

Week 4

Entropy and the Second Law of Thermodynamics

4.1 Entropy Equations

- 1/31:
- We define a new state function S by $dS = \delta q_{\text{rev}}/T$ and call it **entropy**.
 - See notes from last time for why this is a state function.
 - Verify that the same definition of entropy is a state function for any system.
 - Consider an ideal gas system in thermal equilibrium with an arbitrary system and drive the ideal gas system along a loop.
 - Around the cycle: $\Delta S_{\text{total}} = 0$.
 - Ideal gas:

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_1 + \Delta S_2 \\ &= \int \frac{\delta q_{\text{rev}_1}}{T} - \int \frac{\delta q_{\text{rev}_1}}{T} \\ &= \int \frac{\delta q_{\text{rev}_1}}{T} + \int \frac{\delta q_{\text{rev}_2}}{T}\end{aligned}$$

- We must devise a reversible process to calculate the entropy changes for an irreversible process leading to the same final state.

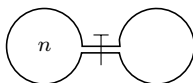


Figure 4.1: Two linked containers.

- Imagine two linked containers, one filled with n moles of gas and the other vacuumed.
- Opening the two containers to each other results in an adiabatic expansion. All vibrational/rotational energy of the molecules is consumed and used for translation.
- Measuring the temperature with spectroscopy (the Maxwell-Boltzmann distribution of each spectral line, plus only the ground rovibrational states are occupied now) shows a drastic drop in temperature.
- We have $\delta q = 0$ and $\delta w = 0$ so that $dU = 0$ and $\Delta T = 0$ overall?
- An isothermal expansion is a reversible process leading to the same final state.

- $dU = 0$ implies $\delta q_{\text{rev}} = -\delta w = P dV$.
- We have that

$$\Delta S = \int \frac{\delta q_{\text{rev}}}{T} = \int_{V_0}^{2V_0} \frac{P dV}{T} = \int_{V_0}^{2V_0} \frac{nRT}{V} \frac{1}{T} dV = nR \ln 2$$

- Using entropy as a state function to predict the vapor pressure in equilibrium with its liquid, from the enthalpy at boiling and the boiling temperature.



Figure 4.2: Vapor pressure thermodynamic loop.

- Consider the above thermodynamic loop, where T is the temperature of the water and P is the pressure above the water.
- We have that

$$\Delta S_1 = \int_T^{T_b} \frac{C_{P_l}}{T} dT \quad \Delta S_2 = \frac{\Delta H_{\text{vap}}}{T_b} \quad \Delta S_3 = nR \ln \frac{P_0}{P} \quad \Delta S_4 = \int_{T_b}^T \frac{C_{P_g}}{T} dT$$

and that

$$\Delta S_0 = \frac{\Delta H_{\text{vap}}}{T}$$

- We know that ΔS around the loop is zero since S is a state function. We neglect the heat capacity effect. Thus,

$$\begin{aligned} \frac{\Delta H_{\text{vap}}}{T_b} + nR \ln \frac{P_0}{P} - \frac{\Delta H_{\text{vap}}}{T} &= 0 \\ \ln \frac{P_0}{P} &= \frac{\Delta H_{\text{vap}}}{nR} \left(\frac{1}{T} - \frac{1}{T_b} \right) \\ P &= P_0 e^{-\Delta H_{\text{vap}}/nR(1/T - 1/T_b)} \end{aligned}$$

- The above equation gives the vapor pressure at T in terms of the vapor pressure P_0 at T_b .

- **Trouton's rule:** The statement that

$$\frac{\Delta H_{\text{vap}}}{T_b} \approx 85 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$$

- Discovered this rule as an undergrad after an afternoon's manipulation of data from a book of tables.
- This rule reflects the fact that

$$\frac{\Delta H_{\text{vap}}}{T_b} = \Delta S_{\text{vap}}$$

and implies that ΔS_{vap} is approximately a constant.

- Example of entropy change: The direction of heat flow between two systems (1 and 2) only in thermal contact.

- We have

$$\begin{aligned}\delta q_{\text{rev}_1} &= \delta q_{\text{rev}_2} \\ C_{V_1} dT_1 &= -C_{V_2} dT_2\end{aligned}$$

- Thus,

$$\begin{aligned}dS &= dS_1 + dS_2 \\ &= \frac{\delta q_{\text{rev}_1}}{T_1} + \frac{\delta q_{\text{rev}_2}}{T_2} \\ &= \frac{C_V dT_1}{T_1} - \frac{C_V dT_1}{T_2} \\ &= C_V dT_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)\end{aligned}$$

- The conclusion is that if $dT_1 > 0$, then $dS > 0$. This is the spontaneous direction, the direction that nature chooses, the one in which entropy increases.
- The maximum of S is the equilibrium temperature between the two systems.
- Entropy change of the isothermal mixing of two ideal gases at the same temperature.
 - Consider the same two-container setup from Figure 4.1.
 - We have that

$$\begin{aligned}\Delta S &= Rn_1 \ln \frac{V_1 + V_2}{V_1} + Rn_2 \ln \frac{V_1 + V_2}{V_2} \\ &= R(n_1 + n_2) \left(\frac{n_1}{n_1 + n_2} \ln \frac{V_1 + V_2}{V_1} + \frac{n_2}{n_1 + n_2} \ln \frac{V_1 + V_2}{V_2} \right) \\ &= R(n_1 + n_2)(-y_1 \ln y_1 - y_2 \ln y_2) \\ &= R(n_1 + n_2)[-y_1 \ln y_1 - (1 - y_1) \ln(1 - y_1)]\end{aligned}$$

■ Note that $y_1 = n_1/(n_1 + n_2) = V_1/(V_1 + V_2)$ is the mole fraction, and similarly for y_2 .

- The conclusion is that $\Delta S > 0$.
- The maximum of ΔS is at $y_1 = y_2 = 1/2$.
- **Gibb's paradox:** Suppose you have the same gas on both sides of the containers. Then $\Delta S = nR \ln 2$ for an indistinguishable gas.
 - This is wrong.
 - Resolved by knowing that the gases *must* be distinguishable.