

Question 1:

n moles of an ideal gas initially at T_i degrees C and P_i atm pressure undergo an ISOTHERMAL expansion against a constant pressure of P_{ext} atm. The final pressure of the gas is P_f atm. Calculate the entropy change, ΔS for the gas (in J/K).

$$\Delta S = \int \frac{dq_{rev}}{T} = \int \frac{dE + PdV}{T} = \int_{T_i}^{T_f} nC_v \frac{dT}{T} + \int_{T_i}^{T_f} nR \frac{dV}{V} = nC_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

for $T = \text{const.}$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$P_f V_f = nRT = P_i V_i$$

$$\Delta S = nR \ln \frac{P_i}{P_f}$$

Question 2:

n moles of an ideal gas with $C_v = 3R/2$, initially confined to a container of volume V_i litre and at temperature T_i C, expand (or are compressed) against a constant external pressure of P_{ext} atm until the final pressure of the gas is equal to the external pressure. During this process the system does w_{by} J of work on the surroundings. Calculate the change in entropy, ΔS , of the gas.

$$\Delta S = \int \frac{dq_{rev}}{T} = \int \frac{dE + PdV}{T} = \int_{T_i}^{T_f} nC_v \frac{dT}{T} + \int_{T_i}^{T_f} nR \frac{dV}{V} = nC_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

From the equation for work w V_f can be calculated:

$$w = -w_{by} = - \int_{V_i}^{V_f} P_{ext} dV = -P_{ext} \int_{V_i}^{V_f} dV = -P_{ext} (V_f - V_i)$$

$$\therefore V_f = V_i + \frac{w_{by}}{P_{ext}}$$

Only missing parameter is T_f which can be calculated from the ideal gas law applied to the final state $T_f = \frac{P_f V_f}{nR}$.

Question 3:

The process in the previous question is spontaneous, reversible or impossible?

In order to answer the question you need to calculate $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$. Under the assumption that $T_{surr} = T_i$ an expression for ΔS_{surr} becomes:

$$\Delta S_{surr} = \frac{-q}{T_i} = \frac{\Delta E - w}{T_i} = \frac{nC_v \Delta T}{T_i}$$

If $\Delta S_{tot} > 0$ process is spontaneous.

If $\Delta S_{tot} = 0$ process is reversible.

If $\Delta S_{tot} < 0$ process is impossible.

Question 4:

Given that ΔH (fusion) of water is 6025 J/mol, $C_p(\text{ice}) = 37.7$ J/Kmol and $C_p(\text{water}) = 75.3$ J/Kmol calculate ΔG for the freezing of n moles of water at 1 atm pressure and constant temperature T C.

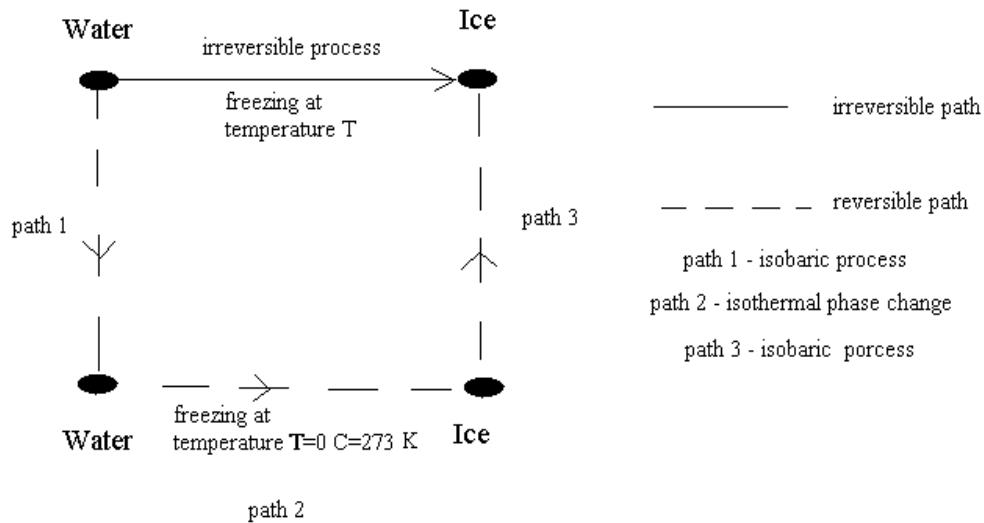
$$\Delta G_{freez} = \Delta H_{freez} - T \Delta S_{freez}$$

In order to calculate ΔS_{freez} defined as

$$\Delta S = \int \frac{dq_{rev}}{T}$$

for an irreversible process of freezing of water, a hypothetical reversible path must be considered for a given process.

In this case irreversible process of freezing water at temperature T can be considered as a process of isobaric cooling of water from temperature T to 0 °C (path 1), then at temperature 0 °C process of freezing, phase change from water to ice (path 2) and finally isobaric heating of ice from 0 °C to temperature T (path 3).



$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_1 = nC_p(\text{water}) \ln \frac{273}{T}$$

$$\Delta S_2 = \frac{\Delta H_{\text{freezing}}}{T_{\text{freezing}}} = -\frac{\Delta H_{\text{fusion}}}{T_{\text{freezing}}}$$

$$\Delta S_3 = nC_p(\text{ice}) \ln \frac{T}{273}$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_1 = nC_p(\text{water})\Delta T = nC_p(\text{water})(273 - T)$$

$$\Delta H_2 = \Delta H_{\text{freezing}} = -\Delta H_{\text{fusion}}$$

$$\Delta H_3 = nC_p(\text{ice})\Delta T = nC_p(\text{ice})(T - 273)$$

Question 5 :

Which of the following BY ITSELF gives a criterion for the spontaneity of the process in the previous question?

1. ΔS
2. ΔH
3. $\Delta G \iff$ In previous example process is done under constant pressure and temperature so $\Delta G = (\Delta G)_{P,T}$ can be a criterion for the spontaneity of the process.
4. ΔT
5. q
6. w
7. ΔE
8. ΔS (surroundings)