

**Chemistry 366  
Thermodynamics  
Midterm Exam  
March 8, 2006**



Name van der Wark

**Full credit will be given to correct answers only when ALL the necessary steps are shown. DO NOT GUESS THE ANSWER.**

**This is a closed book exam, and you are responsible to be sure that your exam has no missing pages ( 6 pages).**

**If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.**

*But surely this is an old tale you tell, they say;  
But surly this is a new tale you tell, other say.  
Tell it once again, they say;  
Or, do not tell it yet again, others say.  
But I have heard all this before, say some;  
Or, but this is not how it was before, say the rest*

Naqshbandi recital, from The Way of the Sufi, by Idries Shah

**Once you start the exam, you have up to 2 hours to solve it.**

**Honor Statement**

**I have neither give nor received aid in this examination.**

**Full signature \_\_\_\_\_**

**P1.** , A rigid vessel of volume  $0.500 \text{ m}^3$  containing  $\text{H}_2$  at  $20.5^\circ\text{C}$  and a pressure of  $611 \times 10^3 \text{ Pa}$  is connected to a second rigid vessel of volume  $0.750 \text{ m}^3$  containing  $\text{Ar}$  at  $31.2^\circ\text{C}$  at a pressure of  $433 \times 10^3 \text{ Pa}$ . A valve separating the two vessels is opened and both are cooled to a temperature of  $14.5^\circ\text{C}$ . What is the final pressure in the vessels?

$$n_{\text{H}_2} = \frac{PV}{RT} = \frac{611 \times 10^3 \text{ Pa} \times 0.500 \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (273.15 + 20.5) \text{ K}} = 125 \text{ mol}$$

$$n_{\text{Ar}} = \frac{PV}{RT} = \frac{433 \times 10^3 \text{ Pa} \times 0.750 \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (273.15 + 31.2) \text{ K}} = 128 \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{(125 + 128) \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (273.15 + 14.5) \text{ K}}{(0.500 + 0.750) \text{ m}^3} = 4.84 \times 10^5 \text{ Pa}$$

**P2.** , For 1 mol of an ideal gas,  $P_{\text{external}} = P = 200 \times 10^3 \text{ Pa}$ . The temperature is changed from  $100^\circ\text{C}$  to  $25.0^\circ\text{C}$ , and  $C_{V,m} = 3/2R$ . Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$ .

$$\Delta U = nC_{V,m}\Delta T = \frac{3}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (298 \text{ K} - 373 \text{ K}) = -935 \text{ J}$$

$$\begin{aligned} \Delta H &= nC_{p,m}\Delta T = n(C_{V,m} + R)\Delta T \\ &= \frac{5}{2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (298 \text{ K} - 373 \text{ K}) \\ &= -1.56 \times 10^3 \text{ J} \\ &= q_p \end{aligned}$$

$$w = \Delta U - q_p = -935 \text{ J} + 1.56 \times 10^3 \text{ J} = 624 \text{ J}$$

**P3** Because  $V$  is a state function,  $\left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right)_P$ . Using this

relationship, show that the isothermal compressibility and isobaric expansion coefficient are related by  $\left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_P$ .

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right)_P$$

$$\text{Because } \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial [V\beta]}{\partial P}\right)_T = -\left(\frac{\partial [V\kappa]}{\partial T}\right)_P \text{ or } \left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial T}\right)_P = V\beta$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -V\kappa$$

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T = \left(\frac{\partial V\beta}{\partial P}\right)_T$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right)_P = -\left(\frac{\partial V\kappa}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial P}\right)_T \beta + V\left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \kappa - V\left(\frac{\partial \kappa}{\partial T}\right)_P$$

$$-\cancel{V\kappa\beta} + \cancel{V}\left(\frac{\partial \beta}{\partial P}\right)_T = -\cancel{V}\beta\kappa - \cancel{V}\left(\frac{\partial \kappa}{\partial T}\right)_P$$

14) Calculate  $w$ ,  $q$ ,  $\Delta H$ , and  $\Delta U$  for the process in which 1 mol of water undergoes the transition  $\text{H}_2\text{O}(l, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(g, 460 \text{ K})$  at 1 bar pressure. The volume of liquid water at 373 K is  $1.89 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$  and the volume of steam at 373 and 460 K is 3.03 and  $3.74 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$ , respectively. For steam,  $C_{p,m}$  can be considered constant over the temperature interval of interest at  $33.58 \text{ J mol}^{-1} \text{ K}^{-1}$ .

$$q = \Delta H = n\Delta H_{\text{vaporization}} + nC_{p,m}^{\text{steam}}\Delta T$$

$$= 40656 \text{ J} + 1 \text{ mol} \times 33.58 \text{ J mol}^{-1} \text{ K}^{-1} \times (460 \text{ K} - 373 \text{ K}) = 4.35 \times 10^4 \text{ J}$$

$$w = -P_{\text{external}}\Delta V = -10^5 \text{ Pa} \times (3.03 \times 10^{-2} \text{ m}^3 - 1.89 \times 10^{-5} \text{ m}^3) - 10^5 \text{ Pa} \times (3.74 \times 10^{-2} \text{ m}^3 - 3.03 \times 10^{-2} \text{ m}^3)$$

$$= -3028 \text{ J} - 710 \text{ J} = -3.74 \times 10^3 \text{ J}$$

$$\Delta U = w + q = 4.35 \times 10^4 \text{ J} - 3738 \text{ J} = 3.98 \times 10^4 \text{ J}$$

Examples. - A Berthelot gas is a gas whose  $P, V, T$  behavior is described by the eq. of state

$$V = n \frac{RT}{P} + na \left[ 1 + \frac{b}{T^2} \right] \left( P + \frac{a}{TV^2} \right) (V - b) = RT$$

where  $a$  and  $b$  are const. characteristic of a particular gas.

Obtain an expression for the change in enthalpy  $\Delta H$  of  $n$  moles of a Berthelot gas that undergoes the change in state  $P_1, T$  to  $P_2, T$ .

Hint: ~~We will prove that~~  
Consider the following relation.

$$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P$$

Solution:

$$\Delta H = H(P, T)$$

Thus

$$dH = \left( \frac{\partial H}{\partial P} \right)_T dP + \left( \frac{\partial H}{\partial T} \right)_P dT,$$

but  $dT = 0$ , and therefore

$$dH = \left( \frac{\partial H}{\partial P} \right)_T dP$$

Using the hint

$$dH = \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP.$$

$$\begin{aligned} \left( \frac{\partial V}{\partial T} \right)_P &= \left( \frac{\partial}{\partial T} \left( n \frac{RT}{P} + na + \frac{nab}{T^2} \right) \right)_P = \left( \frac{nR}{P} \frac{\partial}{\partial T} T + na \frac{\partial}{\partial T} 1 + nab \frac{\partial}{\partial T} \frac{1}{T^2} \right)_P \\ &= \frac{nR}{P} - \frac{2nab}{T^3} \end{aligned}$$

$$V - T \left( \frac{\partial V}{\partial T} \right)_P = \cancel{\frac{nRT}{P}} + na + \frac{nab}{T^2} - \cancel{\frac{nRT}{P}} + \frac{2nab}{T^2}$$
$$= na + \frac{3nab}{T^2} = na \left[ 1 + \frac{3b}{T^2} \right]$$

$$dH = \left( \frac{\partial H}{\partial P} \right)_T dP = na \left[ 1 + \frac{3b}{T^2} \right] dP$$

$$\int_1^2 dH = \boxed{\Delta H = na \left[ 1 + \frac{3b}{T^2} \right] \Delta P}$$