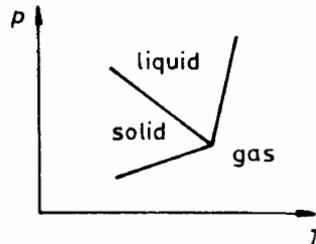


Problem sheet 12

Please hand in your solutions before the lecture on Wednesday, 20th of January.

Problem Problem 1 - Physical and unphysical phases - Vapour pressure

- (a) Some researchers claim to have measured the following phase diagram of a new substance.



Their results show that along the phase lines near the triple point

$$0 < \left(\frac{dP}{dT} \right)_{\text{sublimation}} < \left(-\frac{dP}{dT} \right)_{\text{fusion}} < \left(\frac{dP}{dT} \right)_{\text{vaporization}} \quad (1)$$

if these results are correct, then this new substance has a very unusual property and one property which violates the laws of thermodynamics. What are these two properties? *3 points.*

- (b) Derive an expression for the dependence of the equilibrium vapor pressure of a material with respect to the total pressure (i.e., how does the equilibrium partial pressure of a material depend on the addition of an overpressure of an inert gas.). Use this result to discuss qualitatively the difference between the triple point of and ice point (temperature at which ice and air-saturated water are in equilibrium at 1 atm) of water. *2 points.*
- (c) Calculate the change in specific latent heat with temperature at a point (P, T) along a phase equilibrium line. Express your results in terms of L and the specific heat C_P , coefficient of expansion α , and the specific volume V of each phase at the original temperature and pressure. *2 points.*
- (d) If the specific latent heat at 1atm on the vaporization curve is 540cal/g, estimate the change in latent heat 10°C higher than the curve. Assume the vapour pressure can be treated as an ideal gas with rotational degrees of freedom. *1 points.*

emphNote: The following data apply to the triple point of water:

Temperature: 0.01°C; Pressure: 4.6mmHg.

Specific volume of solid: 1.12cm³/g; Specific volume of liquid 1.00cm³/g.

Heat of melting: 80cal/g; Heat ofvaporization: 600cal/g.

Problem 2 - Occupation numbers

- (a) A system of N identical spinless bosons of mass m is in a box of volume V at temeprature $T > 0$. Write the general expression for the number of particles, $n(\epsilon)$, having an energy between ϵ and $\epsilon + \delta\epsilon$ in terms of their mass and energy, the temperature, chemical potential, volume, and any other relevant quantity. *3 points.*
- (b) Show that in the limit that the average distance, between the particles is very large compared to their de Broglie wavelength, $d \ll \lambda$, the distribution becomes equal to that calculated using the Boltzmann distribution. *2 points.*
- (c) Write the general expression for the mean number of fermions, N_i , occupying a single particle quantum state of energy ϵ . Sketch this expression for $T = 0K$ and $T = \mu/5K$. Label the significant points along both axis. Afterwards obtain and expression for μ in terms of the particle density, n. *3 points.*

- (d) Show that the expression for N_i reduces to the Maxwell-Boltzmann distribution in the limit $n\lambda \ll 1$, where λ is the thermal de Broglie wavelength. *2 points.*

Problem 3 - Quantum Statistics

- (a) We consider an harmonic potential well in which there may be present one or more non-interacting particles. What is the spectrum of the single particle states? What are the changes in the canonical and in the grand canonical partition functions, in the internal energy, and the chemical potential (for fixed particle number) when one changes the zero of the energy, replacing ϵ_q by $\epsilon'_0 = \epsilon_q + \delta$? *2 points.*
- (b) Evaluate the canonical partition function for:
- (α) a single particle, *1 points.*
 - (β) two distinguishable particles, *1 points.*
 - (γ) two spinless fermions, *1 points.*
 - (δ) two spinless bosons, *1 points.*
 - (ϵ) two spin 1/2 fermions. *1 points.*
- (c) Compare the internal energies and the entropies in these cases. Study the limits as $T \rightarrow 0$, as $T \rightarrow \infty$, and as $\hbar \rightarrow 0$. Explain the results. Write the grand partition functions for spin-zero fermions and bosons and for spin 1/2 fermions in the form of a series. *3 points.*
- (d) Calculate the lowest-order corrections due to the Pauli principle to the chemical potential, the equation of state, the internal energy, and the specific heat of ideal gases. *2 points.*