Edlisefnafrædi 2

Midannarpróf, 25. okt. 2006

Leyfileg hjálpargögn: Reiknivélar og stærdfrædihandbækur Prófid samanstendur af 5 spurningum sem eru mislangar og hafa mismikid vægi, en gilda samtals 100 punkta. Aftast er listi yfir jöfnur.

Problem 1: (10 pts)

Consider a gas that can be described by the following equation of state:

$$p(V_m, T) = R\left(\frac{T}{V_m} + q\left(\frac{T}{V_m}\right)^2\right)$$

where q is a constant and V_m is the molar volume.

(a) Find an expression for the compression factor, Z.

(b) At low pressure, the experimentally determined vale of q is found to be negative, while at hight pressure it is found to be positive. Explain these observations by considering the interaction between the gas molecules.

Problem 2: (15 pts)

Compare and contrast two different processes where one mole of a, ideal, monatomic gas is compressed from an initial volume of V_1 at room temperature to a final volume of $V_2 = V_1/2$. In process A the the tank of gas is isolated from the surroundings. In process B the tank of gas is immersed in a water bath at room temperature. In both cases the compression is carried out slowly enough that one can assume the processes are reversible.

(a) Sketch qualitatively how the pressure increases as a function of volume in both processes and mark the two curves clearly.

(b) How much work needs to be done during the compression in the two processes, A and B?

(c) What is the entropy change in the gas in the two processes, A and B?

Problem 3: (25 pts)

The heat of combustion of caffeine was determined by first burning benzoic acid to calibrate the calorimeter and then by burning caffeine. In both cases the calorimeter was filled with 466 g of distilled water. When 0.0717 g of benzoic acid, $C_7H_6O_2(s)$, were burned as well as 1.1 cm of the iron wire used to ignite the sample, the temperature increased from 22.615 °C to 23.487 °C. When 0.0624 g of caffeine, $C_8H_{10}O_2N_4(s)$, were burned, along with 1.8 cm of the wire, the temperature increased from 22.714 °C to 23.346 °C. (The energy change for combustion of benzoic acid is $\Delta U^{\circ} = -26.434 \text{ kJ/g}$, the combustion of the wire gives 9.62 J/cm, and the specific heat of water is 1 cal/g deg).

(a) What is the heat capacity of the calorimeter with and without water?

(b) What is the energy change, ΔU , per mol for the combustion of caffeine?

(c) Write a balanced chemical equation for the combustion of caffeine and find the enthalpy change for the combustion of caffeine.

(d) Find the heat of formation for caffeine (from thermodynamic tables one finds $\Delta H_f^{\circ} = -393.5 \ kJ/mol$ for $CO_2(g)$, $\Delta H_f^{\circ} = -241.8 \ kJ/mol$ for $H_2O(g)$ and $\Delta H_f^{\circ} = -285.8 \ kJ/mol$ for $H_2O(l)$).

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

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

to rewrite the expression for the speed of sound so that the only partial derivatives that appear are partial derivatives of S.

(c) Use Maxwell relations and the chain rule to rewrite the expression obtained in (b) so that the only partial derivatives that appear involve the measureable quantities P, V and T (note: $(\partial S/\partial T)_x = C_x$ where x=V or P).

(d) Use the results obtained in (c) to derive an expression for the speed of sound in an ideal gas.

(e) Predict the speed of sound in SO_2 gas at a temperature of $25^{\circ}C$ and a pressure of 1 bar assuming that equipartition holds except that vibrational degrees of freedom are not excited in the molecules.

Problem 5: (25 pts)

The enthalpy of a certain gas was determined over a range of temperature while pressure was kept constant and the results summarized in the expression

$$H(T) = aT + bT^3$$

where a and b are experimentally determined constants. Consider the process when the gas is heated from temperature T_a to temperature T_b , both within the range of validity of the expression above, while the pressure was kept constant at the value used in the experiments described above. Assume ideal gas behavior.

- (a) Give an expression for the change in constant pressure heat capacity, ΔC_P .
- (b) Give an expression for the change in constant volume heat capacity, ΔC_V .
- (c) Give an expression for the internal energy change, ΔU .
- (d) Give an expression for the entropy change, ΔS .
- (e) Give an expression for the Gibbs free energy change, ΔG .