Fachbereich Physik
Freie Universität Berlin
Theoretische Physik

SoSe 02
Set 10
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Theorie der Wärme – Statistical Physics
(Prof. E. Frey)

Problem set 10

Problem 10.1 *chemical reactions* (5 pts)

For a mixture of r components the fundamental relation for the Gibbs free energy (free enthalpy) reads

$$dG = -SdT - VdP + \sum_j \mu_j dN_j \,,$$

where μ_j, N_j are the chemical potential and particle number of the corresponding species, and the sum runs over all components. Assume that there is a chemical reaction

$$0 \rightleftharpoons \sum_j \nu_j A_j \,,$$

where ν_j are *stoichiometric coefficients* and A_j are the symbols of the chemical components. Introduce a reaction variable $\tilde{N}$ such that the particle changes fulfill $dN_j = \nu_j d\tilde{N}$. Since the reaction variable is not fixed, the Gibbs free energy will adjust $\tilde{N}$ in order to render G minimal. Derive the condition $\sum_j \nu_j \mu_j = 0$ for the chemical potentials in equilibrium.
For dilute gases the chemical potentials can be well approximated by the fundamental equation of a general ideal gas

$$\mu_j = k_B T \left[\chi_j(T) + \ln(c_i P)\right] \,.$$

The quantitiy $\chi_j(T)$ is a function of T only, and $c_j = N_j/N$, $N = \sum_j N_j$ is the concentration of the j-th component. Show that in equilibrium the concentrations satisfy the *mass action law*

$$\prod_j c_j^{\nu_j} = K_c(P,T)$$

and determine the equilibrium constant $K_c(P,T)$. Discuss the pressure dependence of the chemical equilibrium for the reactions $2H_2 + O_2 \rightleftharpoons 2H_2O$, $3H_2 + N_2 \rightleftharpoons 2NH_3$.
Show that the *heat of reaction* is given by

$$\left(\frac{dH}{d\tilde{N}}\right)_P = -T\frac{\partial}{\partial T}\left(\sum_j \nu_j \mu_j\right)_{P,N_j} \,,$$

where H is the enthalpy. Relate the heat of reaction to the equilibrium constant of the chemical reaction. Find the temperature dependence of $K_c(T,P)$ if the heat of reaction is approximately temperature-independent.

Problem 10.2 *dilute solutions* (5 pts)

Consider a mixture of a solvent and a dilute solute at constant pressure and temperature. The Gibbs free energy fulfills

$$dG = -SdT - VdP + \mu dN + \mu' dN' \,,$$

where μ, μ' are the chemical potentials and N, N' the particle numbers of the solvent and solute, respectively. Using the chemical potential of a dilute solute

$$\mu'(T,P,c) = k_B T\left[\psi'(T,P) + \ln c\right] \qquad c = N'/N$$

derive the dependence of the solvent chemical potential $\mu(T,P,c)$ on the concentration c of the solute. [Answer: $\mu(T,P,c) = \mu_0(P,T) - k_B T c$.]

(a) Consider a container with an immobile semipermeable wall, i.e. permeable for the solvent and impermeable for the solute. Determine the osmotic pressure due to different solute concentrations. Since the concentrations are small, you can expand the chemical potential in powers of the pressure difference.

(b) Discuss the reduction of the vapor pressure by the addition of a low concentration of nonvolatile solute, i.e. the change of the liquid-gas coexistence pressure for fixed temperature. Here the solute is confined to the liquid phase of the solvent.

(c) Derive an equation for the rise of the boiling point of a solvent caused by an infinitesimal addition of a nonvolatile solute at fixed pressure.

(d) Similarly, demonstrate the lowering of the freezing point by adding a small amount of a solute confined to the liquid phase.

Problem 10.3 *symmetric mixture* (3 pts)

A simple model for the concentration dependence of the Gibbs free energy of a symmetric mixture is given by

$$G(T, P, c) = G_0(T, P) + Nk_BTc\ln c + Nk_BT(1-c)\ln(1-c) + Nwc(1-c)\,.$$

Here $N = N_A + N_B$ is the total number of particles, $c = N_A/N$ the concentration of the species A, and $1-c = N_B/N$ the concentration of B molecules. Discuss the dependence of G on the concentration c for different values of the dimensionless number w/k_BT. What happens physically when the shape of G changes?

Termine für Übungsgruppen:
Do 12-14 in T3, 1.3.48 (Franosch)
Do 16-18 in T1, 1.3.21 (Parmeggiani, Lattanzi) in englischer Sprache
Fr 12-14 in E2, 1.1.53 (Falcke)
Abgabe: In der Vorlesung vom 3.7.02