

April 8, 2008

1) SHORT ANSWER (30 Pts)

- a) (15 pts): The intermolecular interaction potential between molecules that form hydrogen bonds is sometimes described by the following equation:

$$\Gamma(r) = \frac{6^6}{5^5} \varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{10} \right]$$

In this equation, the parameters ε and σ have the same meaning as for potentials discussed in class. Describe briefly the origin of the two terms in this interaction potential. Do fluids that interact with this kind of potential have a Boyle temperature? Would you expect ε to be larger or smaller in magnitude than for a similar fluid that interacts only through dispersion forces? Explain your answers.

- b) (15 pts) You are told that Gas A obeys the following equation of state:

$$P = \frac{RT}{v - b}$$

Can this gas be liquefied by Joule-Thompson expansion? Justify your answer.

April 8, 2008

Solution to Problem 1 (Short Answer).

- a.) The intermolecular potential function $\Gamma(r)$ describes how much potential energy is associated with a pair of molecules who are a distance r apart. The positive term in $\Gamma(r)$ accounts for the repulsion that occurs when $r \leq \sigma$ due to overlapping electron clouds or electrostatic repulsion between like charges if the molecules are ions. The second, negative term in $\Gamma(r)$ accounts for the attractive energies due to electrostatic attraction of ions of opposite charges, dipole-dipole interactions, hydrogen bonding (a type of dipole-dipole interaction), dispersion, and induction energies present between molecules.

The Boyle temperature is the temperature at which attractive and repulsive intermolecular forces are balanced at a given pressure. In the intermolecular potential function, there are both positive and negative terms which take into account the repulsive and attractive intermolecular forces, respectively. Thus, this fluid can have a Boyle temperature such that the attractive and repulsive forces exactly balance.

The energy parameter ϵ is related to the magnitude of attractive intermolecular attraction between molecules. Hydrogen bonding is a chemical force that is intermediary in strength between van der Waals interactions and covalent bonding. Hydrogen bonding occurs over much shorter distances because of there is some degree of covalent bond character in which lone-pair electrons are shared. Because of the close range nature of hydrogen bonding, the chemical force decays as $(1/r^{10})$ rather than $(1/r^6)$ for van der Waals forces. Dispersion forces are a type of van der Waals interaction present when a molecule has a temporary dipole and induces a dipole in a neighboring molecule. Thus when hydrogen bonding is present, there is a significant increase in intermolecular attraction compared to a fluid that only experience dispersion forces. If the similar fluid only exhibits dispersion forces, the amount of attractive forces between molecules of the original fluid must be greater since hydrogen bonding is a chemical force that is much stronger than van der Waals interactions. Because ϵ scales with the magnitude of attractive forces, ϵ would be larger than for the similar fluid which only interacts through dispersion forces.

- b.) For Joule-Thompson liquefaction to occur, the temperature of the gas must *decrease* such that the gas condenses as the gas undergoes Joule-Thompson expansion. The Joule-Thompson coefficient, μ_{JT} , is defined as

April 8, 2008

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h \quad (1)$$

The Joule-Thompson coefficient must be positive for the temperature to decrease as the pressure is decreased isenthalpically. The change in enthalpy, dh , can be expressed in terms of the changes in pressure and temperature as follows:

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP \quad (2)$$

Simplifying the partial derivatives:

From the definition of heat capacity,

$$\left(\frac{\partial h}{\partial T} \right)_P = c_P$$

Using the fundamental equation for enthalpy,

$$\begin{aligned} \left(\frac{\partial h}{\partial P} \right)_T &= \left(\frac{T \partial s + v \partial P}{\partial P} \right)_T \\ &= T \left(\frac{\partial s}{\partial P} \right)_T + v \end{aligned}$$

Using the Maxwell relation $\left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P$,

$$\left(\frac{\partial h}{\partial P} \right)_T = -T \left(\frac{\partial v}{\partial T} \right)_P + v$$

Substituting these partial derivatives back into Equation 2,

$$dh = c_P dT + \left[-T \left(\frac{\partial v}{\partial T} \right)_P + v \right] dP \quad (3)$$

Joule-Thompson expansion is isenthalpic ($dh = 0$), so we can set Equation 3 equal to zero and rearrange,

$$\left(\frac{\partial T}{\partial P} \right)_h = \frac{\left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right]}{c_P} \quad (4)$$

April 8, 2008

Substituting in Equation 1,

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$$

$$\mu_{JT} = \frac{\left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right]}{c_p} \quad (5)$$

Now we can evaluate the Joule-Thompson coefficient using Equation 5 and the given equation of state. Rearrange the equation of state to make it in explicit in volume:

$$v = \frac{RT}{P} + b \quad (6)$$

Evaluating Equation 5 using Equation 6,

$$\mu_{JT} = \frac{T \left(\frac{\partial v}{\partial T} \right)_P - v}{c_p} \quad (5)$$

$$= \frac{T \left(\frac{R}{P} \right) - \left(\frac{RT}{P} + b \right)}{c_p} \quad (7)$$

$$\mu_{JT} = - \left(\frac{b}{c_p} \right) \quad (8)$$

The heat capacity c_p is always positive, so we only need to consider the sign of b . The parameter b represents a correction term to the ideal gas law, taking into account that the volume available to a particular molecule is less than the total volume of the system due to the hard-sphere volume of other molecules. After examining the original equation of state, b must be a positive term to decrease the volume relative to the ideal gas law. Consequently, the Joule-Thompson coefficient is negative, and the gas cannot undergo liquefaction.

Alternate Solution:

For liquefaction to occur, $\mu_{JT} > 0$ because temperature must decrease while the pressure decreases during expansion. Since the temperature is decreasing while the pressure

April 8, 2008

decreases, the molecular kinetic energy must be converted into potential energy to expand isenthalpically. The increase in molecular potential energy means that the molecules are more stable due to attractive forces, and attractive forces dominate when $\mu_{JT} > 0$. Since the PvT relationship given does not account for attractive forces by a term such as a/V^2 found in the van der Waals equation of state, this gas does not exhibit the nonideal behavior necessary to undergo liquefaction.

Grading Scheme:

Part a.

1. 2 points for stating that the positive term is associated with repulsive forces (or 1 point for stating repulsive forces are present but not identifying it with the positive term).
2. 1 point for explaining the origin of repulsive forces (one example needed).
3. 2 points for stating that the negative term is due to attractive forces (or 1 point for stating attractive forces are present but not identifying it with the negative term).
4. 1 point for explaining the origin of attractive forces (one example needed).
5. 2 points for stating that at the Boyle temperature, attractive and repulsive intermolecular forces are in balance or that it is the temperature at which $B(T)=0$.
6. 2 points for stating that this fluid does have a Boyle temperature since the intermolecular potential function includes terms that accounts for both attractive and repulsive forces.
7. 2 points for stating that the parameter ϵ scales with the magnitude of attractive intermolecular forces (or 1 point for stating that ϵ scales with intermolecular forces).
8. 3 points for stating that since the original fluid interacts via hydrogen bonding which is a *short-ranged* chemical force, which is much stronger than dispersion forces, ϵ is higher (or 1 point for stating that ϵ is higher because hydrogen bonding is present in addition to dispersion forces).

April 8, 2008

Part b.

1. 1 point for Equation 1 $\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$ or stating that expansion is isenthalpic
2. 3 points for stating that the Joule-Thompson coefficient must be positive for liquefaction to occur because the gas must cool as it expands
3. 2 points for Equation 5 $\mu_{JT} = \frac{T \left(\frac{\partial v}{\partial T} \right)_P - v}{c_p}$
4. 2 points for Equation 7 $\mu_{JT} = \frac{T \left(\frac{R}{P} \right) - \left(\frac{RT}{P} + b \right)}{c_p}$
5. 1 point for Equation 8 $\mu_{JT} = - \left(\frac{b}{c_p} \right)$
6. 3 points for stating that b is always positive since it lowers the system volume to account for the hard-sphere volume of molecules (or 1 point for stating b is positive based on expression for b used in the van der Waals, Redlich-Kwong and other equations of state)
7. 3 points for stating that the gas cannot undergo liquefaction because the Joule-Thompson coefficient, $\mu_{JT} = - \left(\frac{b}{c_p} \right)$, is always negative.

Alternative solution

1. [10 pts] for stating that a term accounting for intermolecular forces is not found in the EOS, thus it is not possible for attractive forces to be dominate as is required when $\mu_{JT} > 0$. Also, an explanation of why $\mu_{JT} > 0$ is required. (Partial credit is received here because b accounts for the repulsive forces due to the overlap of electron clouds.)
2. [15 pts] for stating that a term accounting for attractive forces is not found in the EOS, thus it is not possible for attractive forces to be dominating as is required when $\mu_{JT} > 0$. Also, an explanation of why $\mu_{JT} > 0$ is required.