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Chemistry 2: Thermodynamics
Exam Solution:

Exercise 1

$$(H_2O,s) \xrightarrow{\Delta H_1^\circ} (H_2O,s) \xrightarrow{\Delta H_2^\circ} (H_2O,l) \xrightarrow{\Delta H_3^\circ} (H_2O,l) \xleftarrow{\Delta H_4^\circ} (H_20,l)$$

258K	**273K**	**273K**	**Te**	**298K**
1mol	1mol	1mol	5mol	4mol

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

a) The enthalpy of heating one mole of ice from -15°C (T_1) to 0°C (T_2) is:

$$Q_1 = \Delta H_1^\circ = n_1 \int_{T_1}^{T_2} C_p(H_20,s)dT$$

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

$Q_1 = 564{,}3$ J

b) The enthalpy of fusion of ice is:

$\Delta H^\circ_2 = Q_2 = 6{,}0510^3$J.

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

$$Q_3 = \Delta H_3^\circ = n_1 \int_{T2}^{Teq} C_p(H_20,l)dT$$

$$Q_3 = \Delta H_3^\circ = 1.\int_{273}^{Teq} 75{,}24\, dT$$

$Q_3 = 75{,}24\ (T_e - 273)$ J

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

$\Delta H^\circ_4 = Q_4 = 4.75{,}24\ (T_{eq} - 298)$

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

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

$\Sigma Q_i = 564{,}3 + 6{,}05\ 10^3 + 75{,}24\ (T_{eq} - 273) + 4.75{,}24\ (T_{eq} - 298)$

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

Exercise 2

The enthalpy $\Delta H^\circ_{r,298}$ of the reaction:

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

$CO (g) + 1/2O_2 (g) \rightarrow CO_2 (g)$ $\Delta H°_{r,298}$ (1) = -283 kJ

(3) x [$H_2(g) + 1/2O_2(g) \rightarrow H_2O (g)$] 3$\Delta H°_{r,298}$ (2) = 3 (-241,8)kJ

(-1) x [$CH_4(g) + 2O_2 (g) \rightarrow CO_2(g) + 2H_2O(g)$] -1$\Delta H°_{r,298}$ (3) = +803,2 kJ

$CO (g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$ $\Delta H°_{r,298}$ (4)

$\Delta H°_{r,298}$ (4) = $\Delta H°_{r,298}$ (1) + 3$\Delta H°_{r,298}$ (2) - $\Delta H°_{r,298}$ (3)

$\Delta H°_{r,298}$ (4) = -283+ 3 (-241,8) +803,2 = -206,23 kJ

$\Delta H°_{r,298}$ (4) = -206,23 kJ

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

$\Delta H^{\circ}_{r,298} = \Delta U^{\circ}_{r,298} + RT\Delta n_g$;

Δn_g is the change in stoichiometric coefficients of the gaseous products and reactants.

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

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

$\Delta U^{\circ}_{r,298} = -206.23 - (8.31/1000) \cdot (298) \cdot (-2) = -201.28\,\text{kJ}$

$\Delta U^{\circ}_{r,298} = -201.28\,\text{kJ}$

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

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. $V_1 = V_2$

$$G.P \Rightarrow \frac{P_1V_1}{T_1} = nRT_1 \Rightarrow \frac{P_2V_2}{T_2} = nRT_2 \Rightarrow T_2 = \left(\frac{P_2}{P_1}\right) T_1$$
$$A.N \quad T = 2T_1 = 100^\circ C$$

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

The relation to use is $(TV^{\gamma-1} = \text{const}) \Rightarrow T_2V_2^{\gamma-1} = T_3V_3^{\gamma-1} \Rightarrow V_3 = V_2\left(\frac{T_2}{T_3}\right)^{\frac{1}{\gamma-1}}$

$$A.N \quad V_2 = V_1 \quad \text{so} \quad V_3 = 0.633 \text{ liter}$$

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

$$\frac{P_3V_3}{T_3} = nRT_3 \Rightarrow \frac{P_4V_4}{T_4} = nRT_4 \Rightarrow \frac{V_4}{V_3} = \frac{T_4}{T_3} \Rightarrow V_4 = \frac{T_4}{T_3}V_3$$
(1)

- (4 to 1): adiabatic expansion

$$T_4V_4^{\gamma-1} = T_1V_1^{\gamma-1}$$

(2)

Multiplying (1) by (2) eliminates T_4 and we get $V_4 \Rightarrow V_4 = \frac{V_3T_1V_1^{\gamma-1}}{T_3} \Rightarrow V_4 = \left(\frac{V_3T_1}{T_3}\right)^{\frac{1}{\gamma-1}} V_1^{\frac{\gamma}{\gamma-1}}$

$$A.N \quad V_4 = 0.386 \text{ liter} \quad and \quad T_4 = \frac{V_4T_3}{V_3} = 73.17^\circ C$$

2nd method to calculate V_4

- (2 to 3): adiabatic expansion $P_2V_2^\gamma = P_3V_3^\gamma$
- (4 to 1): adiabatic expansion $P_4V_4^\gamma = P_1V_1^\gamma$

$$V_1 = V_2 \quad and \quad P_3 = P_4$$

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: $a = P_2/P_1 = 4; V_1 = 1; T_1 = 50°C; T_3 = 120°C; \gamma = 1.4.$

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

- (1 to 2): isochoric compression

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

- (2 to 3): adiabatic compression

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

- (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 ΔU 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 $\Delta U = 0$