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Problems set # 2 **Physics 303** September 9, 2014

1. Van der Waals equation of state for a non-ideal gas describing its transition to liquid has the form

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT,$$

where a describes attraction of the gas molecules and b describes the volume occupied by the molecules and thus excluded from their motion. *(i)* Plot isotherms of this gas for diferent T, setting $a = b = R = 1$. Verify that at high T isotherms are close to those for an ideal gas, but for lower T they become distorted. Show that below a critical temperature $T < T_C$ there is a local maximum and minimum of P. The transition between the two types of curves (that is where $T = T_C$) is a curve having an inflection point called the critical point (CP). This transition curve is known as the critical curve. *(ii)* Calculate the isothermal compressibility of the van der Waals gas in terms of (v, T). Obtain its high-temperature limit. What happens with it at the critical point? *(iii)* Find the critical point parameters using the analysis in *(i)* as a hint.

2. Using the Berthelot equation of state,

$$P = \frac{RT}{v - b} - \frac{a}{Tv^2}\,,$$

show that $v_C = 3b$, $T_C = \sqrt{\frac{8a}{27bR}}$, and $P_C = \frac{1}{12b}\sqrt{\frac{2aR}{3b}}$. Compare the numerical value of $RT_C P_C^{-1} v_C^{-1}$ with the experimental values given below.

3. Using the Dieterici equation of state,

$$P = \frac{RT}{v - b} \exp\left\{-\frac{a}{RTv}\right\},$$

show that $v_C = 2b$, $T_C = \frac{a}{4Rb}$, $P_C = \frac{a}{4e^2b^2}$, and find the numerical value of $RT_C P_C^{-1} v_C^{-1}$. How does this compare with the tabulated experimental values?

4. Making use of the triple product find the expansivity β of a substance obeying the Dieterici equation of state. *(ii)* At high temperature and high specific volumens (low densities) all gases approximate an ideal gas. Show that for large values of T and v, the expression for β obtained in *(i)* goes over to the corresponding equation for an ideal gas.

5. Show that β and κ_T are infinite at the critical point.

Substance	$RT_C P_C^{-1} v_C^{-1}$
He	3.06
H_2	3.27
O_2	3.42
CO_2	3.61
H_2O	4.29