

**T IV: Thermodynamik und Statistik**  
(Prof. E. Frey)

**Problem set 10**

**Problem 10.1** *chemical reactions*

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  $\mu_j, N_j$  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  $\nu_j$  are *stoichiometric coefficients* and  $A_j$  are the symbols of the chemical components. Introduce a reaction variable  $\xi$  such that the particle changes fulfill  $dN_j = \nu_j d\xi$ . Since the reaction variable is not fixed, the Gibbs free energy will adjust  $\xi$  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

$$\mu_j = k_B T [\chi_j(T) + \ln(c_j P)].$$

The quantity  $\chi_j(T)$  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  $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$ ,  $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$ .

Show that the *heat of reaction* is given by

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

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.

\* A mean field model for the dynamics towards equilibrium is given in terms of a rate equation for the reaction coordinate

$$\frac{d\xi}{dt} = k_{\rightarrow} \prod_{j, \nu_j < 0} c_j^{-\nu_j} - k_{\leftarrow} \prod_{j, \nu_j > 0} c_j^{\nu_j}$$

with positive kinetic rates  $k_{\rightarrow} > 0, k_{\leftarrow}$  for the forward and backward reaction.

Discuss the gain and loss terms in the rate equation and motivate the ansatz for the respective rates. Derive rate equations for the change of species number for the two example reactions specified above.

Show that in the kinetic rates  $k_{\rightarrow}, k_{\leftarrow}$  are connected to the equilibrium constant  $K_c(P, T)$ .

Demonstrate that for such a reaction kinetics the Gibbs free energy is decreasing

$$\left( \frac{dG}{dt} \right)_{T,P} \leq 0$$

and equality holds in equilibrium only.

Consider the reaction for concentrations close to equilibrium  $c_j = c_j^{eq} + \delta c_j$  to show that the rate equation reduces to

$$\frac{d\xi}{dt} = \frac{-L}{k_B T} \left( \frac{\partial G}{\partial \xi} \right)_{T,P}$$

where the *Onsager* coefficient  $L$  is positive.

### Problem 10.2 critical properties of the van-der Waals fluid

The empirical equation of state of a van-der Waals fluid reads

$$\left( P + \frac{N^2 a}{V^2} \right) (V - Nb) = N k_B T,$$

where  $P, V = Nv, T$  and  $N$  denote the pressure, volume, temperature, and the number of particles, respectively, and  $a, b$  are some non-universal constants. Show that by introducing reduced variables  $\hat{P} = P/P_c, \hat{v} = v/v_c, \hat{T} = T/T_c$  with  $P_c = a/27b^2, v_c = 3b, k_B T_c = 8a/27b$  one obtains a parameter-free form

$$\left( \hat{P} + \frac{3}{\hat{v}^2} \right) (3\hat{v} - 1) = 8\hat{T}.$$

Demonstrate that  $\hat{P} = \hat{v} = \hat{T} = 1$  corresponds to a critical point, i.e.  $(\partial P / \partial v)_T = (\partial^2 P / \partial v^2)_T = 0$ . Expand the reduced pressure for small  $t = \hat{T} - 1, \phi = \hat{v} - 1$  [Answer:  $\hat{P} = 1 + 4t - 6t\phi - 3\phi^3/2 + \mathcal{O}(\phi^4, t\phi^2)$ ]. Derive the free energy per particle close to the critical point. Convince yourself that one has to use a Maxwell construction for  $t < 0$  and discuss the shape of the coexistence curve in a  $P$ - $v$  diagram. Evaluate the specific heat per particle  $c_V = C_V/N$  above and below  $T_c$  at  $v = v_c$ . Calculate the isothermal compressibility  $\kappa_T$

(a) at  $v = v_c$  for temperatures  $T > T_c$ .

(b) at the coexistence boundary for  $T < T_c$ .