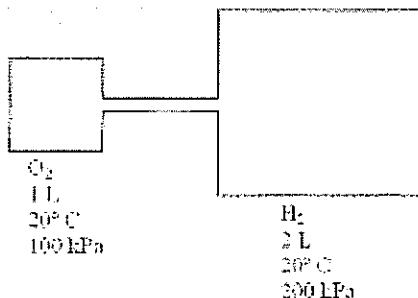


**Example on applying Dalton's law:**

Part 1: A flask with volume of 1 L is filled with oxygen at 20°C and 100 kPa. A second flask with volume of 2 L is filled with hydrogen at the same temperature and 200 kPa. The two flasks are then joined by a narrow tube and the two gases mix. Calculate the partial pressures of the two gases and the total pressure in each of the two flasks.

Part 2: Assume that a spark inside the flasks ignites the mixture. After cooling the flasks to 20°C, calculate the partial pressures of gases and the total pressure in each of the flasks. State clearly any additional assumptions/simplifications you need to make.



(a) After they are connected, P is the total pressure of the system and it is the same at any point.

$$n_{O_2} = \frac{P_{O_2} V_{O_2}}{RT} = \frac{100 \times 1 \times 10^{-3} \text{ Pa} \times 1 \times 10^{-3} \text{ m}^3}{8.314 \times 293.15 \text{ K}} = 0.041 \text{ mol}$$

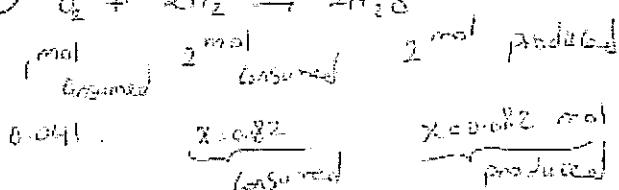
$$n_{H_2} = \frac{200 \times 2 \times 10^{-3} \text{ Pa} \times 2 \times 10^{-3} \text{ m}^3}{8.314 \times 293.15 \text{ K}} = 0.1641 \text{ mol}$$

$$n_{\text{Final}} = \frac{PV}{RT} = \frac{P \times 3 \times 10^{-3} \text{ m}^3}{8.314 \times 293.15} = 1.2381 \cdot 10^{-6} P$$

$$(n_{O_2} + n_{H_2})_{\text{initial}} = n_{\text{Final}} \rightarrow 0.2051 = 1.2381 \cdot 10^{-6} P \rightarrow P = 166.748 \text{ Pa} = 166.75 \text{ kPa}$$

$$\left( \begin{array}{l} P_{O_2} = \frac{P_{\text{tot}} \cdot P}{n} \\ = \frac{0.041 \times 166.75}{0.2051} = 33.43 \text{ kPa} \\ P_{H_2} = \frac{P_{\text{tot}} \cdot P}{n} = 133.42 \text{ kPa} \end{array} \right)$$

$$(b) O_2 + 2H_2 \rightleftharpoons 2H_2O$$



$$(n_{O_2})_f = 0 \quad (n_{H_2})_f = 0.082 \text{ mol}$$

$$(n_{H_2O})_f = 0 \quad [\text{because at } 25^\circ\text{C, water is in liquid phase.}]$$

$$P_t = P_{H_2} = \frac{0.082 \times R \times 293.15}{2 \times 10^{-3}} = 666.99 \text{ Pa}$$

Example on ideal and real gases:

A closed system with volume of  $0.15 \text{ m}^3$  contains 40 kg ethylene in the gas phase. Calculate the pressure of the gas at  $25^\circ\text{C}$  in the system using:

- ideal gas law
- virial equation of state
- Van der Waals equation of state

$$a = \frac{27R^2T_c^2}{64P_c}$$

$$b = \frac{RT_c}{8P_c}$$

For ethylene:  $T_c=282.3 \text{ K}$        $M_N = 28 \text{ g/mol}$

$P_c=50.4 \text{ bar}$

$B=242 \text{ cm}^3/\text{mol}$

$C=25200 \text{ cm}^6/\text{mol}^2$

$$m = 40 \text{ kg} \rightarrow n = \frac{40 \times 10^3}{28} = 1428.6 \text{ mol}$$

$$\textcircled{1} \quad p = \frac{nRT}{V} = \frac{1428.6 \times 8.314 \times 298.15}{0.15} = 2.36683 \times 10^7 \text{ Pa}$$

$$\textcircled{2} \quad Z = 1 + \frac{nB}{V} + \frac{n^2C}{V^2} = 1 + \frac{1428.6 \times 242 \times 10^{-6}}{0.15} + \frac{(1428.6)^2 \times 25200 \times 10^{-12}}{(0.15)^2} = 0.98$$

$$Z = \frac{PV}{nRT} \rightarrow p = Z \left( \frac{nRT}{V} \right) = 0.98 \times 2.36683 \times 10^7 = 2.3136 \times 10^7 \text{ Pa}$$

$$\textcircled{3} \quad p = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

$$a = \frac{27R^2T_c^2}{64P_c} = 0.4611 \quad b = \frac{RT_c}{8P_c} = 5.82 \times 10^{-5} \text{ m}^3/\text{mol}$$

$$\therefore \frac{1428.6 \times R \times 298.15}{0.15 - (1428.6 \times 5.82 \times 10^{-5})} - \frac{0.4611 \times (1428.6)^2}{(0.15)^2} = 1.1146 \times 10^7 \text{ Pa}$$

Example on first law:

A piston which applies a constant pressure of 5 bar is used to compress 3 moles of an ideal gas at constant temperature of 25°C from an initial pressure of 0.5 bar to a final pressure of 3 bar. Assume that C<sub>v</sub> for this ideal gas is 3/2R.

- How much work is done to compress the gas?
- How much heat will be transferred in this process?
- What is the sign of W and Q. Define whether heat is transferred from the system to the surroundings or vice versa? What about work?

$$n = 3 \text{ mol} \quad P_{ext} = 5 \text{ bar} = 5 \times 10^5 \text{ Pa} \quad V_1 = \frac{nRT_1}{P_1} = \frac{3 \times 8.314 \times 298.15}{5 \times 10^5} = 0.1487 \text{ m}^3$$

$$\left\{ \begin{array}{l} T_1 = 25^\circ\text{C} = 298.15 \text{ K} \\ P_1 = 0.5 \text{ bar} \end{array} \right. \xrightarrow{\text{compress}} \left\{ \begin{array}{l} T_2 = T_1 = 25^\circ\text{C} \\ P_2 = 3 \text{ bar} \end{array} \right. \quad V_2 = \frac{nRT_2}{P_2} = 0.0248 \text{ m}^3$$

(a)  $W = -P_{ext}(V_2 - V_1) = -5 \times 10^5 \text{ Pa} (0.0248 - 0.1487) \text{ m}^3 = +61955.9 \text{ J}$   
 (Work should be positive because it is done on the system by the surroundings)

(b)  $\Delta T = 0 \rightarrow nC_V \Delta T = \Delta U = 0$

$$\Delta U = Q + W \rightarrow Q = -W = -61955.9 \text{ J}$$

The heat is transferred from the system to the surroundings (Q is negative)

Example on first law:

The molar heat capacity at constant volume for water vapour varies with temperature according to

$$C_v = 22.23 + 0.0103T$$

where  $C_v$  is in (J/mol/K) and  $T$  is the temperature in Kelvin.

Calculate  $W$ ,  $Q$  and  $\Delta U$  when one mole of water vapour is heated at constant volume from 25 to 200°C. Assume water vapour has ideal gas behaviour.

$$n = 1 \text{ mol}$$

$$\left\{ T_1 = 25^\circ\text{C} = 298.15 \text{ K} \quad \xrightarrow{\text{Const. } V} \quad \right\} \quad \left\{ T_2 = 200^\circ\text{C} = 473.15 \text{ K} \right\}$$

$$\text{Const. } V \longrightarrow \Delta V = 0 \longrightarrow W = -P_{\text{ext}} \Delta V = 0$$

$$\Delta U = Q + \int \overset{W}{\cancel{W}} = \int_{T_1}^{T_2} n C_V dT \quad \begin{array}{l} (\text{because } C_V \text{ is not constant and it is} \\ \text{a function of } T, \text{ so you cannot take it} \\ \text{out of integral in this problem}) \end{array}$$

$$= 1 \times \int_{T_1}^{T_2} (22.23 + 0.0103 T) dT = 22.23(T_2 - T_1) + \frac{0.0103}{2} (T_2^2 - T_1^2) \quad \left. \begin{array}{l} T_2 = 473.15 \\ T_1 = 298.15 \end{array} \right. =$$

$$4585.4 \text{ J} = 4585.4 \text{ K}\cdot\text{J}$$

Example on first law:

A perfectly insulated cylinder arrangement of initial volume  $2 \text{ m}^3$  contains argon which may be assumed to behave as an ideal monatomic gas at 300K and 1 bar pressure. The whole apparatus is located in a vacuum chamber (i.e., the external pressure is zero). By applying an adjustable external force, the gas is reversibly compressed to a final temperature of 1200 K.

- What is the final volume of the gas?
- What is the total work that was done on the gas?

$$C_V = 3/2R$$

Ar

$$\left\{ \begin{array}{l} V_1 = 2 \text{ m}^3 \\ T_1 = 300 \text{ K} \\ P_1 = 1 \text{ bar} \end{array} \right. \xrightarrow[\substack{\text{Ad.} \\ \text{Rev.}}]{\text{Re.V.}} \left\{ \begin{array}{l} T_2 = 1200 \text{ K} \\ V_2 = ? \end{array} \right.$$

[insulated]  $\rightarrow Q = 0 \rightarrow$  Adiabatic

$$n = \frac{PV_1}{RT_1} = 80.19 \text{ mol}$$

$$\Delta U = Q + W \rightarrow W = \Delta U = n C_V \Delta T = 80.19 \times \frac{3}{2} R \times (1200 - 300) = \underline{\underline{9 \times 10^5 \text{ J}}}$$

Adiabatic and reversible process of ideal gases:

$$\frac{T_2}{T_1} = \left( \frac{V_2}{V_1} \right)^{-\frac{R}{C_V}} \rightarrow \frac{1200}{300} = \left( \frac{V_2}{2} \right)^{-\frac{2}{3}} \rightarrow V_2 = 0.25 \text{ m}^3$$

Note: In a compression process, system has its maximum volume initially and then at final conditions it reaches min. volume but max. temperature and max. pressure.

Example on different types of processes:

One mol air is compressed from an initial condition of 1 bar and 25 °C to a final state of 5 bar and 25°C by three different mechanically reversible processes in a closed system:

- heating at const. volume followed by cooling at const. pressure
- isothermal compression
- adiabatic compression followed by cooling at const. volume

Assume air to be an ideal gas with const. heat capacities of  $C_v = 5/2R$  and  $C_p = 7/2R$ . Calculate work required, heat transferred and the changes in internal energy and enthalpy of the air for each process.

$$n = 1 \text{ mol}$$

$$\begin{cases} P_1 = 1 \text{ bar} \\ T_1 = 25^\circ\text{C} \end{cases} \xrightarrow{\text{Comp.}} \begin{cases} P_2 = 5 \text{ bar} \\ T_2 = 25^\circ\text{C} \end{cases}$$

$$\begin{cases} P_1 = 1 \text{ bar} \\ T_1 = 25^\circ\text{C} \end{cases} \xrightarrow{\text{Const. } V} \begin{cases} P_2 = P_3 = 5 \text{ bar} \\ T_2 = T_3 = 25^\circ\text{C} \\ V_2 = V_1 \\ V_3 \end{cases}$$

$$V_1 = \frac{RT_1}{P_1} = 0.025 \text{ m}^3$$

$$T_2 = \frac{P_2 V_2}{nR} = 149.0 \text{ K}$$

$$\textcircled{1} \quad W_1 = 0 \quad (\text{const. } V)$$

$$Q_1 = \Delta U = n C_v \Delta T = n \times \frac{5}{2} R \times (149.0 - 298.15) = 24788.2 \text{ J}$$

$$\textcircled{2} \quad Q_2 = Q_P = n C_p \Delta T = n \times \frac{7}{2} R \times (298.15 - 149.0) = -34705.5 \text{ J}$$

$$Q_T = Q_1 + Q_2 = -9915 \text{ J}$$

$$\Delta U_T = n C_v \Delta T_T = 0 \quad (25^\circ\text{C} \rightarrow 25^\circ\text{C})$$

$$\Delta U_T = Q_T + w_T \rightarrow w_T = -Q_T = +9915 \text{ J}$$

$$\textcircled{3} \quad \text{Rev. Isothermal: } w = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2} = -1 \times R \times 298.15 \ln \frac{1}{5} = +3989.5 \text{ J}$$

$$\Delta T = 0 \rightarrow \Delta U = 0 \rightarrow Q = -w = -3989.5 \text{ J}$$

$$\textcircled{4} \quad \begin{cases} 1 \text{ bar} \\ 25^\circ\text{C} \\ V_1 = 0.025 \text{ m}^3 \end{cases} \xrightarrow{\text{Adi. Rev.}} \begin{cases} P_2 \\ T_2 \\ V_1 \end{cases} \xrightarrow{\text{Const. } V} \begin{cases} P_3 = 5 \text{ bar} \\ T_3 = 25^\circ\text{C} \\ V_3 = \frac{nRT_3}{P_3} = 0.00496 \text{ m}^3 \\ V_3 - V_2 \\ V_2 = V_3 = 0.00496 \text{ m}^3 \end{cases}$$

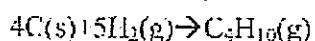
$$\frac{T_2}{T_1} = \left( \frac{V_2}{V_1} \right)^{\frac{R}{C_v}} \rightarrow \frac{T_2}{298.15} = \left( \frac{0.00496}{0.025} \right)^{\frac{2}{5}} \rightarrow T_2 = 569.5 \text{ K}$$

$$\textcircled{5} \quad \{ \quad W_1 = \Delta U_1 + Q_1 = n C_v (T_2 - T_1) = 1 \times \frac{5}{2} R \times (569.5 - 298.15) = 5640.2 \text{ J}$$

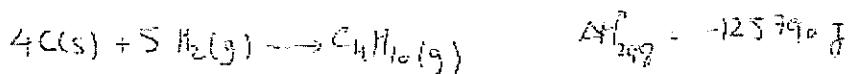
$$\textcircled{6} \quad \{ \quad W_2 = 0 \leftarrow \text{const. } V \rightarrow w_T = W_1, \quad w_2 = 5640.2 \text{ J}$$

$$\Delta U_T = 0 \quad (\text{const. } T)$$

$$Q_T = \Delta U_T - w_T = -5640.2 \text{ J}$$

Example on thermochemistry:Calculate  $\Delta H^\circ_{298}$  for the following reaction using data provided in the table:

reaction	$\Delta H^\circ_{298} (\text{J/mol})$
$\text{+ } 4\text{C(s)} + 4\text{O}_2\text{(g)} \rightarrow 4\text{CO}_2\text{(g)}$	4 (-393509)
$\text{+ } 5\text{H}_2\text{(g)} + 1/2\text{O}_2\text{(g)} \rightarrow \text{5H}_2\text{O(l)}$	5 (-285830)
$\text{+ } 4\text{CO}_2\text{(g)} + 5\text{H}_2\text{O(l)} \rightarrow \text{C}_5\text{H}_{10}\text{(g)} + 13/2\text{ O}_2\text{(g)}$	2877396

Example on the first law:

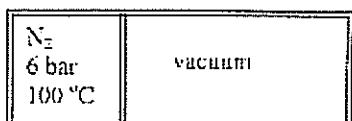
An insulated 4 m<sup>3</sup> tank is divided to two unequal parts with a membrane. The smaller part contains nitrogen gas at 100 °C and 6 bar and its volume is 1/3 of the total volume. The other 2/3 of the tank is under vacuum. In a process, the membrane is removed and nitrogen gas fills up the tank.

a. What is the final temperature of the gas? Is this process reversible or not?

b. Calculate the minimum amount of work required to restore the gas to its initial conditions in an isothermal process?

$$W = \frac{P_1 V_1}{R T_1} \times \frac{1}{3} \times \frac{P_1 V_1}{8.314 \times 373.15} = 257.9 \text{ J}$$

Assume nitrogen behaves as an ideal gas.  $C_p = 7/2 R \text{ J/mol/K}$



(A)  $P_{ext} = 0 \rightarrow dW = -P_{ext} dV = 0 \rightarrow dW = \frac{Q}{T} dT = 0 \rightarrow \Delta T = 0 \rightarrow T_2 = T_1 = 100^\circ\text{C}$   
insulated  $\rightarrow Q = 0$

(B)  $W_{min} = W_{rev} = -nRT \ln \frac{V_2}{V_1} = -1.01 \times 10^4 \text{ mol} \times 8.314 \times 373.15 \times \ln \frac{4/3}{1} \approx 8788.9 \text{ J}$

### Example on the first law:

1 m<sup>3</sup> of an ideal gas which is initially at 1000 kPa and 600 K is expanded to 5 times of its volume under three different processes. For each process, calculate final temperature, pressure and work produced by the gas.  $C_p = 21 \text{ J/mol/K}$

- a. an isothermal reversible process
  - b. an adiabatic reversible process
  - c. an adiabatic irreversible process against constant external pressure of 100 kPa

$$\left\{ \begin{array}{l} V = 1 \text{ m}^3 \\ T = 600 \text{ K} \\ P = 10^{-6} \text{ Pa} \end{array} \right. \xrightarrow{\text{expansion}} \left\{ \begin{array}{l} V_2 = 5 \text{ m}^3 \\ T_2 = ? \\ P_2 = ? \end{array} \right.$$

Note: in an expansion process, system goes from max. T and max. p to max. Volume.

<u>initial</u>	<u>final</u>
Condition	Condition

$$n = \frac{P_1 V_1}{RT_1} = 2_{\text{mole}}$$

③ rev. isothermal

$$T_2 = T_1 = 600 \text{ K} \quad P_1 V_1 = P_2 V_2 \implies P_2 = \frac{P_1 V_1}{V_2} = 2 \times 1.5 \text{ Pa}$$

$$W = -nRT \ln \frac{V_2}{V_1} = -200.5 \times 8.314 \times 600 \ln \frac{5}{1} = \dots \checkmark$$

b) Rev., adiabatic

$$b) \text{ Rev, adiabatic} \quad \frac{T_2}{T_1} = \left( \frac{V_2}{V_1} \right)^{\frac{-R}{C_V}} \rightarrow T_2 = 600 \left( \frac{5}{7} \right)^{\frac{-R}{C_V}} = \dots \rightarrow P_2 = \frac{P_1 R T_2}{V_2} = \sqrt{ } \quad \text{Ans}$$

$$w = \Delta U - \cancel{q} = n C_V \Delta T = \checkmark$$

$$C_p = C_V + R \rightarrow C_V = 12.686 \text{ J/mol.K}$$

(C) Erev, Ad.

三

$$W = -P_{ext} \Delta V = -100 \times 10^3 \text{ Pa} \cdot (5-1) m^3 = -4 \times 10^5 J$$

$$\Delta U_{W+Q} \rightarrow nC_V \Delta T = -4 \times 1.5 \text{ J} \rightarrow \Delta T = -157.26 \rightarrow T_2 = 442.7 \text{ K}$$

$$P_2 = \frac{nRT_2}{V_2} = \checkmark$$

Examples on second law:

1. In a process, one mole of an ideal gas is expanded adiabatically from 800K and 8 bar to a final pressure of 1 bar. Calculate  $\Delta S$ ,  $\Delta U$  and  $Q$  for this process for the following conditions ( $C_p=5/2R$ ):

- if the process is reversible
- if the process is irreversible and 3000 J work is produced during the process.
- if the process is irreversible and expansion is made against vacuum (i.e.  $P_{\text{ext}}=0$ )

$$n = 1 \text{ mol}$$

$$\left\{ \begin{array}{l} P_1 = 8 \text{ bar} \\ T_1 = 800 \text{ K} \end{array} \right. \xrightarrow{\text{Ad.}} \left\{ \begin{array}{l} P_2 = 1 \text{ bar} \\ T_2 = ? \end{array} \right.$$

$$(a) \text{ Adiabatic, Rev} \rightarrow Q_{\text{rev}} = 0 \rightarrow \Delta S = \frac{Q_{\text{rev}}}{T} = 0$$

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{R}{C_p}} \rightarrow T_2 = 348 \text{ K}$$

$$\Delta U = nC_V \Delta T = 1 \times \frac{5}{2} R \times (348 - 800) = -5636.9 \text{ J}$$

$$(b) \text{ Adiabatic, Irreversible} \rightarrow Q_{\text{irrev}} = 0$$

$$W = -3000 \text{ J} \quad \Delta U = \cancel{Q} + W \rightarrow nC_V \Delta T = -3000 \text{ J} \rightarrow 1 \times \frac{5}{2} R \times (T_2 - 800) = -3000 \text{ J}$$

$$T_2 = 559 \text{ K}$$

$$\Delta S = nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} = 1 \times \frac{5}{2} R \times \ln \frac{559}{800} - 1 \times R \times \ln \frac{1}{8} = 9.8 \text{ J/K}$$

$$(c) \text{ Adiabatic, irreversible, } P_{\text{ext}} = 0$$

$$Q = 0 \quad \left. \begin{array}{l} \rightarrow \Delta U = \cancel{Q} + W = 0 \\ P_{\text{ext}} = 0 \rightarrow W = 0 \end{array} \right\} \rightarrow \Delta T = 0 \rightarrow T_2 = T_1 = 800 \text{ K}$$

$$\Delta S = nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} = -1 \times R \times \ln \frac{1}{8} = 17.2 \text{ J/K}$$

2. A 300 mL cup of hot coffee initially at 60°C is placed on the table and allowed to cool to room temperature (25°C). Estimate the entropy change of the universe as a result of this process. Do you expect the values be positive or negative? Why?

$$C_p, \text{coffee} = C_p, \text{water} = 4.18 \text{ J/g/K} \quad \rho = 1 \text{ g/mL} \quad \rho = \frac{m}{V} \quad m = \rho \times V = 300 \text{ g}$$

Note : for liquids and solids :  $C_p \sim C_V \sim C$  and the effect of volume or pressure change on the properties is negligible :  $\Delta P \sim \Delta V \sim 0$

$$\Delta S_{\text{sys}} = m C_p \ln \frac{T_2}{T_1} = 300 \text{ g} \times 4.18 \text{ J/g.K} \times \ln \frac{298.15}{333.15} = -139.17 \text{ J/K}$$

$$Q_{\text{sys}} = m C_p (T_2 - T_1) = 300 \times 4.18 \times (298.15 - 333.15) = -43890 \text{ J}$$

$$\Delta S_{\text{surr.}} = \frac{Q_{\text{surr. rev}}}{T_{\text{surr}}} = \frac{-Q_{\text{sys}}}{T_{\text{surr}}} = \frac{43890}{298.15} = 147.21 \text{ J/K}$$

$$\Delta S_{\text{uni.}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr.}} = +8.2 \text{ J/K} > 0 \quad \text{positive because it is a spontaneous process.}$$

3. One mole of an ideal gas is initially at 0 °C and 1 bar undergoes different reversible processes. For each process, calculate W, Q, ΔU, ΔH and AS. Cp=5/2R:

- cooling at const. V to -100°C
- isothermal compression to 100 bar
- heating at const. pressure up to 100°C
- adiabatic expansion to 0.1 bar pressure

$$n = 1 \text{ mol} \quad T_1 = 273.15 \text{ K} \quad P_1 = 1 \text{ bar} = 10^5 \text{ Pa}$$

(a)  $V = \text{const.} \rightarrow W = -P_{\text{ext}} \Delta V = 0$

$$\Delta U = Q + \cancel{W} = n C_V \Delta T = 1 \times \frac{5}{2} R \times (173.15 - 273.15) = -1247.1 \text{ J}$$

$$\Delta H = n C_p \Delta T = -2078.5 \text{ J}$$

$$\Delta S = n C_V \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1} = -5.7 \text{ J/K}$$

(b)  $\Delta T = 0 \rightarrow \Delta U = \Delta H = 0$

$$W = -nRT \ln \frac{V_2}{V_1} = -nR \tau \ln \frac{P_1}{P_2} = -1 \times R \times 273.15 \times \ln \frac{1}{100} = 10458.2 \text{ J}$$

$$Q = -W = -10458.2 \text{ J}$$

$$\Delta S = n C_p \ln \frac{T_2}{T_1} - n R \ln \frac{P_2}{P_1} = -38.29 \text{ J/K}$$

(c)  $P = \text{const.} \rightarrow Q_p = \Delta H = n C_p \Delta T = 1 \times \frac{5}{2} R \times (373.15 - 273.15) = 2078.5 \text{ J}$

$$\Delta U = n C_V \Delta T = 1 \times \frac{5}{2} R \times (373.15 - 273.15) = 1247.1 \text{ J}$$

$$W = \Delta U - Q = -831.4 \text{ J}$$

$$\Delta S = n C_p \ln \frac{T_2}{T_1} - n R \ln \frac{P_2}{P_1} = 6.48 \text{ J/K}$$

(d)  $Q_{\text{rev}} = 0 \rightarrow \Delta S = 0 \quad \text{?} \quad \frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{1}{k_p}} \rightarrow T_2 = 108 \text{ K}$

$$\Delta U = W + \cancel{Q} = n C_V \Delta T = 1 \times \frac{5}{2} R \times (108 - 273.15) = -2059.6 \text{ J}$$

$$\Delta H = n C_p \Delta T = -3432.6 \text{ J}$$

4. One mole of an ideal gas is compressed isothermally but irreversibly at 400K from 3 bar to 7 bar in a piston/cylinder device. The work required is 48% greater than the work of reversible isothermal compression. The heat transferred from the gas during the compression flows to the surrounding at 25°C. Calculate the entropy change of the gas, the surroundings and  $\Delta S_{\text{univ.}}$  ( $C_p=7/2R$ )

$$n = 1 \text{ mol}$$

$$\left. \begin{array}{l} T_1 = 400 \text{ K} \\ P_1 = 3 \text{ bar} \end{array} \right\} \xrightarrow[\text{Isotherm. Inv.}]{\text{Comp.}} \left. \begin{array}{l} T_2 = 400 \text{ K} \\ P_2 = 7 \text{ bar} \end{array} \right\}$$

$$\Delta S_{\text{sys}} = nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} = -1 \times R_N \ln \frac{7}{3} = -7.044 \text{ J/K}$$

$$\Delta S_{\text{surr}} = \frac{Q_{\text{surr, rev}}}{T_{\text{surr}}} \quad Q_{\text{surr, rev}} = -Q_{\text{sys}}$$

$$\Delta G = Q + W \longrightarrow Q = -W$$

↓  
T = 0

$$W_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2} = -1 \times 8.34 \times 400 \times \ln \frac{3}{7} = 2817.8 \text{ J}$$

$$W_{\text{real}} = 1.18 \times W_{\text{rev}} = 4170.3 \text{ J} \longrightarrow Q_{\text{real}} = -W_{\text{real}} = \underbrace{-4170.3 \text{ J}}$$

$$\rightarrow Q_{\text{surr}} = -Q_{\text{sys}} = +4170.3 \text{ J} \longrightarrow \Delta S_{\text{surr}} = \frac{4170.3 \text{ J}}{298.15 \text{ K}} = 13.99 \text{ J/K}$$

$$\Delta S_{\text{univ.}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 6.9 \text{ J/K}$$

Examples on phase equilibria:

1. The normal melting point of mercury is  $-38.87^{\circ}\text{C}$ . At  $-38.87^{\circ}\text{C}$  and 1 atm pressure, the density of the liquid and that of the solid are 13.69 and  $14.19 \text{ g/cm}^3$ , respectively. The molar heat of fusion at the normal melting point is  $2.42 \text{ kJ/mol}$ . Calculate the change in the melting point if the pressure is increased by 100 atm. ( $M_w, \text{Hg}=200 \text{ g/mol}$ )  $\text{Hg}_{\text{solid}} \rightarrow \text{Hg}_{\text{liquid}}$ )

$$P_1 = 1 \text{ atm} \rightarrow T_{mp} = -38.87^{\circ}\text{C} = 234.28 \text{ K}$$

Assumptions:  $\Delta H_{\text{fus}}$  and  $\Delta V_{\text{fus}}$  are constant over the temperature and pressure range involved.

$$\frac{dP}{dT} = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \rightarrow \int_{T_1}^{T_2} \frac{dP}{T} = \int_{P_1}^{P_2} \frac{\Delta V_{\text{fus}}}{\Delta H_{\text{fus}}} dP \rightarrow \ln \frac{T_2}{T_1} = \frac{\Delta V_{\text{fus}}}{\Delta H_{\text{fus}}} \Delta P$$

$$\Delta V_{\text{fus}} = \bar{V}_{\text{liquid}} - \bar{V}_{\text{solid}} = \frac{1}{\rho_{\text{liquid}}} - \frac{1}{\rho_{\text{solid}}} = \frac{1}{13.69} - \frac{1}{14.19} = 0.00257 \text{ cm}^3/\text{g}$$

$$\ln \frac{T_2}{T_1} = \frac{(0.00257 \text{ cm}^3/\text{g}) \times \frac{1 \text{ m}^3}{1000 \text{ cm}^3} \times 2.42 \times 10^3 \text{ J/mol}}{2.42 \times 10^3 \text{ J/mol}} \times (100 \times 101325) \text{ Pa}$$

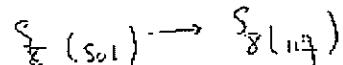
$$\rightarrow T_2 = 234.79 \text{ K} \rightarrow \Delta T = T_2 - T_1 = \approx 5 \text{ K}$$

2. The melting point of monoclinic sulphur ( $S_8$ ) at atmospheric pressure is  $119.3^{\circ}\text{C}$ , the change in volume during fusion is  $+41 \text{ cm}^3/\text{kg}$  and  $\Delta H_{\text{fus}}=3.376 \text{ kcal/mol}$ . Estimate the melting point of monoclinic sulphur when pressure is increased to 1000 atm. ( $M_w$  for S=32 g/mol)

$1 \text{ kcal} = 4.18 \text{ kJ}$

(Answer:  $T_2=423.17 \text{ K} = 150^{\circ}\text{C}$ )

Note:  $M_w$  for  $S_8=8 \times (M_w, \text{S})$



$$\ln \frac{T_2}{T_1} = \frac{\Delta V_{\text{fus}}}{\Delta H_{\text{fus}}} \cdot \Delta P$$

$$\ln \frac{T_2}{T_1} = \frac{41 \text{ cm}^3/\text{g} \times \frac{1 \text{ m}^3}{1000 \text{ cm}^3} \times (8 \times 32 - 9) \text{ g/mol}}{3.376 \times 10^3 \times 4.18 \text{ kJ/mol}} \times (1000 - 1) \times 101325 \text{ Pa}$$

$$T_2 = 423.17 \text{ K} = 150^{\circ}\text{C}$$

3. What pressure in atm is required to make ice melt at  $-20^{\circ}\text{C}$ . (Answer:  $P_2=2883 \text{ atm}$ )

Data:  $\rho_{\text{ice}}=0.92 \text{ g/cm}^3$ ,  $\rho_{\text{water}}=1.0 \text{ g/cm}^3$ ,  $\Delta H_{\text{fus}}=334 \text{ kJ/kg}$

$\text{ice}_{(\text{sol})} \longrightarrow \text{water}_{(\text{aq})}$

$$T_1 = 273.15 \text{ K} \longrightarrow P_1 = 1 \text{ atm} = 101325 \text{ Pa}$$

$$\ln \frac{T_2}{T_1} = \frac{\Delta V_{\text{fus}}}{\Delta H_{\text{fus}}} \Delta P$$

$$\Delta V = \bar{V}_{\text{aq}} - \bar{V}_{\text{sol}} = \frac{1}{\rho_{\text{aq}}} - \frac{1}{\rho_{\text{sol}}} = -0.08696 \text{ cm}^3/\text{g}$$

$$\Delta P = \frac{\Delta H_{\text{fus}}}{-0.08696 \times 10^3 \text{ m}^3/\text{K}} \times \ln \frac{253.15}{273.15} = \checkmark$$

$$P_2 = \Delta P + P_1 = \dots$$

4. The saturated steam table lists pressures of 0.467 atm and 1.96 atm for temperatures of  $80^{\circ}\text{C}$  and  $120^{\circ}\text{C}$ , respectively. Using this information, estimate the value of the heat of vaporization of water at  $100^{\circ}\text{C}$ .

Clausius - Clapeyron :

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$T_1 = 80^{\circ}\text{C} = 353.15 \text{ K} \longrightarrow P_1 = 0.467 \text{ atm}$$

$$T_2 = 120^{\circ}\text{C} = 393.15 \text{ K} \longrightarrow P_2 = 1.96 \text{ atm}$$

$$\ln \frac{1.96}{0.467} = -\frac{\Delta H_{\text{vap}}}{8.314} \left( \frac{1}{393.15} - \frac{1}{353.15} \right) \longrightarrow \Delta H_{\text{vap}} = 41350 \text{ J/mol}$$

5. The vapour pressure of liquid mercury is 96.5 kPa at 354 °C and 107.5 kPa at 360 °C. Calculate the enthalpy change when one mole of liquid Hg vaporizes and determine its normal boiling point. (Answer:  $\Delta H_{\text{vap}}=5.94 \times 10^4 \text{ J/mol}$ ,  $T_{\text{bp}}=356.7 \text{ }^\circ\text{C}$ )

$$T_1 = 354 \text{ }^\circ\text{C} = 627.15 \text{ K} \rightarrow P_1 = 96.5 \text{ kPa}$$

$$T_2 = 360 \text{ }^\circ\text{C} = 633.15 \text{ K} \rightarrow P_2 = 107.5 \text{ kPa}$$

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \rightarrow \Delta H_{\text{vap}} = 5.94 \times 10^4 \text{ J/mol}$$

$$\text{at normal boiling point} \rightarrow P = 1 \text{ atm} = 101.325 \text{ kPa}$$

$$\ln \frac{107.5}{101.325} = -\frac{5.94 \times 10^4}{8314} \left[ \frac{1}{633.15} - \frac{1}{T_1} \right] \rightarrow T_1 = 629.85 \text{ K} \approx 356.7 \text{ }^\circ\text{C}$$

6. The vapour pressure of water at 0.01 °C is 611 Pa; the vapour pressure of ice at -5°C is 402 Pa. Calculate the enthalpy change of sublimation of ice. (Answer:  $\Delta H_{\text{sub}}=5.089 \times 10^5 \text{ J/mol}$ )

( $\text{ice} \xrightarrow{\text{heat}} \text{water (vap)}$ )

$$T_1 = -5 \text{ }^\circ\text{C} = 268.15 \text{ K} \rightarrow P_1 = 402 \text{ Pa}$$

$$T_2 = 0.01 \text{ }^\circ\text{C} = 273.16 \text{ K} \rightarrow P_2 = 611 \text{ Pa}$$

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{sub}}}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\Delta H_{\text{sub}} = 5.089 \times 10^5 \text{ J/mol}$$

