CENG411: HOMEWORK 5

Please write down at the top of the page how many hours you spent on this homework. You may find it useful to use Maxwell’s relations on this problem set.

1. (10 points)
In class we showed that

\[ C_p - C_v = VT \frac{\alpha^2}{\kappa} \]  \hspace{1cm} (1)

where \( \alpha = (1/V)(\partial V/\partial T)_p \) is the volume coefficient of expansion of a substance and \( \kappa = -(1/V)(\partial V/\partial p)_T \) is the isothermal compressibility. \( C_p \) and \( C_v \) are the heat capacities of the substance.

i) In the special case of an ideal gas, use this relation to find \( \gamma = C_p/C_v \). Is this the same as what we derived previously?

ii) Calculate \( \gamma \) for copper at room temperature (298K) and atmospheric pressure. The density of copper is 8.9g/cm\(^3\), its atomic weight is 63.5. Some useful measured values are \( \alpha = 5 \times 10^{-5} \text{K}^{-1} \) and \( \kappa = 4.5 \times 10^{-13} \text{cm}^2\text{dyne}^{-1} \), \( c_p = 24.5 \text{J/K mole} \). What does this show?

2. (10 points)
   i) Show (yes, again) that \( (\partial E/\partial T)_V = C_v \).

ii) Show that

\[ \left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p \] \hspace{1cm} (2)

3. (15 points)
Consider a gas whose equation of state is

\[ \left( p + \frac{a}{V^2} \right) (v - b) = RT \] \hspace{1cm} (3)

where \( v = V/\nu \) is the molar volume. This is an empirical equation known as the van der Waals equations. It represents the behavior of real gases more accurately than the ideal gas law by
introducing two additional positive constants $a$ and $b$. The term $a/v^2$ represents a slight positive pressure i.e. attractive forces between molecules in a real gas tend to keep the molecules closer together than for an ideal gas. The term $b$ represents the volume occupied by the molecules themselves which must be subtracted from the volume available to the molecules in the container.

i) What happens in the limit that $a = b = 0$ or where the gas becomes very dilute i.e. $v \to \infty$?

ii) What is $(\partial E/\partial V)_T$ for a van der Waals gas? for an ideal gas? Express your answers in terms of $a, b, p, R, T$ and $v$.

iii) Show that $c_V$ for a van der Waals gas is only a function of temperature (i.e. it is independent of the molar volume).

iv) Write down an expression for an infinitesimal change in the molar energy $E/v$ in terms of $c_V, T, a$ and $v$ for a van der Waals gas.

v) Use this expression to calculate the change in internal energy in going from one macrostate at temperature $T_0$ and volume $V_0$, to another macrostate at temperature $T$ and volume $V$, for a van der Waals gas. Would your answer be different for an ideal gas?

vi) What is the entropy change for the same process?

4. (10 points)

The Third Law of Thermodynamics is the poor cousin of the First and Second Laws. Our discussion of it is relegated to this homework problem. The Third Law of Thermodynamics states:

The entropy, $S$, for a system has the limiting property that as $T \to 0^+, S \to S_0$ where $S_0$ is independent of all the other parameters in the system.

For a perfectly crystalline substance, $S_0 = 0$.

i) What does this imply about the behavior of the the specific heats at absolute zero?

ii) What about $\alpha$ and $\kappa$?

iii) What about the ratio $(C_p - C_V)/C_V$? Does this contradict the statement that $C_p - C_V$ is a constant for an ideal gas?
5. Summarize what you learnt from problems 1, 2 and 3. (3 points)

**Honor Code Reminder**

Obtaining homework problems or homework solutions from previous CENG 411 classes is prohibited. Giving out homework problems or solutions from the present CENG 411 class is also prohibited. An excerpt from the University Honor Code is given below:

“The students are encouraged to talk to each other, the labbies, the instructor, or anyone else about any assignment in the course that is not specifically designated as pledged. This assistance is limited to the discussion of the problem and perhaps sketching of a solution. Consulting another student’s solution (even from a previous class on the same subject) is prohibited, and submitted solutions may not be copied from any source.”