

8 chemical potential

8.1: Triple point

Exercise 8.3 from Reif's book

8.2: Latent heat

Exercise 8.7 from Reif's book

8.3: Chemical reaction

Exercise 8.12 from Reif's book

8.4: Vapor pressure and mixture of gases

A container contains a mixture of two ideal (classical, monatomic) gases, labeled A and B . The numbers of gas molecules in the container is denoted N_A and N_B , respectively. The partial pressures p_A and p_B of the gases in the mixture are defined as the force per unit area that gas exerts on the walls of the container.

- Calculate the Helmholtz Free energy F of the mixture of the two gases. Express your answer in terms of the number of molecules N_A and N_B , the volume V of the container, and the masses m_A and m_B of the molecules.
- For each gas, express the partial pressure in terms of the volume V of the container, the temperature T , and the number of molecules N_A and N_B .
- Calculate the chemical potentials μ_A and μ_B of the two gases. Express your answers in terms of the partial pressures p_A and p_B , the temperature T , and any other variables or constants you may need.

For component A , the gas in the container is in equilibrium with its liquid, which is present at the bottom of the container. The other gas, B , is insoluble in the liquid phase of A . You may continue to consider the gas phases of A and B as ideal gases.

- Argue that, in the presence of the gas B , the pressure $p_{A,\text{liquid}}$ in the liquid phase of A is equal to the combined pressure $p_A + p_B$ of the two gases in the container.
- Use (d) to find an expression for the shift in the vapor pressure of A as a result of the presence of a small amount of the gas B . Express your answer in terms of the specific volume of the liquid v_{liquid} , the temperature T , the vapor pressure of A in the absence of the gas B , and any other observables you may need.

8.5: Diatomic molecules

Exercise 9.8 from Reif's book

Suggested problems for further study:

8.6: Coexistence of solid and gas

A monatomic gas and a solid composed of the same type of atoms are in equilibrium in a container. The atoms in the solid can be thought of as bound to their lattice position by a three-dimensional harmonic oscillator potential with frequency ω and ground state energy $-v + 3\hbar\omega/2$. (The offset $-v$ represents the binding potential in the solid.) The energy of each atom in the solid is thus expressed as

$$\varepsilon_j = -v + \hbar\omega(n_x + 1/2) + \hbar\omega(n_y + 1/2) + \hbar\omega(n_z + 1/2),$$

where n_x , n_y , and n_z are integers describing the number of oscillation quanta for oscillations in the x , y , and z directions. The number of gas atoms is N_g , the number of atoms in the solid is N_s .

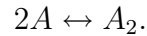
- (a) Assuming the gas is ideal and can be described using classical mechanics, calculate the Helmholtz free energy F_g of the gas. Express your answer in terms of the number N_g of molecules in the gas phase, the temperature T , the volume V , and any constants you may need.
- (b) Calculate the Helmholtz free energy F_s of the solid. Express your answer in terms of T , v , ω , and N_s .
- (c) Using the relation $\mu = (\partial F/\partial N)_{T,V}$, calculate the chemical potentials μ_g and μ_s of the gas and the solid, respectively.
- (d) Derive an expression for the gas pressure p at which gas and solid coexist. Express your answer as a function of T , m , v and ω .

8.7: Equilibrium in inhomogeneous system

Exercise 8.10 from Reif's book

8.8: Chemistry

Consider an element A that can form molecules A_2 through the chemical reaction



The mass of an atoms A is m and the mass of a molecule A_2 is $2m$. We neglect the internal structure of the A_2 molecules and consider both the atoms and the molecules as point particles. We also neglect the interactions between the particles (except for the presence of the chemical reaction mentioned above).

- (a) Calculate the Helmholtz free energy F for a mixture of N_1 A atoms and N_2 A_2 molecules in a container of volume V and temperature T . Use your answer to calculate the chemical potentials μ_1 and μ_2 for the A atoms and the A_2 molecules, respectively. (*Hint: use your answer to exercises 8.13a and 8.13c.*)
- (b) Show that, in equilibrium, the particle densities $n_1 = \bar{N}_1/V$ and $n_2 = \bar{N}_2/V$ satisfy the relation

$$\frac{n_2}{n_1^2} = K(T),$$

and calculate the function $K(T)$.

- (c) If the temperature T is increased by a factor 2 at constant volume, then
1. the pressure p also increases with a factor 2,
 2. the pressure p increases with a factor > 2 ,
 3. the pressure p increases with a factor < 2 .

8.9: Gaussian integrals

Exercise 7.19 from Reif's book

8.10: Specific heat of ideal diatomic gas using classical mechanics

The Hamiltonian function for a single diatomic molecule can be approximated as

$$H = H_{\text{trans}} + H_{\text{rot}} + H_{\text{vibr}},$$

where

$$\begin{aligned}H_{\text{trans}} &= \frac{p_{\text{cm}}^2}{2M}, \\H_{\text{rot}} &= \frac{p_{\theta}^2}{2I} + \frac{p_{\phi}^2}{2I \sin^2 \theta}, \\H_{\text{vibr}} &= \frac{p_r^2}{2\mu} + \frac{k}{2}(r - r_0)^2.\end{aligned}$$

The molecule consists of two different atoms of masses m_1 and m_2 , respectively. Further, $M = m_1 + m_2$ is the total mass of the molecule, $\mu = m_1 m_2 / M$ is the reduced mass for the internal motion, r_0 is the equilibrium distance between the two atoms, and $I = \mu r_0^2$ is the moment of inertia in the rigid-rotator approximation. The momentum \vec{p}_{cm} is the center-of-mass momentum; r is the distance between the atoms; p_r is the internal momentum conjugate to r ; p_{θ} and p_{ϕ} are the canonical momenta conjugate to the polar angles θ and ϕ describing the relative orientation of the two atoms in the molecule.

- (a) Using classical mechanics, calculate the classical one-molecule canonical partition functions $Z_{\text{trans } 1}$, $Z_{\text{vibr } 1}$, and $Z_{\text{rot } 1}$.
- (b) Calculate the contributions E_{trans} , E_{vibr} , and E_{rot} to the (internal) energy of an ideal gas of N such diatomic molecules.
- (c) Calculate heat capacity at constant volume C_V of this ideal gas.
- (d) Compare your results to what you would have obtained using the equipartition theorem and to what was obtained in lecture using quantum mechanics. When do the three results agree?

8.11: Entropy at zero temperature

For a gas of diatomic molecules, using quantum mechanics, show that

$$\lim_{T \rightarrow 0} S_{\text{vibr}} = 0.$$

Here S_{vibr} is that part of the total entropy S that is associated with the vibrational degrees of freedom of the molecules. This is an example that a quantum variable that “freezes” at low temperatures does not contribute to the entropy. (This is the underlying reason for the third law of thermodynamics.)

8.12: Doppler effect

Exercise 7.22 from Reif's book.

8.13: Triple point

Exercise 8.2 from Reif's book. The triple point is that point in the phase diagram where the solid, liquid, and vapor phase are in equilibrium.

8.14: Melting under pressure

Exercise 8.8 from Reif's book.

8.15: The atmosphere

Exercise 8.11 from Reif's book.

8.16: Chemical equilibrium

Exercise 8.12 from Reif's book.

8.17: Effusion

Exercise 8.13 from Reif's book.