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PHYS 119A
Midterm Examination

Wednesday 28 October 2009

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Question 1: Short Answers (10 points)

a. Consider the following change in state: 1 mole of a real gas undergoes a reversible change in state in a Carnot cycle. Will ΔU be greater, smaller or equal than the ΔU for an ideal gas undergoing the same cycle. EXPLAIN (or you will not get full credit).

$\Delta U = 0$ for any cyclic process

$\Delta U_{ideal} = \Delta U_{real} = 0$

b. What is the constant volume heat capacity (C_v) of 1 mole of an ideal diatomic gas at room temperature? Explain. What is the heat capacity at constant pressure (C_p) for this same system? Explain.
Note: at this temperature, the vibrational modes are not excited.

$\left.\begin{array}{l}\text{3 translational moments} \\ \text{\& 2 rotational moments}\end{array}\right\}$ 5 in total

contribute to equipartition result: $U = \frac{5}{2} nRT$

$$\left.\frac{\partial U}{\partial T}\right|_V = \boxed{C_v = \frac{5}{2} nR}$$

$$H = U + PV = \frac{5}{2} nRT + nRT = \frac{7}{2} nRT$$

$$\left.\frac{\partial H}{\partial T}\right|_P = \boxed{C_p = \frac{7}{2} nR}$$

c. Consider a real gas, with attractive intermolecular interactions that undergoes a **free expansion** (the external pressure is zero) in **a thermally insulated** container to twice its initial volume. In this process, will ΔU be positive, negative or zero? Explain.

$w = 0$ free expansion

$q = 0$ adiabatic

$\Delta U = q + w = 0$

$\Delta U = 0$

Question 2: 15 points

Consider a real gas with equation of state:

$$P = \frac{RT}{\overline{V}-b} - \frac{a}{T^{1/2}}\frac{1}{\overline{V}(\overline{V}+b)}$$

and $\overline{V} = \dfrac{V}{n}$

Consider the reversible isothermal expansion at a temperature T of 1 mol of this gas from an initial state with volume V_1 to a final state with volume V_2. Find an expression for w and ΔU for this process. Simplify your expressions (i.e. evaluate all partial derivatives and integrals). Show all your work! Write your final answer in the table below:

	WORK	ΔU
Expression	$-RT\ln\left(\frac{\overline{V}_2-b}{\overline{V}_1-b}\right) + \frac{a}{bT^{1/2}}\ln\left(\frac{\overline{V}_2(\overline{V}_1+b)}{\overline{V}_1(\overline{V}_2+b)}\right)$	$\frac{3}{2}\frac{a}{bT^{1/2}}\ln\left(\frac{\overline{V}_2(\overline{V}_1+b)}{\overline{V}_1(\overline{V}_2+b)}\right)$

The following integral may be useful:

$$\int_{V_1}^{V_2}\frac{dV}{(V-b)} = \ln\frac{(V_2-b)}{(V_1-b)}$$

$$\int_{V_1}^{V_2}\frac{dV}{V(V+b)} = \frac{1}{b}\ln\frac{V_2(V_1+b)}{V_1(V_2+b)}$$

$$\overline{W} = -\int_{V_1}^{V_2} d\overline{V}\,P$$

$$= -RT\int_{V_1}^{V_2} d\overline{V}\frac{1}{(\overline{V}-b)} + \frac{a}{T^{1/2}}\int_{V_1}^{V_2} d\overline{V}\frac{1}{\overline{V}(\overline{V}+b)}$$

$$= -RT\ln\left(\frac{\overline{V}_2-b}{\overline{V}_1-b}\right) + \frac{a}{bT^{1/2}}\left\{\ln\left(\frac{\overline{V}_2(\overline{V}_1+b)}{\overline{V}_1(\overline{V}_2+b)}\right)\right.$$

$$\Delta\overline{U} = \int_{\overline{V}_1}^{\overline{V}_2}\left.\frac{\partial\overline{U}}{\partial\overline{V}}\right|_T d\overline{V} = \int_{\overline{V}_1}^{\overline{V}_2} d\overline{V}\left\{T\left.\frac{\partial P}{\partial T}\right|_{\overline{V}} - P\right\} = \overline{W} + \int_{\overline{V}_1}^{\overline{V}_2} d\overline{V}\,T\left\{\left.\frac{\partial P}{\partial T}\right|_{\overline{V}}\right\}$$

See bonus question

EXTRA PAGE

$$T \frac{\partial P}{\partial T}\Big|_{\bar V} = \frac{RT}{\bar V - b} + \frac{a}{2T^{1/2}} \frac{1}{\bar V(\bar V + b)}$$

$$= P + \frac{3}{2}\frac{a}{T^{1/2}} \frac{1}{\bar V(\bar V + b)}$$

$$\Delta \bar U = \bar w - \bar w + \frac{3}{2}\frac{a}{T^{1/2}} \underbrace{\int_{\bar V_1}^{\bar V_2} d\bar V \frac{1}{\bar V(\bar V + b)}}_{\text{integral from list}}$$

$$= \frac{3}{2}\frac{a}{T^{1/2} b} \ln\left(\frac{\bar V_2(\bar V_1 + b)}{\bar V_1(\bar V_2 + b)}\right)$$

Question 3: DERIVATIONS (10 points)

Consider a real gas with equation of state:

$$\bar{V} = \left(\frac{RT}{P}\right) + B(T)$$

where B(T) means that B is a function of T.

a) Obtain an expression for $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$ in terms of $T, B(T)\ and\ \frac{dB(T)}{dT}$ for one mole of gas.

$$\left.\frac{\partial \bar{V}}{\partial T}\right|_P = \frac{R}{P} + \frac{dB}{dT}$$

$$\left.\frac{\partial \bar{H}}{\partial P}\right|_T = \bar{V} - T\left.\frac{\partial \bar{V}}{\partial T}\right|_P = \underbrace{\bar{V} - \frac{RT}{P}}_{B(T)} - T\frac{dB(T)}{dT}$$

$$\boxed{\left.\frac{\partial \bar{H}}{\partial P}\right|_T = B(T) - T\frac{dB(T)}{dT}}$$

b) Use the properties of mixed derivatives of state functions and the result of part a) to obtain an expression for $\left(\frac{\partial C_P}{\partial P}\right)_T$ for (one mole) of this gas.
Your final expression should contain some (not necessarily all!) of the following terms: $T, B(T), \frac{dB(T)}{dT}\ and\ \frac{d^2B(T)}{dT^2}$.

$$C_p = \left.\frac{\partial H}{\partial T}\right|_P \qquad \left.\frac{\partial C_p}{\partial P}\right|_T = \frac{\partial H}{\partial P\,\partial T} = \frac{\partial}{\partial T}\left(\left.\frac{\partial H}{\partial P}\right|_T\right)_P$$

$$= \frac{\partial}{\partial T}\left[B(T) - T\frac{dB(T)}{dT}\right]$$

$$= \frac{dB(T)}{dT} - \frac{dB(T)}{dT} - T\frac{d^2B}{dT^2}$$

$$\boxed{\left.\frac{\partial C_p}{\partial P}\right|_T = -T\frac{d^2B}{dT^2}}$$

BONUS QUESTION: 2 POINTS

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

Hint: Use the fact that H=U+PV and that $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$$\left.\frac{\partial H}{\partial P}\right|_T = \left.\frac{\partial H}{\partial V}\right|_T \left.\frac{\partial V}{\partial P}\right|_T \quad \text{(chain rule)}$$

$$= \left\{ \left.\frac{\partial U}{\partial V}\right|_T + P + V\left.\frac{\partial P}{\partial V}\right|_T \right\} \left.\frac{\partial V}{\partial P}\right|_T \quad \text{(from } H=U+PV\text{)}$$

$$= \left\{ T\left.\frac{\partial P}{\partial T}\right|_V - P + P + V\left.\frac{\partial P}{\partial V}\right|_T \right\} \left.\frac{\partial V}{\partial P}\right|_T \quad \left(\text{from } \left.\frac{\partial U}{\partial V}\right|_T = \ldots\right)$$

$$= T\left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial V}{\partial P}\right|_T + V$$

$$\boxed{\left.\frac{\partial H}{\partial P}\right|_T = -T\left.\frac{\partial V}{\partial T}\right|_P + V} \quad \text{(cyclic rule)}$$