $\Delta U = 0$