ChE 230
Summer 2003
Midterm Exam #1
Administered: Wednesday June, 18, 2003

A monatomic gas described by the ideal gas equation of state has a pressure and constant-pressure heat capacity given by

$$p = \frac{RT}{\underline{V}}$$

$$\left(\frac{\partial \underline{H}}{\partial T}\right)_p \equiv \underline{C_p} = \frac{5}{2}R$$

A monatomic gas described by the van der Waals equation of state has a pressure and constant-pressure heat capacity given by

$$p = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}$$

$$\left(\frac{\partial \underline{H}}{\partial T}\right)_p \equiv \underline{C_p} = \frac{R}{2}\left(\frac{5p\underline{V}^3 - \underline{V}a + 6ab}{p\underline{V}^3 - \underline{V}a + 2ab}\right)$$

R = 8.314 J/mole/K
1 atm = 101325 Pa

Problem 1.
We perform a Joule-Thomson experiment to measure the Joule-Thomson coefficient,
$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial p}\right)_{\underline{H}}.$$

(a) Find an expression for the partial derivative representing the change in enthalpy per change in pressure under isothermal conditions for the ideal gas.
(b) Find an expression for the partial derivative representing the change in enthalpy per change in molar volume under isothermal conditions for the ideal gas.

Solution:

(a) $\left(\dfrac{\partial \underline{\underline{H}}}{\partial p}\right)_T \left(\dfrac{\partial p}{\partial T}\right)_{\underline{H}} \left(\dfrac{\partial T}{\partial \underline{H}}\right)_p = -1$

$\left(\dfrac{\partial \underline{\underline{H}}}{\partial p}\right)_T = -\left(\dfrac{\partial T}{\partial p}\right)_{\underline{H}} \left(\dfrac{\partial \underline{\underline{H}}}{\partial T}\right)_p = -\mu_{JT}\underline{C_p}$

$\left(\dfrac{\partial \underline{H}}{\partial p}\right)_T = -\mu_{JT}\underline{C_p} = -\mu_{JT}\dfrac{5}{2}R$

(b) $\left(\dfrac{\partial \underline{\underline{H}}}{\partial \underline{V}}\right)_T = \left(\dfrac{\partial \underline{\underline{H}}}{\partial p}\right)_T \left(\dfrac{\partial p}{\partial \underline{V}}\right)_T$

$\left(\dfrac{\partial p}{\partial \underline{V}}\right)_T = -\dfrac{RT}{\underline{V}^2}$

$\left(\dfrac{\partial \underline{\underline{H}}}{\partial \underline{V}}\right)_T = \left(\dfrac{\partial \underline{\underline{H}}}{\partial p}\right)_T \left(\dfrac{\partial p}{\partial \underline{V}}\right)_T = -\mu_{JT}\dfrac{5}{2}R\left(-\dfrac{RT}{\underline{V}^2}\right) = \dfrac{5}{2}\mu_{JT}\dfrac{R}{\underline{V}}\left(\dfrac{RT}{\underline{V}}\right) = \mu_{JT}\dfrac{5}{2}\dfrac{p^2}{T}$

Problem 2.

We have 2 moles of xenon (a monatomic gas) initially at T = 298 K and p = 1 atm.
The gas is heated at constant pressure to 600 K. Find the heat, work, change in molar internal energy, and change in molar enthalpy if we consider the material as an ideal gas.

Solution:

Isobaric heating of an ideal gas.

initial volume: $\quad V_1 = \dfrac{nRT_1}{p_1} = 0.04890 m^3$

final volume: $\quad V_2 = \dfrac{nRT_2}{p_1} = 0.09846 m^3$

heat: $\quad q = \displaystyle\int_{T_1}^{T_2} n\underline{C_p} dT = n\underline{C_p}\int_{T_1}^{T_2} dT = n\underline{C_p}(T_2 - T_1) = \frac{5}{2}nR(T_2 - T_1) = 12554 J$

work: $\quad w_{rev} = -\displaystyle\int_{V_1}^{V_2} p dV = -p\int_{V_1}^{V_2} dV = -p(V_2 - V_1) = -5022 J$

extensive internal energy: $\quad \Delta U = q + w_{rev} = 12554 - 5022 = 7532 J$

intensive internal energy: $\quad \Delta\underline{U} = \dfrac{1}{n}\Delta U = \dfrac{7532}{2} = 3766 J$

extensive enthalpy:
$$\Delta H = \Delta U + \Delta(pV) = \Delta U + p\Delta V = q + w_{rev} + p\Delta V = q - p\Delta V + p\Delta V = q = 12554 J$$

intensive enthalpy: $\quad \Delta\underline{H} = \dfrac{1}{n}\Delta H = \dfrac{12554}{2} = 6272 J$

Problem 3.

We have 2 moles of xenon (a monatomic gas) initially at T = 298 K and p = 1 atm.
(a) The gas is expanded at constant temperature to double the volume. Find the change in molar enthalpy if we consider the material as an ideal gas.
(b) Will we obtain the same result for a van der Waals equation of state? Why or why not?

Solution:

(a) Isothermal expansion of an ideal gas.

For an ideal gas, the enthalpy is only a function of temperature. Therefore, for an ideal gas undergoing an isothermal process, there is no temperature change and thus no enthalpy change.

intensive enthalpy: $\Delta \underline{H} = 0$

(b) Will we obtain the same result for a van der Waals equation of state? Why or why not?

No, we will not get the same result, because we can see from the heat capacity, that the enthalpy of the van der Waals is not just a function of temperature, but also of pressure. The pressure is changing during this isothermal process. Therefore, the enthalpy will also change.

Not part of the exam but interesting all the same:

How would we calculate the change in enthalpy for a van der Waals gas undergoing an isothermal expansion or compression?

Use the Bridgman tables to obtain a convenient form of the necessary derivative.

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{T\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T} + V = \frac{T\dfrac{R}{V-b}}{-\dfrac{RT}{(V-b)^2} + \dfrac{2a}{V^3}} + V$$

Integrate over pressure assuming constant T.

$$\Delta H = H(T_1, P_2) - H(T_1, P_1) = \int_{P_1}^{P_2} \left[\frac{T\dfrac{R}{V-b}}{-\dfrac{RT}{(V-b)^2} + \dfrac{2a}{V^3}} + V \right] dP$$

This is an ugly integral because V still varies with p. Probably the safest bet is to integrate it numerically using a Simpson's rule, or a similar method.