Übungen zur Thermodynamik

Computational Science Bachelor

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Teil II: Phasenübergange, Verbrennungsprozesse

(**HA** Punkte in Klammern, ohne Punkte: im Seminar)

1. Derive the Maxwell relations which follow from the energy $U(S,V)$, enthalpy $H[S,p]$, free energy $F[T,V]$ and Gibbs potential $G[T,p]$ respectively.(**HA** 4)

2. The Dieterici equation of state $p = \frac{RT}{V-b} \mathrm{e}^{\frac{-a}{RTV}}$ provides a useful alternative to the van der Waals equation for nonideal classical gases. Note that here V is the molar volume, R is the molar gas constant, and a and b are constants which are properties of the particular gas.

   a) Derive the expressions for the critical pressure, molar volume, and temperature, p_c, T_c, V_c in terms of a and b. Evaluate the critical compressibility factor $\frac{p_c V\_c}{RT_c}$ and show that it is in better agreement with the data for most gases than the corresponding result for the van der Waals equation. (**HA** 3)

   b) Express the Dieterici equation in reduced form. (**HA** 3)

   c) Deduce the virial coefficients for the Dieterici equation. Compare the second virial coefficient with the van der Waals result. (**HA** 3)

3. The heat of vaporization for a van der Waals fluid can be obtained by integrating the heat transfer along an isotherm using

   $$\Delta H = T \int_{V_l}^{V_g} \left(\frac{\partial S}{\partial V} \right)_T dV$$

   where V_l and V_g are the molar volumes for the saturated liquid and vapor phases, as determined by the Maxwell construction. Why ? (**HA** 2)

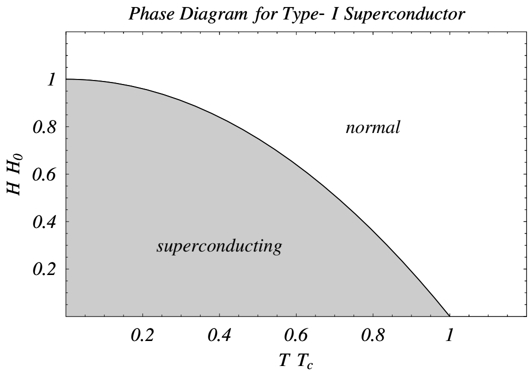
   a) Show that

   $$\Delta H = T \int_{V_l}^{V_g} \left(\frac{\partial p}{\partial T} \right)_V dV$$

   and evaluate using the van der Waals equation of state. (**HA** 2)

   b) Compute ΔH for water at atmospheric pressure given that $\alpha = 0.565$ Pa m^6 mole^{-2} and $b = 3.1 \times 10^{-5}$ m^3 mole^{-1}. Compare with experimental data. (**HA** 2)

4. The phase diagram for a typical type-I superconductor is sketched.



Experimentally one finds that the coexistence curve separating the normal and superconducting phases is well-approximated by the parabolic curve

$$\frac{H_c[T]}{H_c} = 1 - \left(\frac{T}{T_c}\right)^2$$

where the parameters H_c and T_c depend on the particular metal. The metal is nonmagnetic in its normal phase but in its superconducting phase expels any applied magnetic field H smaller than the critical field $H_c[T]$. Thus, the magnetization per unit volume, M, satisfies

$$\begin{aligned} T > T_c \quad &or \quad H > H_c[T] \rightarrow M_n = 0 \\ T < T_c \quad &and \quad H < H_c[T] \rightarrow M_s = -\frac{H}{4\pi} \end{aligned}$$

where the subscripts n and s denote normal and superconducting phases. The fundamental thermodynamic relation for this system is $dF = -SdT - MdH$ where F, S, and M are the free energy, entropy, and magnetization per unit volume.

a) Calculate $F_s[T,H] - F_s[T,H_c]$ for the superconducting phase. (**HA** 2)

b) Show that the superconducting phase has lower free energy than the normal phase when $H < H_c[T]$. (**HA** 2)

c) Compute the latent heat of transformation between normal and superconducting phases. (**HA** 2)

d) Determine the temperature dependence of the difference between the constant-H specific heats for the normal and superconducting phases, $\Delta_H[T,H] = C_{H,n}[T,H] - C_{H,s}[T,H]$, and show that there is a discontinuity in C_H at T_c. (**HA** 2)

5. Thermodynamics of van der Waals gas

a) Evaluate $C_p - C_V$ for the van der Waals equation of state.

b) Determine the relationships between T and V and between p and V that apply to isentropic transformations of a gas that obeys the van der Waals equation of state assuming that C_V is constant. (**HA** 3)?

Max 30 Punkte