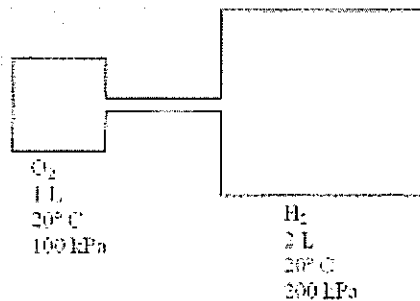


**Example on applying Dalton's law:**

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.

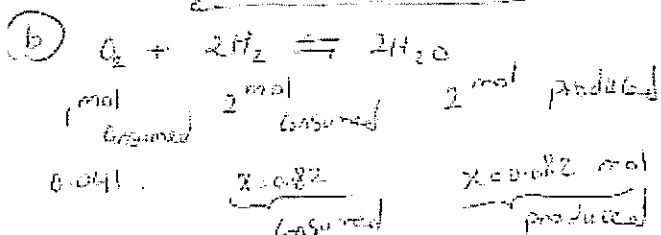
$$n_{\text{O}_2} = \frac{P_{\text{O}_2} V_{\text{O}_2}}{RT} = \frac{100 \times 10^3 \text{ Pa} \times 10^{-3} \text{ m}^3}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 293.15 \text{ K}} = 0.041 \text{ mol}$$

$$n_{\text{H}_2} = \frac{200 \times 10^3 \text{ Pa} \times 2 \times 10^{-3} \text{ m}^3}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 293.15 \text{ K}} = 0.1641 \text{ mol}$$

$$n_{\text{Final}} = \frac{PV}{RT} = \frac{P \times 3 \times 10^{-3} \text{ m}^3}{8.314 \times 293.15} = 1.23 \times 10^{-6} P$$

$$(n_{\text{O}_2} + n_{\text{H}_2})_{\text{initial}} = n_{\text{Final}} \rightarrow 0.2051 = 1.23 \times 10^{-6} P \rightarrow P = 166748 \text{ Pa} = 166.75 \text{ kPa}$$

$$\begin{aligned}
 P_{\text{O}_2} &= \frac{n_{\text{O}_2}}{n} P \\
 &= \frac{0.041}{0.2051} \times 166.75 = 33.33 \text{ kPa} \\
 P_{\text{H}_2} &= \frac{n_{\text{H}_2}}{n} P = 133.42 \text{ kPa}
 \end{aligned}$$



$$(n_{\text{O}_2})_f = 0$$

$$(n_{\text{H}_2})_f = 0.1641 - 0.082 = 0.082 \text{ mol}$$

$$(n_{\text{H}_2\text{O}})_f = 0 \text{ [because at 25°C, water is in liquid phase.]}$$

$$P^e = P_{\text{H}_2} = \frac{0.082 \times R \times 293.15}{3 \times 10^{-3}} = 66699 \text{ Pa}$$

$$P_{\text{O}_2} = P_{\text{H}_2\text{O}} = 0$$

Example on ideal and real gases:

A closed system with volume of  $0.15 \text{ m}^3$  contains  $40 \text{ kg}$  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

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

$$b = \frac{R T_c}{8 P_c}$$

For ethylene:  $T_c = 282.3 \text{ K}$   $M_N = 28 \text{ g/mol}$   
 $P_c = 50.4 \text{ bar}$   
 $B = -242 \text{ cm}^3/\text{mol}$   
 $C = 25200 \text{ cm}^6/\text{mol}^2$

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

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

$$b) \quad Z = 1 + \frac{nB}{V} + \frac{n^2 C}{V^2} = 1 + \frac{1428.6 \times -242 \times 10^{-6} \text{ m}^3/\text{mol}}{0.15} + \frac{(1428.6)^2 \times 25200 \times 10^{-12} \text{ m}^6/\text{mol}^2}{(0.15)^2}$$

$$= 0.98$$

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

$$c) \quad p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

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

$$p = \frac{1428.6 \times 8.314 \times 298.15}{0.15 - (1428.6 \times 5.82 \times 10^{-5})} - \frac{0.4611 \times (1428.6)^2}{(0.15)^2} = 1.1144 \times 10^7 \text{ Pa}$$

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  $C_v$  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?

$$n = 3 \text{ mol} \quad P_{\text{ext}} = 5 \text{ bar} = 5 \times 10^5 \text{ Pa}$$

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

$$V_1 = \frac{nRT_1}{P_1} = \frac{3 \times 8.314 \times 298.15}{5 \times 10^5} = 0.1487 \text{ m}^3$$

$$V_2 = \frac{nRT_2}{P_2} = 0.0248 \text{ m}^3$$

$$(a) \quad W = -P_{\text{ext}}(V_2 - V_1) = -5 \times 10^5 \text{ Pa} (0.0248 - 0.1487) \text{ m}^3 = +61955.9 \text{ J}$$

(Work should be positive because it is done on the system by the surroundings)

$$(b) \quad \Delta T = 0 \longrightarrow nC_v \Delta T = \Delta U = 0$$

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

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.

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

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

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

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

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

$$4585.4 \text{ J} = 1.585 \text{ kJ}$$

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  $300 \text{ K}$  and  $1 \text{ bar}$  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  $1200 \text{ K}$ .

- What is the final volume of the gas?
  - What is the total work that was done on the gas?
- $C_V = 3/2 R$

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

insulated  $\rightarrow Q = 0 \rightarrow \text{Adiabatic}$

$$n = \frac{P_1 V_1}{R T_1} = 80.19 \text{ mol}$$

$$\Delta U = \underbrace{Q}_0 + W \rightarrow W = \Delta U = n C_V \Delta T = 80.19 \times \frac{3}{2} R \times (1200 - 300) = \underline{\underline{9 \times 10^5 \text{ J}}}$$

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.

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

$$\left[ \begin{array}{l} P_1 = 1 \text{ bar} \\ T_1 = 25^\circ\text{C} \end{array} \right] \xrightarrow{\text{Comp.}} \left[ \begin{array}{l} P_2 = 5 \text{ bar} \\ T_2 = 25^\circ\text{C} \end{array} \right]$$

$$\text{a) } \left[ \begin{array}{l} 1 \text{ bar} \\ 25^\circ\text{C} \\ V_1 \end{array} \right] \xrightarrow[\text{①}]{\text{const. } V} \left[ \begin{array}{l} P_2 = P_3 = 5 \text{ bar} \\ T_2 \\ V_2 = V_1 \end{array} \right] \xrightarrow[\text{②}]{\text{const. } P} \left[ \begin{array}{l} P_3 = P_2 = 5 \text{ bar} \\ T_3 = 25^\circ\text{C} \\ V_3 \end{array} \right]$$

$$V_1 = \frac{nRT_1}{P_1} = 0.025 \text{ m}^3$$

$$T_2 = \frac{P_2 V_2}{nR} = 1490 \text{ K}$$

$$\text{① } \left\{ \begin{array}{l} W_1 = 0 \quad (\text{const } V) \\ Q_1 = \Delta U = nC_V \Delta T = n \times \frac{5}{2} R \times (1490 - 298.15) = 24788.2 \text{ J} \end{array} \right.$$

$$\text{② } \left\{ \begin{array}{l} Q_2 = Q_P = nC_P \Delta T = n \times \frac{7}{2} R \times (298.15 - 1490) = -34705.5 \text{ J} \end{array} \right.$$

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

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

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

$$\text{b) Rev. Isothermal: } W = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2} = -1 \times R \times 298.15 \ln \frac{1}{5} = +3989.5 \text{ J}$$

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

$$\text{c) } \left[ \begin{array}{l} 1 \text{ bar} \\ 25^\circ\text{C} \\ V_1 = 0.025 \text{ m}^3 \end{array} \right] \xrightarrow[\text{①}]{\text{Ad. rev.}} \left[ \begin{array}{l} P_2 \\ T_2 \\ V_2 \end{array} \right] \xrightarrow[\text{②}]{\text{const. } V} \left[ \begin{array}{l} P_3 = 5 \text{ bar} \\ T_3 = 25^\circ\text{C} \\ V_3 = V_2 \end{array} \right]$$

$$V_3 = \frac{nRT_3}{P_3} = 0.00496 \text{ m}^3$$

$$V_2 = V_3 = 0.00496 \text{ m}^3$$

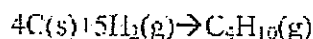
$$\frac{T_2}{T_1} = \left( \frac{V_2}{V_1} \right)^{\gamma} \rightarrow \frac{T_2}{298.15} = \left( \frac{0.00496}{0.025} \right)^{5/3} \rightarrow T_2 = 569.5 \text{ K}$$

$$\text{① } \left\{ \begin{array}{l} W_1 = \Delta U_1 = nC_V (T_2 - T_1) = 1 \times \frac{5}{2} R \times (569.5 - 298.15) = 5640.2 \text{ J} \end{array} \right.$$

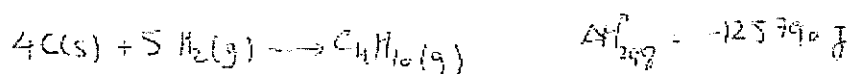
$$\text{② } \left\{ \begin{array}{l} W_2 = 0 \leftarrow \text{const. } V \end{array} \right. \rightarrow W_T = W_1, W_2 = 5640.2 \text{ J}$$

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

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

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

reaction	$\Delta H_{298}^\circ \text{ (J/mol)}$
$4\text{C(s)} + 4\text{O}_2\text{(g)} \rightarrow 4\text{CO}_2\text{(g)}$	4 (-393509)
$5\text{H}_2\text{(g)} + 1/2\text{O}_2\text{(g)} \rightarrow 5\text{H}_2\text{O(l)}$	5 (-285830)
$4\text{CO}_2\text{(g)} + 5\text{H}_2\text{O(l)} \rightarrow \text{C}_4\text{H}_{10}\text{(g)} + 13/2\text{O}_2\text{(g)}$	2877396

**Example on the first law:**

An insulated  $4 \text{ m}^3$  tank is divided to two unequal parts with a membrane. The smaller part contains nitrogen gas at  $100^\circ\text{C}$  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.

- What is the final temperature of the gas? Is this process reversible or not?
- Calculate the minimum amount of work required to restore the gas to its initial conditions in an isothermal process?

$$n = \frac{P_1 V_1}{R T_1} = \frac{(6 \times 10^5 \text{ Pa}) \times \frac{4}{3} \text{ m}^3}{8.314 \times 373.15} = 257.9 \text{ mol}$$

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

$\text{N}_2$ 6 bar $100^\circ\text{C}$	vacuum
--	--------

a)  $P_{\text{ext}} = 0 \rightarrow w = -P_{\text{ext}} \Delta V = 0 \rightarrow \Delta U = Q + w = 0 \rightarrow \Delta T = 0 \rightarrow T_2 = T_1 = 100^\circ\text{C}$   
 insulated  $\rightarrow Q = 0$

b)  $w_{\text{min}} = w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -257.9 \text{ mol} \times 8.314 \times 373.15 \times \ln \frac{4}{1} = 878890 \text{ J}$

**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.  $C_p = 21 \text{ J/mol}\cdot\text{K}$

- an isothermal reversible process
- an adiabatic reversible process
- an adiabatic irreversible process against constant external pressure of 100 kPa

$$\begin{cases} V_1 = 1 \text{ m}^3 \\ T = 600 \text{ K} \\ P = 10^6 \text{ Pa} \end{cases} \xrightarrow{\text{expansion}} \begin{cases} V_2 = 5 \text{ m}^3 \\ T_2 = ? \\ P_2 = ? \end{cases}$$

Note: in an expansion process, system goes from max. T and max. P to max. Volume.  
initial condition      final condition

$$n = \frac{P_1 V_1}{RT_1} = 200.5 \text{ mol}$$

a) rev, isothermal

$$T_2 = T_1 = 600 \text{ K}$$

$$P_1 V_1 = P_2 V_2 \longrightarrow P_2 = \frac{P_1 V_1}{V_2} = 2 \times 10^5 \text{ Pa}$$

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

b) Rev, adiabatic

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{-\frac{R}{C_V}} \longrightarrow T_2 = 600 \left(\frac{5}{1}\right)^{-\frac{R}{C_V}} = \dots \longrightarrow P_2 = \frac{nRT_2}{V_2} = \checkmark$$

$$W = \Delta U - Q = nC_V \Delta T = \checkmark$$

$$C_p = C_V + R \longrightarrow C_V = 12.686 \text{ J/mol}\cdot\text{K}$$

c) Irrev, Ad.

$$Q = 0$$

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

$$\Delta U = W + Q \longrightarrow nC_V \Delta T = -4 \times 10^5 \text{ J} \longrightarrow \Delta T = -157.26 \longrightarrow T_2 = 442.7 \text{ K}$$

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



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.  $P_{\text{ext}} = 0$ )

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

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

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

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{R}{C_p}} \rightarrow T_2 = 548 \text{ K}$$

$$\Delta U = n C_v \Delta T = 1 \times \frac{3}{2} R \times (548 - 800) = -5636.9 \text{ J}$$

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

$$W = -3000 \text{ J} \quad \Delta U = \cancel{Q} + W \rightarrow n C_v \Delta T = -3000 \text{ J} \rightarrow 1 \times \frac{3}{2} R \times (T_2 - 800) = -3000 \text{ J}$$

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

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

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

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

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

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

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

$$\rho_{\text{coffee}} = 1 \text{ g/mL}$$

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:  $\Delta p \sim \Delta V \sim 0$

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

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

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

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = +8.02 \text{ J/K} > 0 \quad \text{positive because it is a spontaneous process.}$$

3. One mole of an ideal gas is initially at 0 °C and 1 bar undergoes different reversible processes. For each process, calculate  $W$ ,  $Q$ ,  $\Delta U$ ,  $\Delta H$  and  $\Delta S$ .  $C_p = 5/2R$ :

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

$$\Delta U = Q + W = n C_V \Delta T = 1 \times \frac{3}{2} R \times (173.15 - 273.15) = -1247.1 \text{ J}$$

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

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

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

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

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

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

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

$$\Delta U = n C_V \Delta T = 1 \times \frac{3}{2} R \times (373.15 - 273.15) = 1247.1 \text{ J}$$

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

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

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

$$\Delta U = W + Q = n C_V \Delta T = 1 \times \frac{3}{2} R \times (108 - 273.15) = -2059.6 \text{ J}$$

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

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  $\Delta S_{\text{univ}}$ . ( $C_p = 7/2R$ )

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

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

$$\Delta S_{\text{sys}} = n C_p \ln \frac{T_2}{T_1} - n R \ln \frac{P_2}{P_1} = -1 \times R \times \ln \frac{7}{3} = -7.014 \text{ J/K}$$

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

$$\Delta U = Q + W \rightarrow Q = -W$$

$$T = 0$$

$$W_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2} = -1 \times 8.314 \times 400 \times \ln \frac{3}{7} = 2837.8 \text{ J}$$

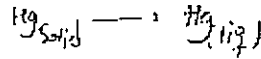
$$W_{\text{real}} = 1.48 \times W_{\text{rev}} = 4170.3 \text{ J} \rightarrow Q_{\text{real}} = -W_{\text{real}} = -4170.3 \text{ J}$$

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

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

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. ( $M_w, \text{Hg} = 200 \text{ g/mol}$ )



$$P_1 = 1 \text{ atm} \longrightarrow T_{m,1} = -38.87^\circ\text{C} = 234.28 \text{ K}$$

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

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

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

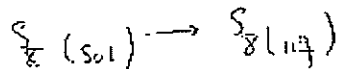
$$\ln \frac{T_2}{T_1} = \frac{(0.00257 \text{ cm}^3/\text{g}) \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \times 200 \text{ g/mol}}{2.42 \times 10^3 \text{ J/mol}} \times (100 \times 101325) \text{ Pa}$$

$$\longrightarrow T_2 = 234.79 \text{ K} \longrightarrow \Delta T = T_2 - T_1 = 0.5 \text{ K}$$

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  $S = 32 \text{ g/mol}$ )  
1 kcal = 4.18 kJ

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

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



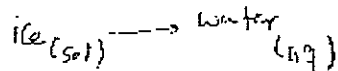
$$\ln \frac{T_2}{T_1} = \frac{\Delta \bar{V}_{\text{fus}}}{\Delta H_{\text{fus}}} \Delta P$$

$$\ln \frac{T_2}{392.45} = \frac{41 \text{ cm}^3/\text{g} \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \times (8 \times 32 \text{ g/mol})}{3.376 \times 10^3 \times 4.18 \text{ kJ/mol}} \times (1000 - 1) \times 101325 \text{ Pa}$$

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

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

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



$$T_1 = 273.15 \text{ K} \longrightarrow P_1 = 1 \text{ atm} = 1.01325 \text{ bar}$$

$$\ln \frac{T_2}{T_1} = \frac{\Delta \bar{V}_{\text{fus}}}{\Delta H_{\text{fus}}} \Delta P$$

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

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

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

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:  $\Delta H_{\text{vap}} = 5.94 \times 10^4 \text{ J/mol}$ ,  $T_{\text{bp}} = 356.7^\circ\text{C}$ )

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

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

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

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

$$\ln \frac{107.5}{101.325} = -\frac{5.94 \times 10^4}{8.314} \left[ \frac{1}{633.15} - \frac{1}{T_1} \right] \rightarrow T_1 = 629.85 \text{ K} = 356.7^\circ\text{C}$$

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:  $\Delta H_{\text{sub}} = 5.089 \times 10^4 \text{ J/mol}$ )

ice  $\xrightarrow{\text{subl.}}$  water (vap)

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

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

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

$$\Delta H_{\text{sub}} = 5.089 \times 10^4 \text{ J/mol}$$

