

7 Increase of entropy when mixing two gases

Given are two isolated containers A and B with a volume of 3 resp. 1 m^3 .

Container A contains argon at a temperature of $T_A = 100$ K and a pressure $p_A = 1$ bar.

- What are the degrees of freedom of the gases and the mass unit¹ in container A ?

Container B contains fluor molecules (F_2) at a temperature of $T_B = 1200$ K and a pressure $p_B = 0.1$ bar. Above 1000 K they have 6 degrees of freedom, below 800 K they have 5 degrees of freedom and a mass of 38 units per atom.

- Which container contains more particles (atoms resp. molecules)? How many?
- Which container contains more mass? How much?
- Which container contains more energy (consider the degrees of freedom)? Calculate the energy for each container.
- Calculate the entropy of each container.

The containers are connected now (a wall between them is removed).

- Calculate the new temperature T and the new pressure p .
- Calculate the mixing entropy S .

8 Joule–Thomson process

If the gas penetrates through the porous partition between two vessels ($P_1 > P_2$), in other respects insulated from each other and from the surroundings, then the value of the enthalpy $H_1 = U_1 + p_1 V_1$ before the process is started is equal to the value of the enthalpy H_2 after the process is finished. The process is assumed to occur adiabatically, i.e. $\delta Q = 0$ during the entire process. The resulting change in the temperature is determined by Joule–Thomson coefficient $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$.

- Show that $dH = TdS + VdP$ and thus $\mu_{JT} = \frac{C}{C_P}(T\alpha - 1)$.
You can use Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha$, where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ is a coefficient of thermal expansion.
- Show that $\mu_{JT} = 0$ for an ideal gas.
- For a real gas, either warming $\mu_{JT} < 0$ or cooling $\mu_{JT} > 0$ can occur. The limit between these two effects is defined by the *inversion curve*, when $\alpha = \frac{1}{T}$.
Calculate and plot in the P-T diagram the inversion curve for the gas with the *van der Waals* equation of state:

$$P = \frac{kT}{v - b} - \frac{a}{v^2}, \quad v = \frac{V}{N}.$$

¹1 mol · 1 unit = 1 g, Avogadro constant $N_A = 6.022 \cdot 10^{23}$

9 Ergodic hypothesis

An ergodic² system is a system for which the time average of a quantity is equal to the average over the configuration space Ω . Argue if the following systems with the given configuration space are ergodic or not. Discuss this property considering elastic and inelastic collision between particles and also in the case of no collision.

- a) Ideal gas of N particles in a cubic box of volume 1, $\Omega = [0, 1]^{3N} \times R^{3N}$.
- b) Ideal gas of N particles in a container of volume 1, $\Omega = \text{energy shell}$.
- c) Gas of N gravitating particles in a cubic box, $\Omega = \text{energy shell}$.

Also determine the conserved quantity in the above systems, how this conservation constraint the configuration space, and find a practical description of the configuration space in each case. For the case of b sketch one element of the configuration space, and how does this depend on the initial condition.



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²The phrase “ergodic”, greek combination of “ergon” (work) and “odos” (path), was introduced by Ludwig Boltzmann who was a professor in Graz from 1869–1873 and 1876–1890.