

Problem set 3 – The Second Law of Thermodynamics

Exercise Maths 3

- Determine $\int_{x_1}^{x_2} \left(\frac{a}{x} + b + cx\right) dx$, where a, b and c are constants,
- Show that $\frac{(T_1+T_2)^2}{4T_1T_2} = 1 + \frac{(T_1-T_2)^2}{4T_1T_2}$,
- Determine $\left(\frac{\partial f}{\partial x}\right)_y$ with $f(x, y) = hy^2x^2 \ln(gx)$, where g and h are constants,
- Integrate on both sides: $\frac{3}{2} \int_{T_1}^{T_2} \frac{1}{T} dT = - \int_{V_1}^{V_2} \frac{1}{V} dV$, to show that $\frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{3/2}$.

Exercise 11

- How is entropy defined (i) thermodynamically and (ii) statistically?
- What role does ΔS play in determining the direction of spontaneous change?
- On cold nights, water spontaneously freezes to form ice. How is this change consistent with your answer to (b)?
- Given that $C_p(\text{H}_2\text{O}) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta_{\text{fus}}H^\ominus(\text{H}_2\text{O}) = 6.00 \text{ kJ mol}^{-1}$, calculate the change in entropy of a system comprising 1 mole of water at 10°C that is cooled to 0°C and then freezes to form ice at 0°C .
- Comment on the sign of ΔS you obtained in (d) in light of the microscopic changes occurring in the system.

Exercise 12

- Calculate the molar entropy of a constant volume sample of 1 mole of $\text{Ne}(\text{g})$ at 500 K, given that it is 146.22 J K^{-1} at 298 K. Assume $\text{Ne}(\text{g})$ is a perfect gas.
- Calculate the entropy change of 3 moles of CH_4 that is heated from 298 K to 1098 K at a pressure of 1 atm, given that

$$C_p(\text{CH}_4)/\text{J K}^{-1} \text{ mol}^{-1} = 23.64 + 4.79 \times 10^{-2} T - 1.93 \times 10^{-5} T^2$$

over the temperature range 298–2000 K.

- The entropy change of 2 moles of a perfect gas when it was expanded isothermally from V_A to V_B was found to be 5.595 J K^{-1} . Calculate the ratio V_B/V_A .

Exercise 13

- Starting from the thermodynamic definition of entropy show that the entropy change ΔS when n moles of a perfect mono-atomic gas expands isothermally from volume V_1 to volume $V_2 = 2V_1$ is given by

$$\Delta S = nR \ln 2.$$

- b) Write the answer to part a), $\Delta S = nR \ln 2$, in the form of Boltzmann's statistical definition of entropy, $S = k_B \ln W$, hence, show that $\frac{W_2}{W_1} = 2^N$. How does the number of possible ways to realise a given configuration change due to the expansion?

Exercise 14

Two equal amounts of the *same* liquid are brought in thermal contact with each other (without mixing) at constant pressure and without loss of heat (i.e. adiabatically) to the surroundings. The initial temperatures are T_1 and T_2 , with $T_1 < T_2$. We assume that the constant pressure heat capacity of the liquids C_P is constant between T_1 and T_2 and the final temperature T_f of both liquids will be equal.

- a) By considering the transfer of heat between the two liquids, i.e. $q_{1 \rightarrow 2}$ and $q_{2 \rightarrow 1}$, show that the final temperature T is given by $T_f = \frac{1}{2}(T_1 + T_2)$.
- b) Show that the entropy change during this process is given by $\Delta S = C_p \ln \frac{T_f^2}{T_1 T_2}$.
- c) **Bonus:** Use the Second Law of Thermodynamics to show that this process proceeds spontaneously, as one would expect.

Exercise 15

In a Carnot cycle a system is first expanded reversibly and isothermally, then expanded reversibly and adiabatically, after that compressed reversibly and isothermally, and finally compressed reversibly and adiabatically to the initial state. Sketch the Carnot cycle, including the direction of the process, in a

- a) $p - V$ diagram b) $p - T$ diagram c) $T - S$ diagram d) $U - S$ diagram

Note that the exact shape of the 'curved' processes in these figures does not have to be determined.