ENV-413: Thermodynamics of the Earth systems

Exercise session for Lecture 6

1. No. Because living systems are open systems, we should check the change of the universe entropy to see if the entropy of an irreversible process in living systems increases. $\rightarrow \Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$.

Although the entropy of living systems remains small, the heat lost by living systems and gained from outside, such as solar radiation, would be released into the surrounding and increase the entropy of the surrounding, so $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ would be positive. For example, the entropy decreases during a process of synthesis of complex protein molecules from individual amino acids, but the process also releases amount of heat into the surrounding. Hence, the second law of thermodynamics is not invalid for living system.

2.

$$dU = -PdV + TdS = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS \qquad \therefore \left(\frac{\partial U}{\partial S}\right)_V = T$$

$$dH = VdP + TdS = \left(\frac{\partial H}{\partial P}\right)_S dP + \left(\frac{\partial H}{\partial S}\right)_P dS \qquad \therefore \left(\frac{\partial H}{\partial P}\right)_S = V \qquad \left(\frac{\partial H}{\partial S}\right)_P = T$$

$$dG = VdP - SdT = \left(\frac{\partial G}{\partial P}\right)_T dP - \left(\frac{\partial G}{\partial T}\right)_P dT \qquad \therefore \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T = \left(\frac{\partial H}{\partial S}\right)_P \qquad \left(\frac{\partial H}{\partial P}\right)_S = V = \left(\frac{\partial G}{\partial P}\right)_T$$

3.

a) for a reversible process $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

for an isothermal process

$$\Delta S_{sys} = n\,R\ln\frac{V_2}{V_1} = 1 \times 8.314 \times \ln\frac{10}{5} = 5.763\,JK^{-1}$$

$$\Delta S_{surr} = -\Delta S_{sys} = -5.763\,JK^{-1}$$

b) S is a state function, and ds is an exact differential, so we can use a reversible path to calculate Δs_{sys} in an irreversible process.

$\rightarrow \Delta S_{sys} = 5.763\,JK^{-1}$

We can calculate q_{sys} from the work done by the system

For an isothermal process, $\Delta u_{sys} = w_{sys} + q_{sys} = 0$

$$\therefore q_{surr} = -q_{sys} = w_{sys} = -P_{ex}\Delta V = -2 \times 101325 \times (10-5) \times 10^{-3}$$
$$= -1013.25\,J$$

$$\rightarrow \Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-1013.25}{300} = -3.377\,JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 5.763 - 3.377 = 2.386\,JK^{-1}$$

4.

From 1st law of thermodynami~~s~~cs $C_p dT = dq + vdp$

For constant pressure $\rightarrow dq = C_p dT$

$$\therefore \Delta S = \int_{T_1}^{T_2} \frac{dq}{T} = \int_{T_1}^{T_2} \frac{C_P dT}{T}$$

$$= \int_{300}^{425} 2 \times \frac{(31+0.008T)}{T} dT = \int_{300}^{425} 2 \times \left(\frac{31}{T} + 0.008\right) dT = 2 \times [31 \ln T + 0.008T]_{300}^{425}$$
$$= 2 \times [(31 \ln 425 + 0.008 \times 425) - (31 \ln 300 + 0.008 \times 300)]$$
$$= 23.595\,JK^{-1}$$

5.

$T_1 = 17 + 273.15 = 290.15\,K$ $T_2 = 35 + 273.15 = 308.15K$

$C_v = \frac{3}{2}R$ for a monoatomic ideal gas

a) For a reversible process at constant volume

$$\Delta s_{sys} = nC_v \ln\frac{T_2}{T_1} = n\frac{3}{2}R \ln\frac{T_2}{T_1} = 6 \times \frac{3}{2} \times 8.314 \times \ln\frac{308.15}{290.15} \cong 4.504\,JK^{-1}$$

b) S is a state function, and ds is an exact differential

Δs_{sys} in an irreversible process = Δs_{sys} in a reversible process = $4.504\,JK^{-1}$