

Homework-01

(Submit yours to TA at the beginning of the class on October 1)

*1: Some problems are taken from a textbook (D.A. McQuarrie and J.D. Simon, "Physical chemistry – a molecular approach-"). For example, if you see "#19-5" at around the problem number, like "HW01-01", it means that this problem is of problem #5 in chapter 19 in the textbook.

*2: Please define the signs of q (heat) and w (work) so that they have positive values when the internal energy of the system is increased by the process.

[HW01-01] Please explain the following 4 systems: (1) open system, (2) closed system, (3) isolated system, and (4) thermally isolated system. Please describe in 300 words or less.

[HW01-02] Please explain path function and state function. Please describe in 300 words or less.

[HW01-03] Please explain the definitions of heat and work in thermodynamics. Please describe in 300 words or less.

[HW01-04] Please write down an appropriate form of the equation representing the first law of thermodynamics in the following processes: (1) reversible isothermal expansion process, (2) reversible constant-volume heating process.

*<hint> For example, in the case of "reversible adiabatic expansion process", the answer should not be " $dU = \delta q + \delta w$ " but be " $dU = \delta w = -PdV$ " with some appropriate explanations.

[HW01-05:#19-5, #19-4, #19-6] Please calculate (i) ΔU (the internal energy change of the system), (ii) q (heat) and (iii) w (work) for the following processes. If necessary, please assume that the ideal gas is monatomic (like He), and thus the internal energy is expressed as $U(T) = \frac{3}{2}nRT$.

(1) A process where the system composed by 10.0 moles of an ideal gas is reversibly expanded from 0.0100 m^3 to 0.0300 m^3 at a constant temperature of 400 K.

(2) A process where the system composed by 10.0 moles of an ideal gas is reversibly compressed from $1.00 \times 10^5 \text{ Pa}$ to $4.00 \times 10^5 \text{ Pa}$ at a constant temperature of 300 K.

(3) A process where the system composed by 50.00 moles of an ideal gas at 400 K is reversibly and isothermally compressed from a volume of 0.0200 m^3 to 0.0100 m^3 .

(4) A process where the system composed by 50.0 moles of an ideal gas at 400 K is reversibly and adiabatically compressed from a volume of 0.0200 m³ to 0.0100 m³.

[HW01-06:#19-8]

(1) Using Redlich-Kwong equation as the equation of state, derive an equation to evaluate the work required for an isothermal reversible expansion from a molar volume of \bar{V}_1 to \bar{V}_2 (\bar{V} is a molar volume defined as " $\bar{V} = V/n$ " where n is the amount of gas in mole). The Redlich-Kwong equation can be written as

$$P = \frac{RT}{\bar{V}-B} - \frac{A}{\bar{V}(\bar{V}+B)T^{1/2}}$$

where A and B are constants and $A=3.2205 \text{ m}^6 \text{ Pa mol}^{-2} \text{ K}^{1/2}$, $B=2.985 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$.

(2) Then, using the derived equation above, calculate the work involved in the isothermal reversible expansion of 1 mole of CH₄ gas from a volume of 1.00x10⁻³ m³ to 5.00x10⁻³ m³ at 300 K.

[HW01-07]

(1) Using the Van der Waals equation as the equation of state, derive an equation to evaluate the work required for an isothermal reversible expansion from a molar volume of \bar{V}_1 to \bar{V}_2 (\bar{V} is a molar volume defined as " $\bar{V} = V/n$ " where n is the amount of gas in mole).

The van der Waals equation can be written as

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

where a and b are constants and $a=0.23026 \text{ m}^6 \text{ Pa mol}^{-2}$, $b=4.3067 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$.

(2) Then, using the derived equation above, calculate the work involved in the isothermal reversible expansion of 2 moles of CH₄ gas from a volume of 1.00x10⁻³ m³ mol⁻¹ to 5.00x10⁻³ m³ mol⁻¹ at 300 K.

[HW01-08:#19-30, #19-31]

(1) For 1 mole of an ideal gas, assuming that $(\partial U/\partial V)_T = 0$, prove that $(\partial H/\partial V)_T = 0$.

(2) For 1 mole of an ideal gas, assuming that $(\partial U/\partial V)_T = 0$, prove that $(\partial C_V/\partial V)_T = 0$.

[HW01-09:#20-13]

(1) Please show that

$$\Delta S = C_P \ln \frac{T_2}{T_1}$$

for a reversible constant-pressure process if C_P (constant pressure heat capacity) is independent of temperature.

*<Hint> Use the definition of C_P ($C_P = (\partial H/\partial T)_{N,P}$), S ($dS = \frac{\delta q_{rev}}{T}$) and H ($H = U + PV$).

(2) Using the equation above, please calculate the change in the entropy of 1.00 mole of H_2O (liquid) ($C_P=75.2 \text{ J K}^{-1}$) when it is heated from 300 K to 360 K.

[HW01-10:#20-14]

(1) Please show that

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

when 1 mole of an ideal gas is taken from state-1 (T_1, V_1) to state-2 (T_2, V_2), assuming that C_V (constant-volume heat capacity) is independent of temperature.

(2) Please calculate the value of ΔS when 1 mole of N_2 (gas) is expanded from $20.0 \times 10^{-3} \text{ m}^3$ at 273 K to $80.0 \times 10^{-3} \text{ m}^3$ at 400 K. Please assume that C_P (constant-pressure heat capacity) is 29.4 J K^{-1} . If necessary, please use the following relationship in the heat capacities of ideal gas: " $C_P - C_V = nR$ ".

[HW01-11:#20-25, #20-26] Please calculate (i) entropy change of the system, (ii) entropy change of the surroundings and (iii) the sum of these entropy changes in the following processes:

(1) A process where 1 mole of an ideal gas is isothermally and reversibly expanded from a pressure of $5.00 \times 10^5 \text{ Pa}$ to $2.00 \times 10^5 \text{ Pa}$ at 400 K.

(2) A process where the system composed by 1 mole of an ideal gas is adiabatically expanded into a vacuum. The initial pressure of the system is 5.00×10^5 Pa and the final pressure of the system is 2.00×10^5 Pa. (Hint: This is an irreversible process. So, in order to calculate the entropy change of the system, we need to consider a corresponding reversible processes which bring the system from the initial state to the final state reversibly.)

[HW01-12: Diesel cycle]

We consider a “Diesel cycle” of n mol of an ideal gas, whose C_p (constant-pressure heat capacity) is $\frac{5}{2}nR$ and whose C_v (constant-volume heat capacity) is $\frac{3}{2}nR$.

The Diesel cycle is composed of the following 4 processes:

- ✓ <Process-1> Reversible constant-pressure expansion from (P_1, T_1, V_1) to (P_1, T_2, V_2) .
- ✓ <Process-2> Reversible adiabatic expansion from (P_1, T_2, V_2) to (P_2, T_3, V_3) .
- ✓ <Process-3> Reversible constant-volume cooling from (P_2, T_3, V_3) to (P_3, T_4, V_3) .
- ✓ <Process-4> Reversible adiabatic compression from (P_3, T_4, V_3) to (P_1, T_1, V_1)

Please answer to the following questions assuming that these 4 processes are reversible.

(1) Please draw V-P diagram and V-T diagram for this cycle.

(2) For each process, please express the following quantities using P, V, T, n, C_p, C_v and R . (“P” means P_1, P_2 , and/or P_3 for example): (i) ΔU (the change in the internal energy of the system), (ii) ΔS (the change in the entropy of the system), (iii) q (heat) and (iv) w (work).

(3) Please describe the efficiency (η) of this cycle using T, C_p, C_v and/or R . Note that η is defined as:

$$\eta = \frac{W_{out}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

where W_{out} is the total work that the system made to the surroundings in a single operation of the cycle (for example, if the system received the work of $W_1 (>0)$ from the surroundings and made the work of $W_2 (>0)$ to the surroundings, $W_{out} = W_2 - W_1$), $Q_H (>0)$ is the heat that the system received from the higher-temperature thermostat, and $Q_L (>0)$ is the heat that the system released to the lower-temperature thermostat. Note that the first law ($\Delta U = q + w = Q_H - Q_L - W_{out} = 0$) is used to change the 2nd term to the 3rd term.

[HW01-13: Brayton cycle]

We consider a "Brayton cycle" of n mol of an ideal gas, whose C_p (constant-pressure heat capacity) is $\frac{5}{2}nR$ and whose C_v (constant-volume heat capacity) is $\frac{3}{2}nR$.

The Diesel cycle is composed of the following 4 processes:

- ✓ <Process-1> Constant-pressure heating from (P_1, T_1, V_1) to (P_1, T_2, V_2) .
- ✓ <Process-2> Adiabatic expansion from (P_1, T_2, V_2) to (P_2, T_3, V_3) .
- ✓ <Process-3> Constant-pressure cooling from (P_2, T_3, V_3) to (P_2, T_4, V_4) .
- ✓ <Process-4> Adiabatic compression from (P_2, T_4, V_4) to (P_1, T_1, V_1)

Please answer to the following questions assuming that these 4 processes are reversible.

(1) Please draw V-P diagram and V-T diagram for this cycle.

(2) For each process, please express the following quantities using P, V, T, n, C_p, C_v and R . ("P" means P_1 , and/or P_2 for example): (i) ΔU (the change in the internal energy of the system), (ii) ΔS (the change in the entropy of the system), (iii) q (heat) and (iv) w (work).

(3) Please describe the efficiency (η) of this cycle using T, C_p, C_v and/or R . Please check HW01-12 for the definition of η .