Chemistry 231 **Assignment #4** (due* Tuesday, 10 October, in class)

*This assignment is *optional.* You lose no marks if you don't hand it in. *Happy Thanksgiving.*

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1. **a)** A tank contains 10.0 L of an ideal gas at 100.0 bar and 300 K. A valve is opened, and the gas expands irreversibly and isothermally against a constant external pressure (p_{ext} = 1.00 bar) to a final pressure of 1.00 bar. Calculate the volume change ΔV and the work $w = -p_{ext}\Delta V$.

[6]

b) A tank contains 10.0 L of a liquid at 100.0 bar and 300 K. A valve is opened, and the liquid expands irreversibly and isothermally against a constant external pressure (p_{ext} = 1.00 bar) to a final pressure of 1.00 bar. Calculate the volume change ΔV and the work $w. = -p_{ext}\Delta V$. *Data*: the isothermal compressibility of the liquid (assumed to be constant) is κ = 0.000046 bar^{-1}.

c) Why is the work done by the expanding gas (part **a**) much larger than the word done by the expanding liquid (part **b**)?

d) Why is a leak from a tank of compressed gas *much more dangerous* than a leak from a tank of compressed liquid?

2. **a)** Why is the isothermal compressibility defined as $\kappa = -V^{-1}(\partial V/\partial p)_T$, not as $\kappa = V^{-1}(\partial V/\partial p)_T$?

[2]

b) Why is it convenient to define the thermal expansivity as $\beta = V^{-1}(\partial V/\partial T)_p$, not as $\beta = (\partial V/\partial T)_p$?

3. **a)** Prove $\beta = 1/T$ for an ideal gas.

b) For a nonideal gas obeying the equation of state $p = RT/(V_m - b)$ prove

[5]

$$\kappa = \frac{1}{1 + (bp/RT)}\,\frac{1}{T}$$

c) Use the results from **c** and **d** to decide if repulsive intermolecular forces increase or decrease the thermal expansivity of a gas

4 **a)** When an ice cube from a freezer is placed in a beverage, a "cracking" sound from the ice is often heard. Why?

[2]

b) A metal lid stuck on a glass jar can often be loosened by using warm water. Why?

5. **a)** The thermal expansivity (also called the cubical expansion coefficient) $\beta = V^{-1}(\partial V/\partial T)_p$ gives the fractional change in volume per degree. The linear expansion coefficient $\beta_{linear} = l^{-1}(\partial l/\partial T)_p$ gives the fractional change in length per degree. Show $\beta_{linear} = \beta/3$.

[5]

b) A steel rail is 40.0 feet long at 25.0 °C. Calculate Δl (the change in the length of the rail) if the temperature is changed from 25.0 °C to –20.0 °C. *Data*: $\beta = 25.7 \times 10^{-6}$ K^{-1} (assumed constant)

Chem 231 Assignment #4 (optional!)

Q1 a) 10.0 L of an ideal gas initially at 100.0 bar and 300 K expands irreversibly against P_{ext} = 1.00 bar to a final pressure of 1.00 bar at 300 K. (isothermal expansion)

$P_{ext} < P$

volume change

$$\Delta V = V_{final} - V_{initial} = \frac{nRT}{P_{final}} - \frac{nRT}{P_{initial}}$$

$$= V_{initial}\left(\frac{V_{final}}{V_{initial}} - 1\right)$$

$$= V_{initial}\left(\frac{\frac{nRT}{P_{final}}}{\frac{nRT}{P_{initial}}} - 1\right) = V_{initial}\left(\frac{P_{initial}}{P_{final}} - 1\right)$$

$$= (10.0\ L)\left(\frac{100.0\ bar}{1.00\ bar} - 1\right) = (10.0\ L)(99)$$

$$\boxed{\Delta V = 990\ L}$$

work

$$w = -\int P_{ext}\, dV \qquad (P_{ext} \text{ constant here})$$

$$= -P_{ext}\int_{V_i}^{V_f} dV = -P_{ext}(V_f - V_i)$$

$$= -P_{ext}\,\Delta V$$

$$= -(1.00\ bar)(990\ L) = -990\ L\ bar$$

$$= -(990\ L\ bar)(10^{-3}\ m^3\ L^{-1})(10^5\ Pa\ bar^{-1})$$

$$\boxed{w = -99000\ J}$$

(Q1 cont.)

b) 10.0 L of a <u>liquid</u> initially at 100.0 bar and 300 K expands <u>irreversibly</u> ($p_{ext} < p$) against $p_{ext} = 1.00$ bar to a final pressure of 1.00 bar at 300K.

<u>liquid</u> $pV \neq nRT$!

κ is the <u>isothermal compressibility</u> of the liquid

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$ multiply by dp

$$\kappa\, dp = -\frac{1}{V}\, dV$$ integrate (κ constant)

$$\int \kappa\, dp = \kappa \int_{p_i}^{p_f} dp = -\int_{V_i}^{V_f} \frac{1}{V}\, dV$$

$$\kappa\left(p_{final} - p_{initial}\right) = -\ln\left(\frac{V_f}{V_i}\right)$$

$$\left(0.000046\ \text{bar}^{-1}\right)\left(100.0 - 1.00\right)\text{bar} = -\ln\left(V_f/V_i\right)$$

$$0.004554 = \ln\left(V_f/V_i\right)$$

$$e^{0.004554} = \frac{V_f}{V_i} \qquad V_f = V_i\, e^{0.004554}$$

10.0 L

$$V_f = (10.0\,L) \qquad \Delta V = V_f - V_i = V_i e^{0.004554} - V_i$$

$$= V_i\left(e^{0.004554} - 1\right) = (10.0\,L)(0.00456)$$

$$\boxed{\Delta V = 0.0456\,L} \qquad \boxed{1\ L\,\text{bar} = 100\ J}$$

$$w = -\int p_{ext}\, dV = -p_{ext}\int_{V_i}^{V_f} dV = -p_{ext}\,\Delta V = -(1.00\ \text{bar})(0.0456\,L)$$

$$\boxed{w = -4.56\ J}$$

(Q1 cont.)

c) $w = -\int P_{ext}\, dV = -P_{ext}\, \Delta V$

very small ΔV

$\Delta V_{\text{ideal gas}} = 990\ L$ $\qquad$ $\Delta V_{\text{liquid}} = 0.046\ L$

liquids are "almost" incompressible (very small change in volume with pressure)

$\Delta V_{\text{liquid}} \approx 0$

work done by expanding liquid ≈ 0

d) In this example, 10.0 L of compressed gas expanding from 100.0 bar to 1.00 bar does $(99000 J / 4.56 J) = 21{,}700$ times more work on the surroundings

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Q2 a) $\left(\frac{\partial V}{\partial P}\right)_T$ is always negative

so κ defined as $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is always positive

if κ was defined instead as $\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, all the tabulated and reported κ data would require a minus sign

$\Longrightarrow$ inconvenient!

b) β defined as $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ is an intensive quantity (fractional change in V per degree)

same value for any amount of substance

$\left(\frac{\partial V}{\partial T}\right)_P$ is an intensive quantity (change in volume per degree)

different for different volumes of substances (less convenient)

Q3 a) Thermal expansivity of an ideal gas ($V = nRT/p$)

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left[\frac{\partial}{\partial T}\left(\frac{nRT}{p}\right)\right]_p = \frac{1}{V}\,\frac{nR}{p}\left(\frac{\partial T}{\partial T}\right)_p = \frac{nR}{pV}$$

$$\beta = \frac{nR}{nRT} = \frac{1}{T}$$

b) Thermal expansivity of a nonideal gas with $p = \frac{RT}{V_m - b}$

$$V_m - b = \frac{RT}{p} \Rightarrow V_m = \frac{RT}{p} + b$$ (constant number of moles (n))

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V/n}\left[\frac{\partial (V/n)}{\partial T}\right]_p = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p$$

b constant

$$= \frac{1}{V_m}\left[\frac{\partial}{\partial T}\left(\frac{RT}{p} + b\right)\right]_p = \frac{R}{pV_m}\left(\frac{\partial T}{\partial T} + \frac{\partial b}{\partial T}\right)_p = \frac{1}{V_m}(1+0)$$

$$= \frac{R}{pV_m} = \frac{R}{p\left(\frac{RT}{p} + b\right)} = \frac{R}{RT + bp} = \frac{1}{T + \frac{bp}{R}}$$

$$\boxed{\beta_{\substack{real\\gas}} = \frac{1}{T}\,\frac{1}{1 + \frac{bp}{RT}}}$$

c) $bp/RT > 0$ so $\frac{1}{1+\frac{bp}{RT}} < 1$

$\beta_{\substack{real\\gas}} < \frac{1}{T} = \beta_{\substack{ideal\\gas}}$ (part a)

repulsive intermolecular forces reduce the thermal expansivity

(Q4) a) Ice in a freezer is typically at about −10 °C. When the ice from a freezer is placed in a room-temperature liquid, the outer layers of ice in contact with the warmer liquid warm up and expand away from the colder ice in the interior of the ice cube, causing thermal stress and cracking of the ice.

b) The thermal expansivity of metals is larger than that of glass. Warming the metal lid and glass jar causes the metal lid to expand more than the glass. The lid "pulls away" from the glass jar, becoming "unstuck".

(Q5) a) The volume of a cube of material (length l per side) is $V = l^3$.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{l^3}\left(\frac{\partial l^3}{\partial T}\right)_P = \frac{1}{l^3}\,3l^2\left(\frac{\partial l}{\partial T}\right)_P = \frac{3}{l}\left(\frac{\partial l}{\partial T}\right)_P$$

$$\beta_{linear} = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_P = \frac{\beta}{3}$$

b) A steel rail at 25.0 °C (40.0 feet long) is cooled to −20.0 °C. Change in the length of the rail?

$$\beta_{linear} = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_P \Rightarrow \frac{dl}{l} = \beta_{linear}\, dT$$

$$\int_{l_i}^{l_f} \frac{dl}{l} = \int_{T_i}^{T_f} \beta_{linear}\, dT \qquad \ln\left(\frac{l_f}{l_i}\right) = \beta_{linear}\,\Delta T = \frac{\beta}{3}\Delta T = \left(\frac{25.7\times10^{-6}\ \frac{1}{K}}{3}\right)(-45\text{ K})$$

$$\ln\left(\frac{l_f}{l_i}\right) = -3.855\times10^{-4} \qquad \frac{l_f}{l_i} = e^{-0.0003855} = 0.99961 \qquad -0.0385\%\ \text{length change}$$

$$\boxed{\Delta l = -0.0156\text{ ft} = -0.19\text{ inch}}$$