

1. Give the ordinary derivatives df/dx of the following functions:

[3] a) $f(x) = -11 + 41x + 3x^3$ b) $f(x) = 15x \ln x$ c) $f(x) = 16/(1 - x)$

2. Evaluate the following integrals:

[3] a) $\int_{-1}^3 12 dx$ b) $\int_{-1}^3 (-1 - 9x + 8x^3) dx$ c) $\int_5^{15} \frac{7}{x} dx$

3. a) Use the thermodynamic equation of state $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$

[3] to show $(\partial U/\partial V)_T = 0$ for an ideal gas.

b) Is $(\partial U/\partial V)_T$ an extensive quantity? Explain.

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

[2] b) Show that the virial equation $\frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \dots$

reduces to the ideal gas law in the limit $p \rightarrow 0$.

5. The Stefan-Boltzmann law gives

$$p = \beta T^4 \quad (\beta = 2.522 \times 10^{-16} \text{ Pa K}^{-4})$$

for the pressure of thermal radiation (the "photon gas" mentioned in class).

[2] a) Calculate the pressure of thermal radiation at 20 °C. Give your answer in units of bar. Is radiation pressure significant at room temperature?

b) Calculate the radiation pressure at the center of a thermonuclear explosion ($T \approx 10^8$ K).

6. Work (w) is the energy transferred to a system by a force acting through a displacement. w is positive (the system gains energy) if the force acts in the same direction as the displacement. w is negative (the system loses energy) if the force and displacement are in opposite directions.

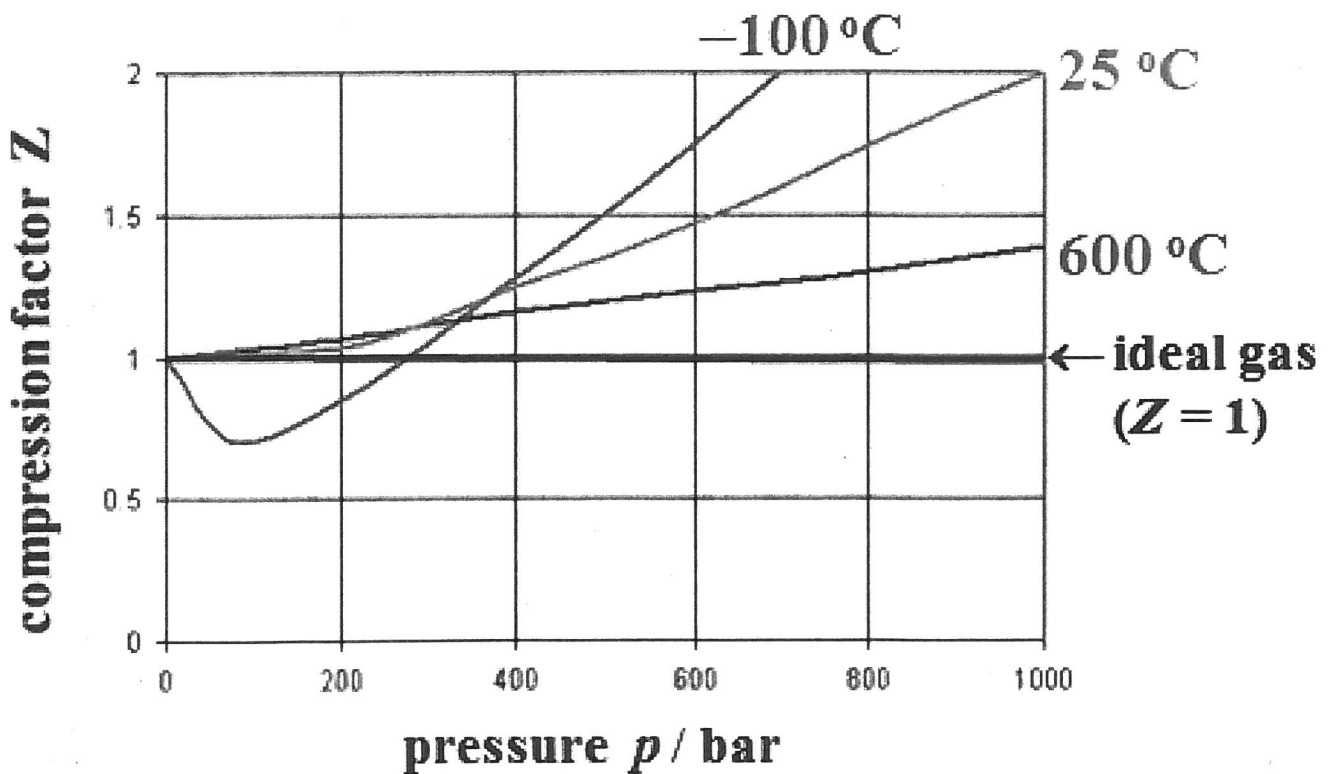
[1] The force acting on mass m in the earth's gravitational field is $-mg$. The minus sign indicates a downward force. g is the gravitational acceleration, 9.81 m s^{-2} near the surface of the earth.

A 1500 kg elevator car (the system) is lifted from the first floor to the third floor in Mulrone Hall, a displacement of 30.0 m. Calculate w for this process.

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7. a) Give the value of the compression factor ($Z = pV_m/RT$) for an ideal gas.
- [2] b) As shown in the graph below, $Z = 1.00$ for methane $-100\text{ }^\circ\text{C}$ and 280 bar. Is methane an ideal gas under these conditions? Explain.
8. A 155.0 L tank is filled with 2000 moles of methane at $25\text{ }^\circ\text{C}$. For safety reasons (to avoid a dangerous *explosion*), the pressure in the tank must not exceed 350 bar.
- a) Calculate the pressure in the tank using the ideal gas law.
- b) Repeat part a using the van der Waals equation ($a = 2.28\text{ bar L}^2\text{ mol}^{-2}$, $b = 0.0427\text{ L mol}^{-1}$)
- [4] c) Repeat part a using the graph of the compression factor (copied below).
- d) Is the tank safe? Justify your answer.

Compression Factor $Z = pV/nRT$ of Methane



Q1

$$a) \frac{d}{dx} (-11 + 41x + 3x^3)$$

$$= \frac{d}{dx} (-11) + \frac{d}{dx} (41x) + \frac{d}{dx} (3x^3)$$

constant
constant

$$= \cancel{\frac{d}{dx} (-11)} + \frac{41 \cancel{dx}}{\cancel{dx}} + 3 \frac{dx^3}{dx} = 41 + 3(3x^2) = \boxed{41 + 9x^2}$$

$$b) \frac{d}{dx} (15x \ln x) = 15x \frac{d \ln x}{dx} + \ln x \frac{d}{dx} (15x) \quad (\text{product rule})$$

$$= 15x \frac{1}{x} + \ln x (15) = \boxed{15 + 15 \ln x}$$

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

$$= \frac{-16 \left(\frac{d1}{dx} - \frac{dx}{dx} \right)}{(1-x)^2}$$

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

(Q2)

$$a) \int_{-1}^3 12 \, dx = 12 \int_{-1}^3 dx = 12(x_f - x_i)$$

$$= 12[3 - (-1)] = \boxed{48}$$

$$b) \int_{-1}^3 (-1 - 9x + 8x^3) \, dx$$

$$= \int_{-1}^3 (-1) \, dx + \int_{-1}^3 (-9)x \, dx + \int_{-1}^3 8x^3 \, dx$$

$$= -\int_{-1}^3 dx - 9\int_{-1}^3 x \, dx + 8\int_{-1}^3 x^3 \, dx$$

$$= -(x_f - x_i) - 9\left(\frac{x_f^2}{2} - \frac{x_i^2}{2}\right) + 8\left(\frac{x_f^4}{4} - \frac{x_i^4}{4}\right)$$

$$= -[3 - (-1)] - 9\left(\frac{9}{2} - \frac{1}{2}\right) + 8\left[\frac{3^4}{4} - \frac{(-1)^4}{4}\right]$$

$$= -4 - 36 + 160 = \boxed{120}$$

$$c) \int_5^{15} \frac{7}{x} \, dx = 7 \int_5^{15} \frac{1}{x} \, dx$$

$$= 7 \int_{\ln 5}^{\ln 15} dx = 7(\ln 15 - \ln 5)$$

$$= 7 \ln\left(\frac{15}{5}\right) = \boxed{7 \ln 3}$$

$$\left(\begin{array}{l} \frac{d \ln x}{dx} = \frac{1}{x} \\ \text{so } \frac{dx}{x} = d \ln x \end{array} \right)$$

Q3 a) thermodynamic equation of state =

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad (\text{any system})$$

for an ideal gas $P = \frac{nRT}{V}$ ← substitute for P in the thermodynamic equation of state

gives:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial}{\partial T} \frac{nRT}{V}\right)_V - \frac{nRT}{V}$$

const. (top) const. (bottom)

$$= T \frac{nR}{V} \left(\frac{\partial T}{\partial T}\right)_V - \frac{nRT}{V}$$

= 1 (above the derivative)

$$= \frac{nRT}{V} - \frac{nRT}{V}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

important conclusion: the energy of an isothermal ideal gas (constant T) is constant

b) $\left(\frac{\partial U}{\partial V}\right)_T \sim \frac{\Delta U}{\Delta V}$ ← extensive ~ intensive (size gets for ΔV ΔU cancel)

← extensive

(Q4)

a) As the pressure of a real gas drops to zero, the molar volume increases to infinity, so the gas molecules become infinitely far apart and do not interact (no attractive or repulsive forces). Also, the molecular volume is negligible compared to the (infinite) volume of the container.

b) As $p \rightarrow 0$, $V_m \rightarrow \infty$ and $\frac{1}{V_m} \rightarrow 0$

$$\lim_{p \rightarrow 0} z = \lim_{V_m \rightarrow \infty} \left(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \dots \right)$$

$$= 1 + \frac{B(T)}{\infty} + \frac{C(T)}{\infty^2} + \frac{D(T)}{\infty^3} + \dots$$

$$z = 1 + 0 + 0 + 0 + \dots$$

$$z = 1 = \frac{pV_m}{RT}$$

ideal gas equation

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

(Q5)

a) at 20°C [$T = (20 + 273.15)\text{K} = 293.15\text{K}$]:

radiation pressure $p = \beta T^4 = (2.522 \times 10^{-16} \text{ Pa K}^{-4})(293.15 \text{ K})^4$
 $= 1.86 \times 10^{-6} \text{ Pa} = (1.86 \times 10^{-6} \text{ Pa})(10^{-5} \text{ bar Pa}^{-1})$
 $= \boxed{1.86 \times 10^{-11} \text{ bar}}$ negligible!

b) at $T = 10^8 \text{ K}$: $p = (2.522 \times 10^{-16} \text{ Pa K}^{-4})(10^8 \text{ K})^4$
 $p = 2.52 \times 10^{16} \text{ Pa} = \boxed{2.52 \times 10^{11} \text{ bar}}$ huge!
(\approx 250 billion atmospheres)

Q6

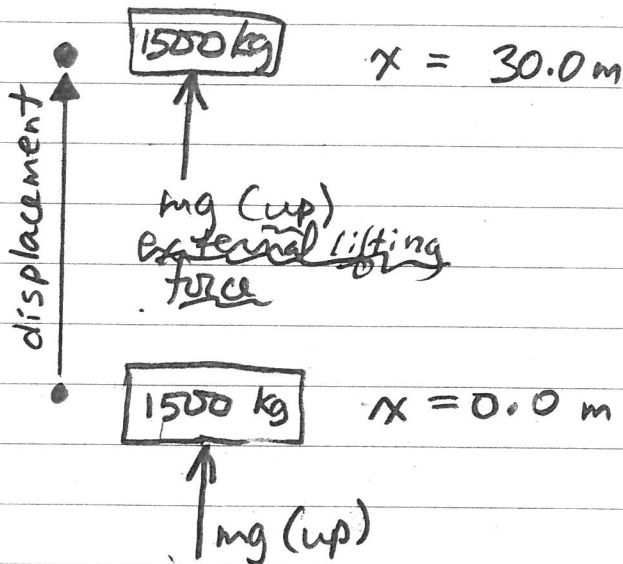
$$\text{work } W = - \int (\text{force}) dx$$

displacement

Sign convention =

W is positive if the force and displacement are in the same direction (e.g., force > 0, dx > 0)

W is negative if the force and displacement act in the opposite directions (e.g., force < 0, dx > 0)



$$W = \int_{x_i}^{x_f} (\text{external force}) dx$$

$$= \int_{x_i}^{x_f} (mg) dx$$

$$W = mg \int_{x_i}^{x_f} dx = mg(x_f - x_i)$$

$$\text{work } W = mg \Delta x$$

$$= (1500 \text{ kg})(9.81 \text{ m s}^{-2}) 30.0 \text{ m}$$

$$W = +4.41 \times 10^5 \text{ J}$$

(+ve work done on the system by the surroundings)

work is positive in this case because

the displacement of the system (+ve, up)

is in the same direction as the externally applied lifting force, so work must be done to lift system against the opposing gravitational force

(Q7) a) compression factor $z = \frac{PV_m}{RT}$

for an ideal gas $PV_m = RT$, so $z = 1$

b) $z = 1.00$ for methane at -100°C , 280 bar

why? repulsive and attractive forces between the methane molecules cancel, but are not zero, so methane is not ideal under these conditions

(for an ideal gas, $z = 1$ at all temperatures and pressures, not just at -100°C , 280 bar)

(Q8) 2000 moles of CH_4 in 155.0 L tank at 25°C
(298.15 K)

methane
molar volume $V_m = \frac{V}{n} = \frac{155.0\text{L}}{2000\text{mol}} = 0.0775 \frac{\text{L}}{\text{mol}}$

a) pressure in the tank using the ideal gas
equation $p = \frac{RT}{V_m}$

$$p = \frac{(0.08314 \text{ kJ bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{0.0775 \text{ L mol}^{-1}}$$

$p = 320 \text{ bar}$ (for an ideal gas)

(Q8 cont.)

b) calculated pressure using the van der Waals equation:

$$p = \frac{RT}{v_m - b} - \frac{a}{v_m^2}$$
$$= \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{0.0775 \text{ mol}^{-1} - 0.0427 \text{ L mol}^{-1}} - \frac{2.28 \text{ bar L}^2 \text{ mol}^{-2}}{(0.0775 \text{ L mol}^{-1})^2}$$
$$= 712 \text{ bar} - 380 \text{ bar}$$

$$p = 332 \text{ bar}$$

c) "guess" $p = 320 \text{ bar}$, then read $z = 1.13$
from the graph at 25° , 320 bar

this gives $v_m = \frac{RT}{p} z$ $(z = \frac{pv_m}{RT})$

$$= \frac{(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{320 \text{ bar}} \cdot 1.13$$

$$v_m = 0.0875 \text{ L mol}^{-1} \quad \text{too large!}$$

\therefore pressure must be higher than 320 bar

$$(\text{actual } v_m = 0.0775 \frac{\text{L}}{\text{mol}})$$

(Q8 c cont.)

"2nd guess" (> 320 bar)

$$\text{try } \frac{0.0875}{0.0775} 320 \text{ bar} = 361 \text{ bar}$$

"illustrates
iterative"
(successive approximations)
solution to
a problem

at 361 bar, read $z = 1.19$

$$\text{and calculate } V_m = \frac{RT}{P} z = \frac{0.08314 (298.15)}{361} 1.19$$

$$V_m = 0.0817 \text{ L mol}^{-1}$$

still too large!
(V_m should be $0.0775 \frac{\text{L}}{\text{mol}}$)

\therefore try a higher pressure

"3rd guess"

$$\text{e.g.: } \frac{0.0817}{0.0775} 361 \text{ bar} = 380 \text{ bar}$$

at 380 bar, read $z = 1.22$

$$\text{as before, calculate } V_m = 0.0796 \text{ L mol}^{-1}$$

still too large

$$\text{4th guess try } P = \frac{0.0796}{0.0775} 380 \text{ bar} = 390 \text{ bar}$$

read $z = 1.24$

$$\text{calc. } V_m = \frac{RT}{P} z = 0.0794 \frac{\text{L}}{\text{mol}}$$

5th guess

$$\text{try } \frac{0.0794}{0.0775} 390 \text{ bar} = \boxed{399 \text{ bar}}$$

read
 $z = 1.25$

$$\text{calc. } V_m = \frac{RT}{P} z = 0.0776 \frac{\text{L}}{\text{mol}} \quad \text{good enough}$$

(Q8 cont.)

d) predicted tank pressures =

320 bar ideal gas equation

332 bar van der Waal's equation

399 bar Z vs p graph

Which estimate of the pressure is most reliable?

399 bar

Why most reliable?

The Z vs p graph is based on actual (measured) values of P , V_m , and T . (Not on theory)

\therefore the tank is not safe

($p > 350$ bar rated pressure)