

1. a) The **Newcomen engine**, the first practical steam engine, operated at atmospheric pressure. This made Newcomen engines relatively easy to build and very safe to operate: no high-pressure steam boilers to *explode*! Using 100 °C for the boiling point of water at 1.00 atm and 20 °C for the temperature of the cooling water, calculate the maximum efficiency of a Newcomen engine.
- b) The **Lingan Generating Station** on Cape Breton Island uses high-pressure steam at 150 atm to run turbine engines, producing 25 % of the electricity used in Nova Scotia. High-pressure engines are much more expensive than atmospheric engines. Why are these costly engines used?
- [3]
2. 5.00 moles of helium (assumed to be an ideal gas) expands adiabatically and reversibly from 300 K and 15.0 L initially to a final volume of 45.0 L.
- a) Calculate q , w , ΔU , ΔH .
- [3] b) Show $\Delta S = 0$.
- c) Expansion of a gas from 15.0 L to 45.0 L should increase the “randomness” and therefore increase the entropy of the gas. But here $\Delta S = 0$! Explain.
3. One mole of liquid water freezes at 0 °C and 1.00 atm. *Data:* $\Delta H_{\text{fus,m}}^\circ(\text{H}_2\text{O,s}) = 6010 \text{ J mol}^{-1}$
- $$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$$
- a) For this process we can assume $\Delta V = 0$ with negligible error. Why?
- b) Calculate q , w , ΔU , ΔH and ΔS .
- [4] c) Because ice is crystalline and more ordered than liquid water, freezing water reduces its entropy. One of your classmates says that according to the Second Law, the entropy can never decrease, so freezing the water violates the Second Law. Is your classmate correct? Explain.
4. a) For an ideal gas undergoing a reversible process, prove (*hint:* start with the First Law)
- $$dS = \frac{C_V}{T}dT + \frac{nR}{V}dV$$
- [3] b) The equation in part a was derived for a reversible process, but it can also be used to calculate entropy changes for irreversible processes! Explain.

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5. This question refers to the conversion of graphite to diamond at 25 °C and 1.00 bar.



Molar enthalpies of formation and molar entropies at 25 °C and 1.00 bar:

$$\begin{array}{ll} \Delta H_{\text{fm}}^{\circ}(\text{graphite, s}) = 0 & S_{\text{m}}^{\circ}(\text{graphite, s}) = 5.740 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta H_{\text{fm}}^{\circ}(\text{diamond, s}) = 1.895 \text{ kJ mol}^{-1} & S_{\text{m}}^{\circ}(\text{diamond, s}) = 2.377 \text{ J K}^{-1} \text{ mol}^{-1} \end{array}$$

- a) The standard enthalpy of formation of diamond is not zero. Why?
- [6] b) Briefly describe how the standard enthalpy of formation of diamond can be measured.
- c) Briefly describe how the entropies of graphite and diamond can be measured.
- d) The molar entropy of diamond is significantly lower than that of graphite. Why? Give a molecular interpretation by comparing the structures of graphite and diamond.
- e) Use the Second Law and the data given above to prove the conversion of graphite to diamond is not spontaneous at 25 °C and 1.00 bar.
6. Question 5 shows that thermodynamics can be used to decide if a process is spontaneous *without actually carrying out the process*. Why is this important?
- [1]

Q1 a) Newcomen Engine

$$T_H = 373 \text{ K } (100^\circ\text{C})$$

$$T_C = 293 \text{ K } (20^\circ\text{C})$$

$$\text{maximum efficiency } \epsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{293 \text{ K}}{373 \text{ K}} = \boxed{0.21}$$

b) The boiling temperature of water increases as the pressure increases.

water boils at 100 °C at 1 atm

look up: water boils at 345 °C (618 K) at 150 atm

$$\text{maximum efficiency } \epsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{293 \text{ K}}{618 \text{ K}} = \boxed{0.52}$$

high-pressure steam engines cost more, but they are more efficient, justifying the higher cost

Q2 Helium has $C_{vm} = \frac{3}{2}R$ and $C_{pm} = C_{vm} + R = \frac{5}{2}R$

$$\text{heat capacity ratio } \gamma = \frac{C_p}{C_v} = \frac{C_{pm}}{C_{vm}} = \frac{(5/2)R}{(3/2)R} = \boxed{\frac{5}{3} = \gamma}$$

for a reversible, adiabatic expansion:

$$P_i V_i^\gamma = P_f V_f^\gamma \quad \Rightarrow \quad P_f = \left(\frac{V_i}{V_f}\right)^\gamma P_i$$

(Q2 cont.)

$$P_i = \frac{nRT_i}{V_i} = \frac{(5.00 \text{ mol})(0.08314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{15.0 \text{ L}}$$

$$P_i = 8.31 \text{ bar}$$

$$P_f = \left(\frac{V_i}{V_f}\right)^\gamma P_i = \left(\frac{15.0 \text{ L}}{45.0 \text{ L}}\right)^{5/3} 8.31 \text{ bar}$$

$$P_f = 1.33 \text{ bar}$$

$$T_f = \frac{P_f V_f}{nR} = \frac{(1.33 \text{ bar})(45.0 \text{ L})}{(5.00 \text{ mol})(0.08314 \text{ J K}^{-1} \text{ mol}^{-1})} = \boxed{144 \text{ K}}$$

$q = 0$ (adiabatic expansion)

$$\Delta U = \overset{0}{q} + w \quad \Delta U = w \quad \left(\begin{array}{l} \Delta T = T_f - T_i \\ = (144 - 300) \text{ K} \\ = -156 \text{ K} \end{array} \right)$$

ideal gas: $dU = C_v dT = n C_{v,m} dT$

$$\Delta U = \int dU = \int C_v dT = \int n C_{v,m} dT = \int n \frac{3}{2} R dT$$

$$= n \frac{3}{2} R \Delta T = (5.00 \text{ mol}) \frac{3}{2} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (-156 \text{ K})$$

$$\boxed{\Delta U = w = -9730 \text{ J}}$$

$$\Delta H = \int C_p dT = n C_{p,m} \Delta T = (5.00 \text{ mol}) \frac{5}{2} R \Delta T$$

$$\boxed{\Delta H = -16200 \text{ J}}$$

(Q2 cont.)

b) the expansion is reversible, so $dq = dq_{\text{rev}}$

$$\text{and } dS = \frac{dq_{\text{rev}}}{T} = \frac{0 \text{ (adiabatic)}}{T} = 0$$

c) expansion of the gas increases its entropy,
but cooling the gas decreases its entropy by
the same amount, so $\Delta S = 0$

$$dS = \frac{C_v}{T} dT + \frac{nR}{V} dV$$

$$\Delta S = \int \frac{C_v}{T} dT + \int \frac{nR}{V} dV$$

$$= C_v \int \frac{1}{T} dT + nR \int \frac{1}{V} dV$$

$$\left(\begin{aligned} C_v &= nC_{vm} \\ &= n \frac{3}{2} R \end{aligned} \right)$$

$$= nC_{vm} \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

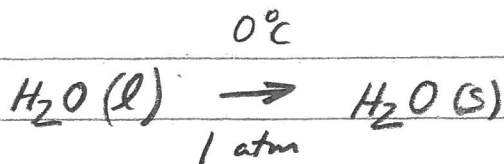
$$= n \frac{3}{2} R \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

$$= nR \left[\frac{3}{2} \ln\left(\frac{T_f}{T_i}\right) + \ln\left(\frac{V_f}{V_i}\right) \right]$$

$$= nR \left[\frac{3}{2} \ln\left(\frac{144}{300}\right) + \ln\left(\frac{45.0\text{L}}{15.0\text{L}}\right) \right]$$

$$\Delta S = nR [-1.10 + 1.10] = 0$$

Q3



a) liquid and solid water are "condensed" phases

unlike gases, liquids and solids have very small molar volumes, and the changes in these volumes are even smaller so $\Delta V \approx 0$

assuming $\Delta V = 0$ leads to negligible errors in the calculation of the work, which is $w = -\int_{\text{ext}} p dV = -p \int dV = -p \Delta V \approx 0$

$$\begin{aligned} \text{b) } q &= \Delta H = n \Delta H_{\text{freezing, m}}^\circ = n (-\Delta H_{\text{fus, m}}) \\ &= (1.00 \text{ mol})(-6010 \text{ J mol}^{-1}) \end{aligned}$$

$$q = \Delta H = -6010 \text{ J}$$

$$w = 0$$

$$\Delta U = q + w = -6010 \text{ J} + 0 = -6010 \text{ J} = \Delta U$$

solid and liquid water are in equilibrium at 0°C and 1.00 atm , so the freezing process is reversible

$$\Delta S = \int_{\text{(T constant)}} \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} = \frac{-6010 \text{ J}}{273.15 \text{ K}}$$

$$\Delta S = -22.0 \text{ J K}^{-1}$$

(Q3 cont.)

c) freezing liquid water at 0°C and 1.00 atm reduces the entropy of the water

but the water (the system) is not isolated!

in addition to the water freezing (with $\Delta S = -22.0 \frac{\text{J}}{\text{K}}$) the surroundings absorbs 6010 J of heat from the freezing of the water

for the system (the water) and the surroundings, which is an isolated "total" system:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}}^{q=-6010\text{J}} + \Delta S_{\text{surrounding}}^{q=+6010\text{J}}$$

$$= -22.0 \frac{\text{J}}{\text{K}} + \frac{6010\text{ J}}{273.15\text{ K}}$$

$$= -22.0 \frac{\text{J}}{\text{K}} + 22.0 \frac{\text{J}}{\text{K}}$$

$\Delta S_{\text{total}} = 0$ for a reversible process in an isolated system (water + surroundings)

The Second Law is not violated!

(Q4) a) for any system $\Delta U = q + w$

specializing to a reversible process: $dS = dq_{rev}/T$
 $(p = p_{ext})$ $dw = -pdV$

for an ideal gas (U depends only on T : $dU = C_v dT$)

the First Law gives $dU = dq + dw$
 $C_v dT = dq_{rev} - pdV$

divide by T to get $\frac{C_v}{T} dT = \frac{dq_{rev}}{T} - \frac{p}{T} dV$

$dS = \frac{C_v}{T} dT + \frac{p}{T} dV = \frac{C_v}{T} dT + \frac{nR}{V} dV$

($\frac{p}{T} = \frac{nR}{V}$ from the ideal gas law)

b) $dS = \frac{C_v}{T} dT + \frac{nR}{V} dV$ was derived

for reversible processes for ideal gases.

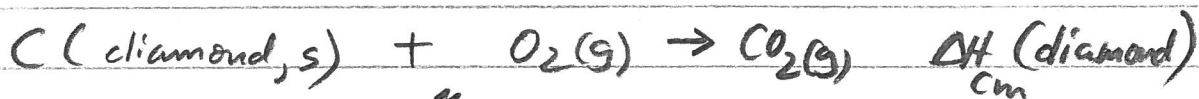
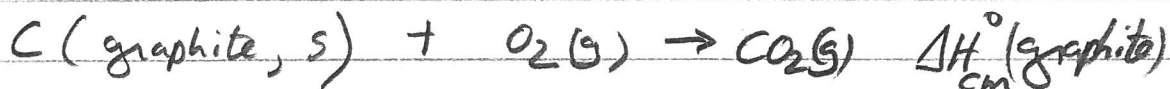
But S is a state function

so any path, reversible or irreversible,
from the initial state to the final state
gives the same value of ΔS

Q5 a) The standard enthalpy of formation of diamond ($\Delta H_{fm}^{\circ}(\text{diamond}, s)$) is not zero because diamond is not the most stable form of carbon at 25 °C, 1 bar.

$\Delta H_{fm}^{\circ}(\text{graphite}, s) = 0$ because graphite is the most stable elemental form of C at 25 °C, 1 bar.

b) burn graphite and burn diamond to measure $\Delta H_{fm}^{\circ}(\text{diamond})$ Details:



= thermochemical algebra:



$$\Delta H_{fm}^{\circ}(\text{diamond}) = \Delta H_{cm}^{\circ}(\text{graphite}) - \Delta H_{cm}^{\circ}(\text{diamond})$$

c) Measure the heat capacities of graphite and diamond.

$$S_m^{\circ}(\text{graphite}, 298.15 K) = \int_0^{298.15 K} \frac{dq_{rev}}{T} = \int_0^{298.15 K} \frac{C_{pm}^{\circ}(\text{graphite})}{T} dT$$

$$S_m^{\circ}(\text{diamond}, 298.15 K) = \int_0^{298.15 K} \frac{C_{pm}^{\circ}(\text{diamond})}{T} dT$$

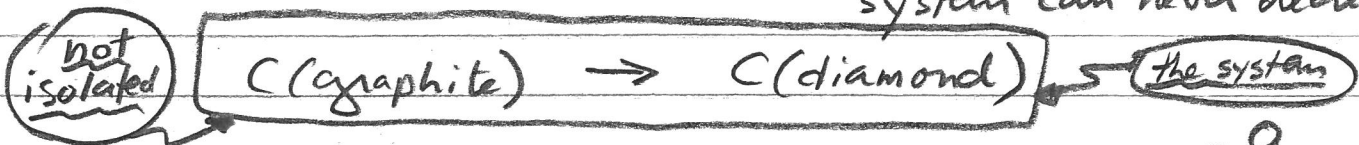
(Q5 cont.)

d) diamond structure: a crystalline 3-dimensional array of tetrahedrally bonded carbon atoms

graphite structure: a crystalline array of 2-dimensional hexagonally bonded planes of carbon atoms

diamond has higher (3-D vs 2-D) symmetry, less disorder, and lower entropy than graphite

e) From the Second Law: the entropy of an isolated system can never decrease



$$\text{heat } q = \Delta H = \Delta H_{\text{fm}}^{\circ}(\text{diamond}) - \Delta H_{\text{fm}}^{\circ}(\text{graphite})$$

(constant pressure)

$$q = 1895 \text{ J mol}^{-1}$$

the system gains 1895 J heat to the surroundings

$$\text{so } q_{\text{surroundings}} = -q = -1895 \text{ J}$$

for the system + surroundings (always an isolated system)

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= S_m^{\circ}(\text{diamond}) - S_m^{\circ}(\text{graphite}) + \frac{q_{\text{surroundings}}}{T_{\text{surroundings}}} \\ &= 2.377 \text{ J K}^{-1} \text{ mol}^{-1} - 5.740 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{-1895 \text{ J}}{298.15 \text{ K}} \end{aligned}$$

$$\Delta S_{\text{isolated system}} = -9.719 \text{ J K}^{-1} \text{ mol}^{-1} < 0 \text{ for an isolated system (IMPOSSIBLE)}$$

Q6 Some chemical reactions, and other processes, are very slow, almost infinitely slow, which means that the observation a process does not occur does not mean the process is impossible.

Important:

Using thermodynamic state functions, and "simple" measurements of ΔH_m and S_m , a process can be determined to be spontaneous or nonspontaneous without actually carrying out the process.