Chemistry 231 **Assignment #1** (due Tuesday, 17 September, in class)

1. Give the ordinary derivatives of the following functions:

[4]

a) $f(x) = 3x + 23x^3$ $\quad df(x)/dx = ?$ $\qquad$ **b)** $f(x) = 15x\ln x$ $\quad df(x)/dx = ?$

c) $f(x) = 16/(1 - x)$ $\quad df(x)/dx = ?$ $\qquad$ **d)** $f(x) = 3e^{-5x}$ $\quad df(x)/dx = ?$

2. Give the partial derivatives of the following functions:

[4]

a) $F(x,y) = 10x^3e^{-0.5y}$ $\qquad (\partial F/\partial x)_y = ?$ $\qquad (\partial F/\partial y)_x = ?$

b) $p(T,V_m) = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$ $\qquad (\partial p/\partial T)_{V_m} = ?$ $\qquad (\partial p/\partial V_m)_T = ?$

3. A 50.0 L tank contains 16.0 kg (1,000 moles) of methane gas at 25 °C. Calculate the pressure in the tank using:

a) the ideal gas law

b) the van der Waals equation with $a = 2.28$ bar L^2 mol^{-2} and $b = 0.0427$ L mol^{-1}

[7] **c)** the graph of the compression factor Z from the course notes (copied on the next page).

d) Which estimate of the pressure (**a**, **b** or **c**) is most reliable? Explain briefly.

e) Do attractive forces between the methane molecules in the tank dominate repulsive forces?

4. **a)** Any real gas becomes ideal as the pressure drops to zero. Why?

[2] **b)** Show that the van der Waals equation $p(T,V_m) = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$

reduces to the ideal gas law $p = RT/V_m$ in the limit $p \to 0$.

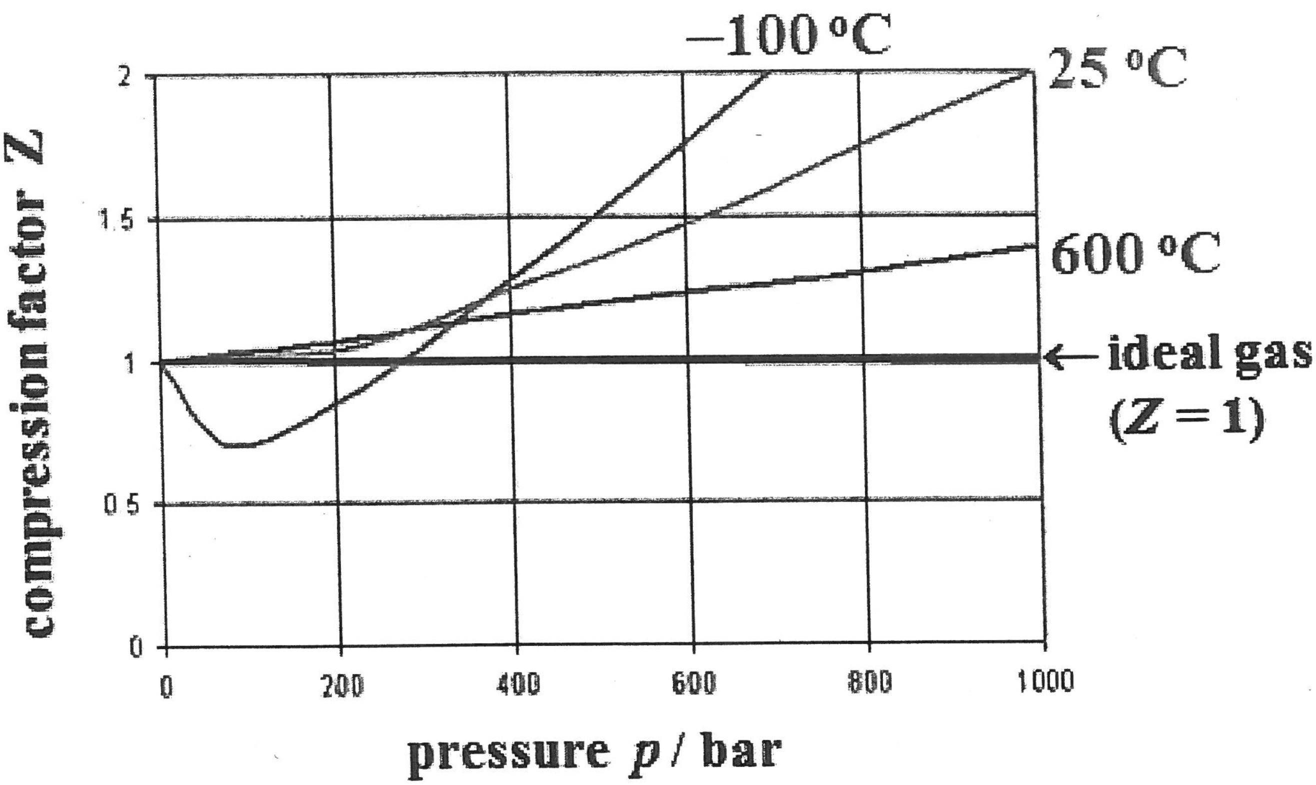
5. **a)** Is $(\partial U/\partial V)_T$ an extensive property? Justify your answer.

[2] **b)** Is V_m an extensive property? Justify your answer.

6. The synthesis of ammonia ($N_2 + 3H_2 = 2NH_3$) was mentioned as an important application of high-pressure gas technology. How important? About half of the world population of 7.5 billion

[1] people would starve without the large scale industrial production of synthetic ammonia! Explain.

Compression Factor $Z = pV/nRT$ of Methane



Chem 231 Assignment #1

Q1 "ordinary" derivatives

a) $$\frac{df(x)}{dx} = \frac{d}{dx}(3x + 23x^3)$$

$$= \frac{d(3x)}{dx} + \frac{d(23x^3)}{dx}$$

$$= 3\frac{dx}{dx} + 23\frac{dx^3}{dx}$$

$$= 3(1) + 23(3x^2)$$

$$\frac{df}{dx} = \boxed{3 + 69x^2}$$

b) $$\frac{df(x)}{dx} = \frac{d}{dx}(15x\ln x) = 15\frac{d(x\ln x)}{dx}$$

$$= 15x\left(\frac{d\ln x}{dx}\right) + 15\ln x\left(\frac{dx}{dx}\right) \quad \left(\begin{array}{c}\text{CHAIN}\\ \text{RULE}\end{array}\right)$$

$$= 15x\left(\frac{1}{x}\right) + 15\ln x\,(1)$$

$$= \boxed{15 + 15\ln x}$$

$$\frac{d[u(x)v(x)]}{dx} = u(x)\frac{dv}{dx} + v(x)\frac{du}{dx}$$

(Q1 cont.)

c) $\frac{d}{dx}\left(\frac{16}{1-x}\right) = 16\,\frac{d\left(\frac{1}{1-x}\right)}{dx}$

here, use $\frac{d\,(u(x))^n}{dx} = n\left[u(x)\right]^{n-1}\frac{du}{dx}$

$= 16\,\frac{d(1-x)^{-1}}{dx}$

$= 16(-1)(1-x)^{-2}\,\frac{d(1-x)}{dx}$

$= -\frac{16}{(1-x)^2}\left(\frac{d(1)}{dx} - \frac{dx}{dx}\right)$

$= -\frac{16}{(1-x)^2}(0-1)$

$= \boxed{\frac{16}{(1-x)^2}}$

d) $\frac{d(3e^{-5x})}{dx} = 3\,\frac{d}{dx}e^{-5x}$

$= (3)(-5)\,e^{-5x}$

$= \boxed{-15e^{-5x}}$

Q2 "partial" derivatives

a) $$F(x,y) = 10x^3 e^{-0.5y}$$

(constants)

$$\left(\frac{\partial F}{\partial x}\right)_y = \left[\frac{\partial}{\partial x}\left(10x^3 e^{-0.5y}\right)\right]_y = 10e^{-0.5y}\left(\frac{\partial x^3}{\partial x}\right)_y$$

$$= 10e^{-0.5y}(3x^2) = \boxed{30x^2 e^{-0.5y}}$$

$$\left(\frac{\partial F}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(10x^3 e^{-0.5y}\right)\right] = 10x^3\left(\frac{\partial e^{-0.5y}}{\partial y}\right)_x$$

$$= 10x^3(-0.5)e^{-0.5y}$$

$$= \boxed{-5x^3 e^{-0.5y}}$$

b) $$p(T, V_m) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

constant here

$$\left(\frac{\partial p}{\partial T}\right)_{V_m} = \left[\frac{\partial}{\partial T}\left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right)\right]_{V_m} = \left[\frac{\partial}{\partial T}\left(\frac{RT}{V_m - b}\right)\right] - \left[\frac{\partial}{\partial T}\left(\frac{a}{V_m^2}\right)\right]_{V_m}$$

$$= \frac{R}{V_m - b}\underbrace{\left(\frac{\partial T}{\partial T}\right)_{V_m}}_{=1} - \underbrace{\left[\frac{\partial}{\partial T}(\text{constant})\right]}_{=0} = \boxed{\frac{R}{V_m - b}}$$

(Q2 b cont.)

$$\left(\frac{\partial p}{\partial V_m}\right)_T = \left[\frac{\partial}{\partial V_m}\left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right)\right]_T$$

$$= \left[\frac{\partial}{\partial V_m}\left(\frac{RT}{V_m - b}\right)\right]_T - \left[\frac{\partial}{\partial V_m}\left(\frac{a}{V_m^2}\right)\right]_T$$

$$= RT\left[\frac{\partial}{\partial V_m}\left(\frac{1}{V_m - b}\right)\right]_T - a\left[\frac{\partial\left(\frac{1}{V_m^2}\right)}{\partial V_m}\right]_T$$

$$= RT\left[\frac{\partial (V_m - b)^{-1}}{\partial V_m}\right]_T - a\left(\frac{\partial V_m^{-2}}{\partial V_m}\right)_T$$

$$= RT(-1)(V_m - b)^{-2}\left[\frac{\partial (V_m - b)}{\partial V_m}\right]_T - a(-2)V_m^{-3}$$

$$= -\frac{RT}{(V_m - b)^2}\left(\underbrace{\frac{\partial V_m}{\partial V_m}}_{=1} - \underbrace{\frac{\partial b}{\partial V_m}}_{=0}\right)_T + 2aV_m^{-3}$$

$$= \boxed{-\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3}}$$

Q3 A 50.0 L tank contains 1000 mol methane at 25 °C ($T = 298.15$ K)

a) pressure in the tank using the ideal gas law

$$p = \frac{nRT}{V} = \frac{(1000\ \text{mol})(0.08314\ \text{L bar K}^{-1}\text{mol}^{-1})(298.15\ \text{K})}{50.0\ \text{L}}$$

$$= \boxed{496\ \text{bar}}$$ ⟹ high pressure, ideal gas law probably not reliable

b) pressure calculated from the van der Waals equation

molar volume $V_m = \frac{V}{n} = \frac{50.0\ \text{L}}{1000\ \text{mol}} = 0.0500\ \frac{\text{L}}{\text{mol}}$

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

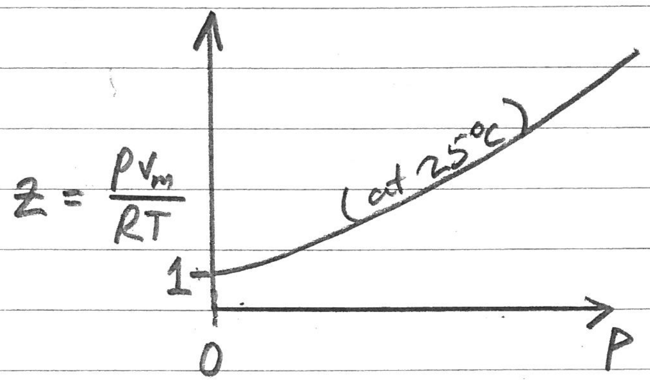
$$= \frac{(0.08314\ \text{L bar K}^{-1}\text{mol}^{-1})(298.15\ \text{K})}{(0.0500 - 0.0427)\ \text{L mol}^{-1}} - \frac{2.28\ \text{bar L}^2\text{mol}^{-2}}{(0.0500\ \text{L mol}^{-1})^2}$$

$$= 3396\ \text{bar} - 912\ \text{bar}$$

$$= \boxed{2484\ \text{bar}}$$ ⟹ very high pressure, even the van der Waals equation is not reliable

(Q3 cont.)

c) Calculate the pressure in the tank using the graph of the compression factor Z plotted against the pressure.



problem!

don't know p!

possible solution : the molar volume $V_m = 0.0500 \frac{L}{mol}$ is known, so replot Z against V_m

example : at $p = 400$ bar, read $Z = 1.25$ (from graph)

calculate $V_m = Z \frac{RT}{p}$

$$= \frac{1.25(0.08314)(298.15)}{400}$$

$$= 0.0775 \frac{L}{mol}$$

repeat:

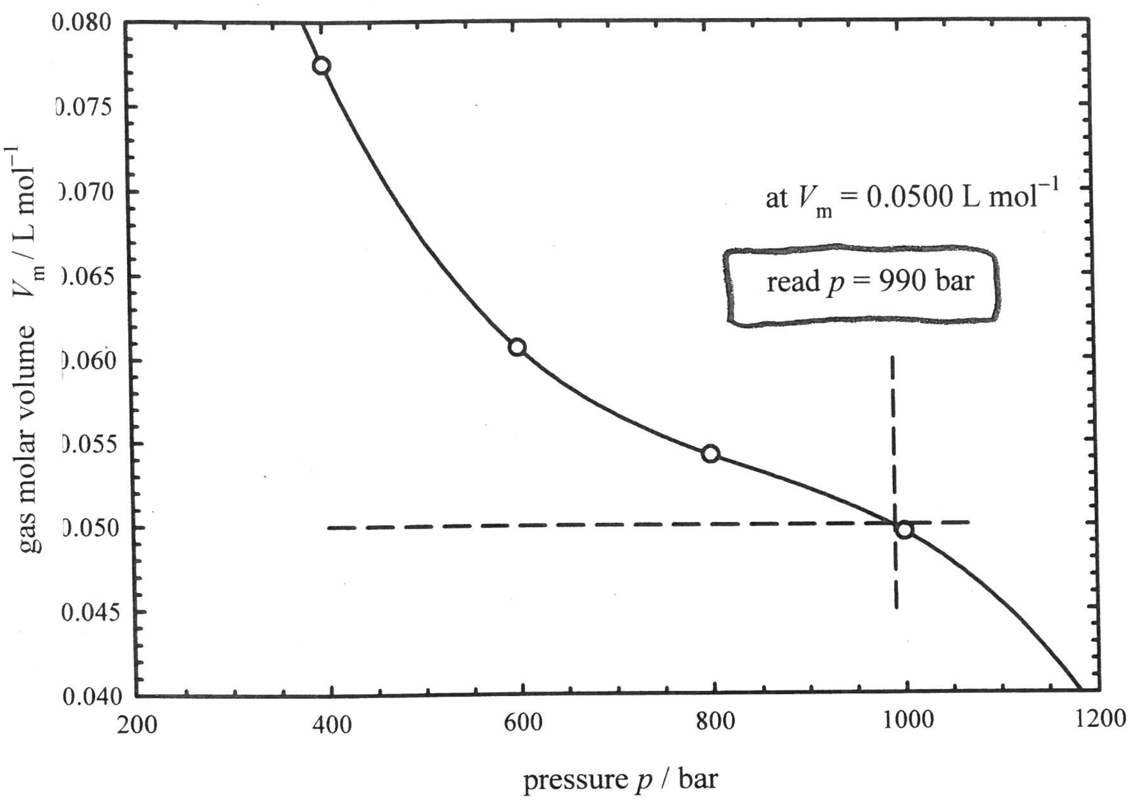
at 600 bar, $Z = 1.47$, $V_m = 0.0607 \ L \ mol^{-1}$

800 bar, $Z = 1.75$, $V_m = 0.0542 \ L \ mol^{-1}$

1,000 bar, $Z = 2.00$, $V_m = 0.0496 \ L \ mol^{-1}$

(Q3 c cont.)

c)



d) The pressure calculated using the compression factor graph (part c) is most reliable because the graph is based on experiment data (measured p, Z values, not predicted values)

e) $Z = \frac{pV_m}{RT} = \frac{(990)(0.0500)}{(0.08314)(298.15)} = 2.00$

$Z = 2.00 = \frac{p}{p_{ideal}}$

$Z > 1$, pressure higher than ideal gas value

$\Rightarrow$ repulsive forces dominate

Q4 a) as the pressure drops to zero, the molar volume increases to infinity, the molecules become infinitely far apart $\Rightarrow$ no interactions

$\Rightarrow$ ideal gas behavior in the limit $p \to 0$

$(V_m \to \infty)$

b) as $p \to 0$ (and $V_m \to \infty$):

$$\lim_{V_m \to \infty} p = \lim_{V_m \to \infty} \left(\frac{RT}{V_m - b} - \frac{a}{V_M^2} \right)$$

$$= \lim_{V_m \to \infty} \frac{RT}{V_m} \left(\frac{V_m}{V_m - b} - \frac{a}{RT} \frac{1}{V_m} \right) = \lim_{V_m \to \infty} \frac{RT}{V_m} \left(\frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RT} \frac{1}{V_m} \right)$$

$$= \frac{RT}{V_m} \left(\frac{1}{1 - \frac{1}{\infty}} - \frac{a}{RT} \frac{1}{\infty} \right) = \frac{RT}{V_m} \left(\frac{1}{1-0} + 0 \right) = \frac{RT}{V_m}$$

Q5 a) internal energy U and volume V are extensive (size-dependent) properties

$$\left(\frac{\partial U}{\partial V} \right)_T \sim \frac{\text{change in } U}{\text{change in } V} = \frac{\text{extensive}}{\text{extensive}} \sim \text{intensive}$$

the size-dependence of U and V cancel, making $\left(\frac{\partial U}{\partial V} \right)_T$ intensive $\left(\left(\frac{\partial U}{\partial V} = \frac{\partial U/n}{\partial V/n} = \frac{\partial U_m}{\partial V_m} \text{ intensive (per mole)} \right) \right)$

(Q5 cont.)

b) Is V_m extensive?

$$V_m = \frac{V}{n} = \frac{\text{extensive property}}{\text{extensive property}} \sim \text{intensive}$$

(size independent)

Q6 $N_2 + 3H_2 \rightarrow NH_3$

from liquefied air

mostly from CH_4 (natural gas)

About 200 million tons of ammonia are synthesized per year

About 160 million tons of ammonia are used to make agricultural fertilizers

(e.g., NH_4OH, NH_4NO_3, urea)

dramatically boosting crop yields for food production

(More than one-half of the nitrogen in your body is from synthetic ammonia!)