Physical Chemistry Cumulative Exam

May 9th, 2017

Topic: thermodynamics

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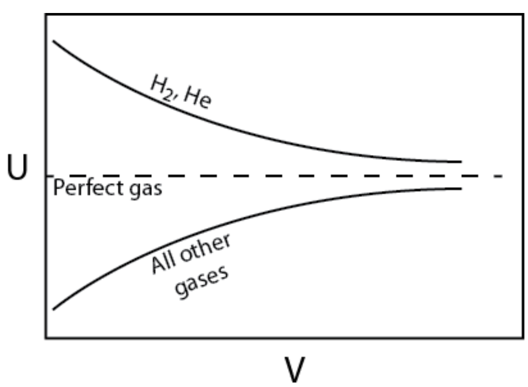
(1) (20 points) In the van der Waals equation: $P = \frac{RT}{V_m - b} - \frac{a}{V_m{}^2}$, the "b" term is always found to be a positive number.

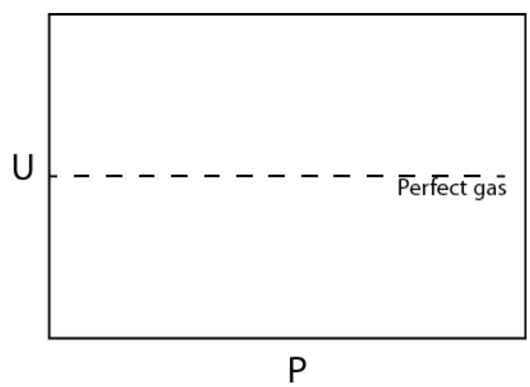
a) Why not add the "b" term to V_m? i.e. Why did van der Waals subtract "b" from V_m?

b) Why should we subtract the second term a/V_m^2?

(2) (20 points) Prove that two reversible adiabatic paths can never cross. Assume that the energy of the system under consideration is a function of temperature only.
(***Hint***: Suppose that the two such paths can intersect and complete the cycle with the two paths plus one isothermal path. Consider the changes accompanying each stage of the cycle and show that they conflict with Kelvin's statement of the Second Law.)

(3) (10 points) Here is a representation for how a perfect gas (dash) and real gases (solid) change with U with respect to volume (left figure). Now can you do the same for how U changes with pressure (right figure)?





(4) (20 points) The osmotic pressure of an unknown substance is measured at 298 K. Determine the molecular weight if the concentration of this substance is 31.5 kg×m^{-3} and the osmotic pressure is 5.30×10^4 Pa. The density of the solution is 997 kg m^{-3}. (ideal gas constant: 8.3144 J mol^{-1} K^{-1})

(5) (30 points) A 22.0 g mass of ice at 273 K is added to 136 g of H_2O (*l*) at 310 K at constant pressure. The final state of the system is liquid water. Calculate Δ*S* for the process. Is the process spontaneous? (ΔH_{fusion} = 6010 J mol^{-1}, $C_{P,m}$ (H_2O) = 75.3 J K^{-1} mol^{-1}, Molecular weight(H_2O) =18.02 g mol^{-1}) ($\Delta S = \frac{q_{rev}}{T}$ (thermodynamic definition of entropy))