Edlisefnafrædi 2

Lokapróf, 11. des. 2006

Leyfileg hjálpargögn: Reiknivélar og stærdfrædihandbækur.

Prófid samanstendur af 6 spurningum sem eru mislangar en gilda samtals 100 stig. Aftast er listi yfir jöfnur.

Problem 1: (10 pts)

The graph below shows the molar heat capacity of a diatomic gas as a function of temperature. Explain the shape of the curve (in particular in the region around inflection points), write the values on the y-axis at each of the dotted, horizontal lines and mark Θ_{vib} and Θ_{rot} at appropriate places on the x-axis.

Problem 2: (15 pts)

The enthalpy of vaporization of a certain liquid is found to be 15 kJ/mol at a boiling point of 300 K. The molar volume of the liquid and the vapor are 150 cm^3/mol and 12.0 dm^3/mol, respectively, under these conditions.

(a) Estimate the slope of the phase boundary between liquid and vapour in the P-T phase diagram, dP/dT, from the Clapeyron equation which in its most basic form can be written as $dP/dT = \Delta S_{vap}/\Delta V_{vap}$. Give the results in units of atm/K.

(b) In the Clausius-Clapeyron equation it is, furthermore, assumed that: (1) the volume of the liquid is negligible compared with the volume of the gas, and (2) that the gas is ideal. How large an error in percent does the neglect of the volume of the liquid introduce in the calculation of dP/dT in this case?

(c) Consider now the effect of non-ideality (corrections to the ideal gas model). Assume the gas can be described by the van der Waals equation with $a = 19.3\ L^2\ bar/mol$ and $b = 0.15\ L/mol$. Estimate how large an error in percent is introduced in the calculation of dP/dT by the assumption of ideal gas behaviour in the Clausius-Clapeyron equation.

Problem 3: (15 pts)

An ice bath is initially made of crushed ice and liquid water at 0°C. Then ethanol is added to the liquid to lower the temperature. (Note that ΔH_{fus} for ice at 273 K is 6.00 $kJ/mol.$).

(a) The desired temperature of the ice bath is -3°C. How many mole percent of ethanol should be in the liquid?

(b) Explain in physical terms why the temperature drops when the ethanol is added.

(c) The temperature of an ice bath made of pure water and ice remains constant at 0°C until all the ice has melted. But, the ice bath with ethanol slowly heats up as the ice melts. Why is that? Explain with reference to a mathematical equation for the temperature of the bath.

Problem 4: (25 pts)

Information about internal degrees of freedom of gas molecules can be obtained by measuring the speed of sound in a gas. From the wave equation it can be shown that the speed of sound, c, satisfies the relationship

$$c^2 = -\frac{V_m^2}{M}\left(\frac{\partial P}{\partial V_m}\right)_S$$

where V_m is the molar volume, M is the molecular weight and the partial derivative is taken with entropy held constant.

(a) Why is the partial derivative taken with entropy being held constant (that is, why is it a good approximation to assume entropy is constant when a sound wave travels in gas)?

(b) Use the Euler chain rule, $(\partial x/\partial y)_z\,(\partial y/\partial z)_x\,(\partial z/\partial x)_y = -1,$ to rewrite the expression for the speed of sound so that only partial derivatives of S appear in the expression.

(c) Rewrite the expression obtained in (b) so that the only partial derivatives that appear involve the measureable quantities P, V and T as well as the heat capacity ratio, $\gamma = C_P/C_V$ (note that $(\partial S/\partial T)_x = C_x$ where C denotes the heat capacity and x is either V or P).

(d) Simplify the results obtained in (c) for the case of an *ideal* gas.

(e) The wavelength of standing sound waves in NO gas at 25 °C and 0.98 atm was measured to be 28.9 cm when the frequency was 1.018 kHz. Find the heat capacity ratio, γ, for the gas under these conditions, assuming ideal gas behaviour.

Problem 5: (20 pts)

Consider a crystal with N identical but distinguishable molecules which have two accessible electronic energy levels separated by an energy gap ϵ. Make the approximation that other, higher energy levels cannot be reached and that these molecular energy levels are unaffected by the presence of other molecules in the crystal. The lower level is three-fold degenerate but the higher level is non-degenerate (see figure below).

(a) What is the molecular electronic partition function and what is the canonical partition function of the system? Simplify as much as possible.

(b) Give an expression for the number of molecules in the excited electronic state as a function of temperature and state explicitly the limit as the temperature goes to zero and the limit as the temperature become very high.

(c) Give an expression for the electronic contribution to the internal energy of the gas as a function of temperature and state explicitly the limit as the temperature goes to zero and the limit as the temperature becomes very high.

(d) Give an expression for the entropy of the system as a function of temperature and state explicitly the limit as the temperature goes to zero and the limit as the temperature become very high.

Problem 6: (15 pts)

Consider the release of hydrogen gas from a solid where the hydrogen atoms are incorporated into holes between metal atoms that can be assumed to be stationary, to first approximation. Assume the energy of a hydrogen atom in the solid is E_b lower than the energy of a hydrogen atom in a gas phase molecule. The hydrogen atoms in the solid can be assumed to be independent harmonic oscillators vibrating at a frequency ν_s which is the same for all vibrational degrees of freedom. Let the vibrational temperature of hydrogen molecules in the gas phase be denoted by Θ_{vib} and the rotational temperature by Θ_{rot}.

(a) Give an expression for the change in enthalpy when the hydrogen is released from the solid to form a hydrogen gas at temperature T and pressure P. Explain all quantities that appear in your expression and relate them to known quantities (in particular, those given above).

(b) Give an expression for the increase in entropy when the hydrogen is released from the solid to form a hydrogen gas at temperature T and pressure P. Explain all quantities that appear in your expression and relate them to known quantities (in particular, those given above).

(c) Give an expression that could be used to predict how much the solid would need to be heated up in order to release hydrogen gas at 1 atm. Explain carefully how you arrive at this expression.