Key points of this lecture EDR Section 5.2-4, 5.10

•Second Law of thermodynamics

•Calculating change in entropy for system
•(and surroundings)

•Calculating change in entropy for mixing of gases

•Calculating change in entropy for chemical reactions at constant pressure and not involving a phase change

Second Law of thermodynamics

$\Delta S \geq 0$ **for spontaneous events in isolated systems**

$\Delta S = 0$ for reversible processes; environmentally isolated

$\Delta S > 0$ for irreversible processes

$\Delta S < 0$ for non-spontaneous processes, highly unlikely

If system is not isolated, we can restate the second law:

The sum of the system and surroundings is greater than or equal to zero,
Because the system plus surroundings is a new isolated system.

S is not a function of time; but S acts to tell us how a system will change in time. ΔS is the difference between two forms of the (adiabatically isolated) system; each form is locally at equilibrium.

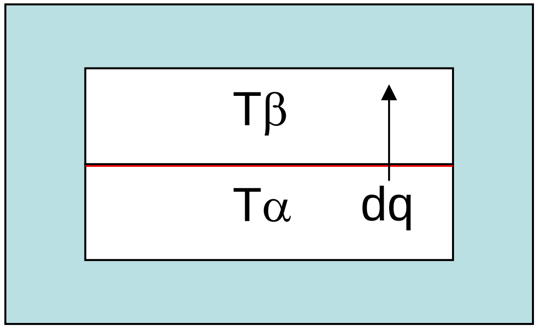
Entropy increases until equilibrium is reached.

Note that the second law does not say anything about how long it would take to reach equilibrium; because entropy is a comparison of the system in two different states. The one with larger entropy is the more probable.

Recall Joule's experiment and how $\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln 2 > 0$

Compare with Boltzmann's idea. $S = k\ln\Omega \quad \frac{\Omega_2}{\Omega_1} = 2^N$

ΔS for an isolated system consisting of two parts, α and β



$$dS = dS_\alpha + dS_\beta$$

Assume each part is the same I.G.; the change is at constant V:

Spontaneous, irreversible
Show:

$$\Delta S > 0 \rightarrow T_\alpha > T_\beta$$

The system starts at equilibrium, with a barrier between the two parts. Then they are allowed to touch and heat will flow from one to the other.

This flow is irreversible.

To compute the entropy we must find a reversible way to bring each part (separately) to the final temperature.

At thermal equilibrium $T = T_F = \frac{1}{2}\left(T_\alpha + T_\beta\right)$

$$q_\alpha^{rev} = \Delta U_\alpha = C_V \Delta T_\alpha$$

$$\Delta S_\alpha = \int_{T_\alpha}^{T_F} \left(\frac{\partial S}{\partial T}\right)_V dT = \int_{T_\alpha}^{T_F} \left(\frac{C_V}{T}\right) dT = C_V \ln\left(\frac{T_F}{T_\alpha}\right)$$

$$\Delta S = \Delta S_\alpha + \Delta S_\beta = C_V \ln\left(\frac{T_F}{T_\alpha}\right) + C_V \ln\left(\frac{T_F}{T_\beta}\right) = C_V \ln\left(\frac{T_F^2}{T_\alpha T_\beta}\right) \approx C_V \left(\frac{\Delta T}{2T_F}\right)^2 > 0$$

Change in entropy for a system + surroundings in a reversible process

One mole of an ideal gas undergoes a reversible isothermal expansion at 298K from V_1=10 L to V_2=20 L. Calculate ΔS_{system}, $\Delta S_{surroundings}$ and ΔS_{total}. The system and surroundings together are a super isolated system.

(a) System $q = -w = PdV$

$$\Delta S = \int_1^2 \frac{q}{T} = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$= \int_{V_1}^{V_2} \frac{P}{T} dV = nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{system} = nRln\left(2\right) = 5.8\ J/K$$

$$q_{rev,system} = T\Delta S = 1.7\ kJ$$

(b) Surroundings

$$q_{surr} = -q_{sys}$$

$$\Delta S_{sur} = \frac{q_{surr}}{T} = \text{-}5.8\ J/K$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Change in entropy for a system + surroundings in an irreversible process

One mole of an ideal gas undergoes a irreversible isothermal expansion at 298K from V_1=10 L to V_2=20 L. Calculate ΔS_{system}, $\Delta S_{surroundings}$ and ΔS_{total}

(a) System

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{system} = 1 \cdot R \cdot \ln(2) = 5.8\ J/K$$

The opportunity to remove heat from the environment was lost because expansion was irreversible (less than "optimal")

(b) Surroundings

$$q_{surr} = -q_{sys} = w_{expansion}$$

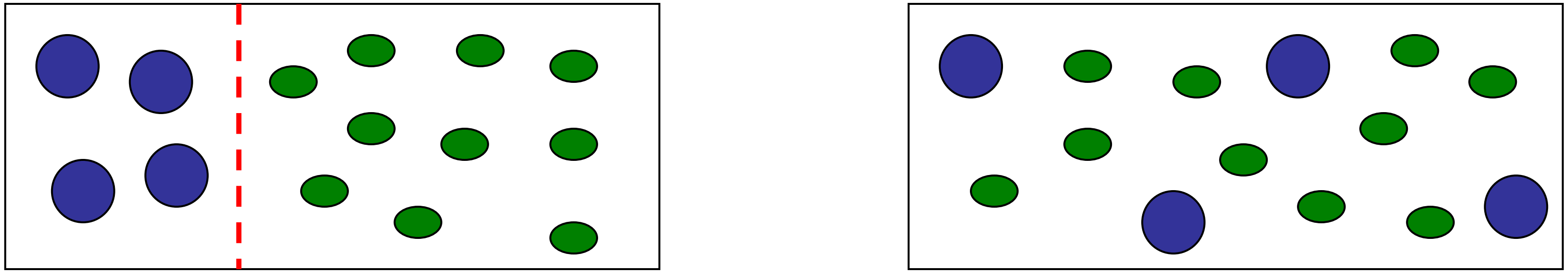
$$q_{surr} = \frac{-nRT}{V_2}(V_2 - V_1) = -1240\ J$$

$$\Delta S_{surroundings} = \frac{q_{surr}}{T} = -4.2\ J/K$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = 1.4\ {}^{J}\!/\!_{K} > 0$$

Entropy of mixing

We have an isolated container of total volume, V separated into two compartments of volume V_1 and V_2 each containing an ideal gas at the same temperature and pressure.



P,T
V_1, n_1

P,T
V_2, n_2

P,T
V_1+V_2, n_1+n_2

Removing the partition is an irreversible process.

To compute the entropy, we must find the reversible path that takes us to the same final state (or an “equivalent” path).

The two gasses must consist of distinguishable molecules.

Because system is isolated: $\Delta S = \Delta S_{sys} = \Delta S_1 + \Delta S_2$

What do we know? $\Delta S = \int \frac{dq_{rev}}{T}; \quad dT = 0; \quad dU = 0$

We can express this irreversible process as the reversible expansion of each gas to $V_{total}=V_1+V_2$

$$\Delta S_{gas1} = \int \frac{dq_{rev}}{T} = -\int \frac{dw_{rev}}{T} = n_1 R \int_{V_1}^{V_{total}} \frac{dV}{V} = n_1 R \ln\left(\frac{V_{total}}{V_1}\right)$$

$$\Delta S_{gas2} = n_2 R \ln\left(\frac{V_{total}}{V_2}\right)$$

$$\Delta S_{sys} = n_1 R \ln\left(\frac{V_{total}}{V_1}\right) + n_2 R \ln\left(\frac{V_{total}}{V_2}\right)$$

Since P and T are constant through the process,

$$\frac{V_2}{V_{total}} = \frac{n_2}{n_{total}} = x_2 \qquad \text{and} \qquad \frac{V_1}{V_{total}} = \frac{n_1}{n_{total}} = x_1$$

The mole fractions of the two gasses: $x_1 \; and \; x_2 \; ; \quad x_1 + x_2 = 1$

$$\Delta S_{gas1} = -n_1 R \ln(x_1) \qquad \Delta S_{gas2} = -n_2 R \ln(x_2)$$

$$\boxed{\Delta S_{system,mixing} = -R\left(n_1 \ln(x_1) + n_2 \ln(x_2)\right)}$$

Is $\Delta S_{total} > 0$?

$$\boxed{\Delta S_{mixing} = -R\sum_{i=1}^{N} n_i \ln(x_i)}$$

A chemical reaction can occur;
How does the entropy change?

- The system entropy is a function of T,P, and the species in the box.

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P,n_k} dT + \left(\frac{\partial S}{\partial P}\right)_{T,n_k} dP + \sum_k \left(\frac{\partial S}{\partial n_k}\right)_{T,p,n_p} dn_k$$

- How the entropy changes now at constant T, and P, and the number of moles changes by a single chemical reaction

$$dn_k = \nu_k dx$$

ν_k ares $\underline{\text{signed}}$ stoichiometric coefficients

- Then the entropy change due to the reaction (dx) at constant P and T is:

$$dS = dx \cdot \sum_k \nu_k \left(\frac{\partial S}{\partial n_k}\right)_{T,p,n_p} \qquad dS = dx \cdot dS_{rxn}$$

Molar standard entropies (at a standard temperature and pressure)

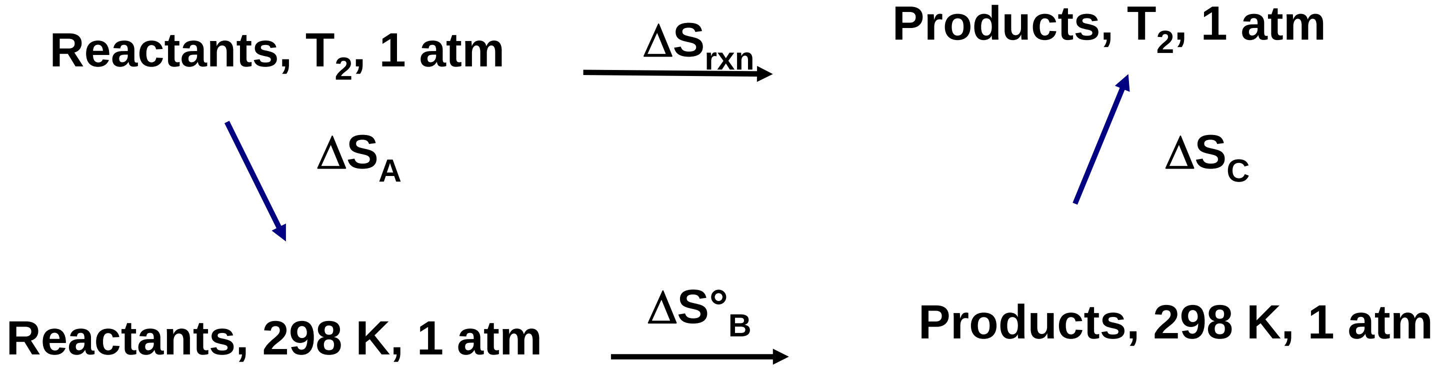
$$\overline{S}_k^o = \left(\frac{\partial S}{\partial n_k}\right)_{T,P} = \int_{T=0}^{T_o=298.15} \frac{\overline{C}_P(T)}{T} dT$$

$$aA + bB \rightarrow cC + dD$$

$$\Delta S^\circ_{rxn} = c\overline{S^\circ_C} + d\overline{S^\circ_D} - a\overline{S^\circ_A} - b\overline{S^\circ_B}$$

What if the reaction does not occur at 298 K?

Use alternate paths!



Reactants, T_2, 1 atm $\xrightarrow{\Delta S_{rxn}}$ **Products, T_2, 1 atm**

ΔS_A

ΔS_C

Reactants, 298 K, 1 atm $\xrightarrow{\Delta S^\circ_B}$ **Products, 298 K, 1 atm**

$$\Delta S_{rxn} = \Delta S_A + \Delta S^\circ_B + \Delta S_C$$

$$\overline{\Delta S} = \overline{\Delta S}_A + \overline{\Delta S}^{\circ}_B + \overline{\Delta S}^{\circ}_C$$

$$\overline{\Delta S} = \int_{T_2}^{298K} \frac{\overline{C}_{P,reac}\,dT}{T} + \overline{\Delta S}^{\circ}_B + \int_{298K}^{T_2} \frac{\overline{C}_{P,prod}\,dT}{T}$$

$$\overline{\Delta S} = \overline{\Delta S^{\circ}_B} + \left(\overline{C}_{P,prod} - \overline{C}_{P,reac}\right) \int_{298K}^{T_2} \frac{dT}{T}$$

$$\overline{\Delta S_{rxn}} = \overline{S}^{\circ}_{products} - \overline{S}^{\circ}_{reactants} + \left(\overline{C}_{P,prod} - \overline{C}_{P,reac}\right) \ln\left(\frac{T_2}{298K}\right)$$

$$\boxed{\overline{\Delta S_{rxn}}\left(T_2\right) = \Delta\overline{S}^{\circ}_{rxn}\left(T_0\right) + \ln\left(\frac{T_2}{T_o}\right) \sum_k \nu_k \overline{C}_P\left(k\right)}$$