

1. CHAPTER 1 PROBLEMS: INTRODUCTION

Short Questions/Problems

Problem 1.1

If a differential is exact, does this mean that it is related to a point function?

Solution:

Yes; it could be integrated and point function can be obtained

Problem 1.2

Can the electron mass be ignored when it crosses the system boundary, but still treat a system as closed during electric heating?

Solution: The mass of electrons crossing the boundary is negligible compared to the system mass; yes treat as closed system.

Problem 1.3

Air sacs in lungs are called Alveoli from which O₂ enter blood. The dia of each alveoli is 0.125 mm and O₂ % is 14 % (by mole %). At 37 C, 1 bar, the number of **molecules** of O₂ in each alveolus is given as

- a) 2.7×10^{13}
- b) 3.3×10^{12}
- c) 6.02×10^{26}
- d) None of above within 10 %

Solution:

Volume 1.022×10^{-12} m³; $PV = NRT$, $N = 3.97 \times 10^{-14}$, $n = 2.38 \times 10^{13}$ molecules or 3.33×10^{12} molecules of O₂

Problem 1.4

This differential sum $3x^2dy + 2y^2dx$ can be written as

- a) dZ , an exact differential
 - b) δZ , an inexact differential
- $\partial M/\partial y = 2y$, $\partial N/\partial x = 6x$; inexact

Problem 1.5

Consider a pan of water at 91.76 C kept at sea level. It does not boil; however when the same pan is taken to Denver (altitude 1610.4 m) where pressure is 75 kPa, it starts boiling. Explain why.

Solution:

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Sat temp at sea level: 100 C; given $T < T_{\text{sat}}$; however at $T_{\text{sat}} = 91.76$ C; hence it will boil

Problem 1.6

Let the molal internal energy of diatomic gas (say O_2 gas) be \bar{u}_d while the molal internal energy of monatomic gas (say "O" gas) be \bar{u}_m . Then

- $\bar{u}_d < \bar{u}_m$ since diatomic species has higher molecular weight compared to monatomic gas
- $\bar{u}_d > \bar{u}_m$ since diatomic species has lower molecular weight
- $\bar{u}_d > \bar{u}_m$ since monatomic species has vibrational and rotational energies in addition to translational energies.
- $\bar{u}_d > \bar{u}_m$ since diatomic species has vibrational and rotational energies in addition to translational energies.
- None of the above

Solution:

Ans. (d) since diatomic species has vibrational and rotational energies in addition to translational energies.

Problem 1.7

Steam at 200C, 100 kpa has a specific volume (m^3/kg) of

- 2.172
- 1.673
- 0.127

Solution:

Ans. (a) , Table A.4c

Problem 1.8

Consider a relation for property B in terms of U, internal energy (kJ), volume V (m^3), N number of moles:

$$B = \frac{C_1 V^{1/3} U^{1/2}}{N^{5/6}}$$

Where C_1 is a constant; the property B is

- extensive
- intensive
- neither of above since insufficient information is given.

Solution:

$$\text{Ans(b) since } B = \frac{C_1 (\lambda V)^{1/3} (\lambda U)^{1/2}}{(\lambda N)^{5/6}} = \frac{\lambda C_1 (V)^{1/3} (U)^{1/2}}{(N)^{5/6}} = \lambda^0 B$$

Mathematical background

Problem 1.9

Compute the partial derivative $(\partial v / \partial T)_P$ for the relation $P(T, \bar{v}) = \bar{R} T / (\bar{v} - \bar{b}) - \bar{a} / (T^{1/2} \bar{v} (\bar{v} + \bar{b}))$ when $T = 873 \text{ K}$, $\bar{R} = 0.08314 \text{ bar m}^3/\text{kmole}$, and $\bar{v} = 0.245 \text{ m}^3 \text{ kmol}^{-1}$, assuming that $\bar{a} = 142.64 \text{ bar m}^6 \text{ K}^{1/2} \text{ kmol}^{-2}$ and $\bar{b} = 0.0211 \text{ m}^3 \text{ kmol}^{-1}$.

Solution:

$$P(v, T) = \frac{RT}{v - b} - \frac{a}{T^{1/2} v(v + b)} \quad (\text{A})$$

$$P = P(v, T) \quad (\text{B})$$

For given values of T and v, and known parameters a and b, P is uniquely fixed in any given system or P is called a point function of T and v. Using total differentiation $P = P(v, T)$

$$dP = (\partial P / \partial v)_T dv + (\partial P / \partial T)_v dT \quad (\text{B})$$

a) We will adopt total differentiation to evaluate $\left(\frac{\partial v}{\partial T} \right)_P$

From (A)

$$\left(\frac{\partial P}{\partial v} \right)_T = \frac{-RT}{(v - b)^2} + \bar{a} T^{1/2} \frac{[2v + b]}{v^2 (v + b)^2} \quad (\text{C})$$

And

$$\left. \frac{\partial P}{\partial T} \right)_v = \frac{R}{(v-b)} + \frac{1}{2} \frac{a}{T^{3/2} v (v+b)} \quad (D)$$

Use (C) and (D) in (B):

$$dP = \left\{ \frac{-RT}{(v-b)^2} + \frac{a}{T^{1/2}} \frac{(2v+b)}{v^2(v+b)^2} \right\} dV + \left\{ \frac{R}{v-b} + \frac{1}{2} \frac{a}{T^{3/2} v (v+b)} \right\} dT \quad (E)$$

Use (E) to find $(\partial v / \partial T)_P$ or $(\partial v / \partial P)_T$. At constant P, (E) yields

$$0 = \left\{ -RT/(v-b)^2 + [a/ \{T^{1/2}\} [2v+b] / \{v^2(v+b)^2\}] \right\} dv_p + [R/(v-b) + [a/ \{2 T^{3/2} v(v+b)\}]] dT_p \quad (F)$$

From (F)

$$dv_p/dT_p = [R/(v-b) + [a/ \{2 T^{3/2} v(v+b)\}]] / \{RT/(v-b)^2 - [a/ \{T^{1/2}\} [2v+b] / \{v^2(v+b)^2\}]\} \quad (G)$$

b) $T = 873 \text{ K}$, $v = 0.245 \text{ m}^3/\text{kmole}$, $a = 142.64 \text{ baes m}^3 \text{ K}^{1/2}/\text{kmole}$ $b = 0.0305 \text{ m}^3/\text{kmole}$

$$dv_p/dT_p = [0.08314 \text{ bar m}^3/\text{kmole K} / (0.245 - 0.0211) + 142.64 / \{2 \cdot 873^{3/2} \cdot 0.245(0.245 + 0.0211)\}] / \{ [0.08314 \cdot 873 / (0.245 - 0.0211)^2 - [142.64 / \{873^{1/2}\} [2 \cdot 0.245 + 0.0211] / [0.245^2 (0.245 + 0.0211)^2]] \} = (0.3713 - 0.0424) / (1447.8 + 579.8) = 0.000477 \text{ m}^3/\text{kmole K}$$

Problem 1.10

a) Perform line integration of the following differentials, first along constant values of x and then along constant values of y from (2, 5) to (4, 7): $xy^3 dx + 3x^2y^2 dy$, and $2e^x y dy + e^x y^2 dx$ and determine which one is path independent. b) Verify your results employing the mathematical criteria for exact differentials. c) Obtain an expression for $z(x, y)$ for any one of the above differentials that can be expressed as dz .

Solution:

a)

$$xy^3 dx + 3x^2y^2 dy \quad \text{Eq. (1)}$$

$$2e^x y dy + e^x y^2 dx \quad \text{Eq. (2)}$$

Integrating Eq. (1) and keeping x constant from (2, 5) to (2, 7) we follow:

$$[x^2y^3]_{2,5}^{2,7} = 1372 - 500 = 872 \quad (A)$$

Integrating Eq. (1) and keeping y constant from (2, 7) to (4, 7) we follow:

$$[x^2y^3/2]_{2,7}^{4,7} = 2744 - 686 = 2058 \quad (B)$$

Adding both (A) and (B) together gives:

$$2058 + 872 = 2930 \quad (C)$$

Similarly with Eq. (1) we will now first keep y constant from (2, 5) to (4, 5):

$$[x^2y^3/2]_{2,5}^{4,5} = 1000 - 250 = 750 \quad (D)$$

Integrating Eq. (1) and keeping x constant from (4, 5) to (4, 7) we follow:

$$[x^2y^3]_{4,5}^{4,7} = 5488 - 2000 = 3488 \quad (E)$$

Adding both (D) and (E) together gives:

$$750 + 3488 = 4238 \quad (F)$$

Notice that (F) and (C) are not equal:

$$\boxed{2930 \neq 4238}$$

Eq. (1) is not path independent

Following the same procedure for Eq. (2) Integrating and holding x constant from (2, 5) to (2, 7):

$$[e^xy^2]_{2,5}^{2,7} = 49e^2 - 25e^2 = 24e^2 \quad (G)$$

Integrating Eq. (2) and keeping y constant from (2, 7) to (4, 7) we follow:

$$[e^xy^2]_{2,7}^{4,7} = 49e^4 - 49e^2 \quad (H)$$

Adding both (G) and (H) together gives:

$$24e^2 + 49e^4 - 49e^2 = 49e^4 - 25e^2 = 2667.92 \quad (I)$$

Similarly with Eq. (2) we will now first keep y constant from (2, 5) to (4, 5):

$$[e^xy^2]_{2,5}^{4,5} = 25e^4 - 25e^2 \quad (J)$$

Integrating Eq. (2) and keeping x constant from (4, 5) to (4, 7) we follow:

$$[e^xy^2]_{4,5}^{4,7} = 49e^4 - 25e^4 = 24e^4 \quad (K)$$

Adding both (J) and (K) together gives:

$$24e^4 + 25e^4 - 25e^2 = 49e^4 - 25e^2 = 2667.92 \quad (L)$$

Notice that (I) and (L) are equal:

$$\boxed{2667.92 = 2667.92}$$

Eq. (2) is path independent

b) To verify this result we will impose the mathematical criteria for exact differentials. We will now put Eq. (2) into the following form:

$$dZ = M(x, y)dx + N(x, y)dy$$

Where the following is shown:

$$M(x, y) = e^x y^2 \quad (M)$$

$$N(x, y) = 2 e^x y \quad (N)$$

Taking the following differentials:

$$\frac{\partial M}{\partial y} = 2e^x y \quad (O)$$

$$\frac{\partial N}{\partial x} = e^x y^2 \quad (P)$$

Since the two differentials are equal:

$$\boxed{\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}}$$

Eq. (2) is path independent

C) Note that $M = \frac{\partial Z}{\partial y}$, $N = \frac{\partial Z}{\partial x}$ and hence integrating Eq. (O) with y

$$Z = e^x y^2 + f(x) \quad (Q)$$

Differentiating (Q) and comparing with (P), $\frac{\partial Z}{\partial x} = f'(x) + e^x y^2 = e^x y^2$, $f'(x) = 0$ or $f(x) = C$. Thus

$$Z(x, y) = e^x y^2 + C$$

Problem 1.11

Consider the function $\phi = x^3 y/t + x^2 y^2/t^3 + x y^3/t^7$. Is this a fully homogeneous function? Is this function partly homogeneous and, if so, with respect to what variables? Show that the Euler equation applies if this is a partly homogeneous function.

Solution:

$$\phi = x^3 y/t + x^2 y^2/t^3 + x y^3/t^7$$

$\phi(\lambda x, \lambda y, \lambda t) = \lambda^3 x^3 y/t + \lambda^1 x^2 y^2/t^3 + \lambda^{-3} x y^3/t^7$. ; not fully homogeneous since λ powers are not same

$\phi(\lambda x, \lambda y, t) = \lambda^4 x^3 y/t + \lambda^4 x^2 y^2/t^3 + \lambda^4 x y^3/t^7$; partly homogeneous with x and y, 4th order

$$x \frac{\partial \phi}{\partial x} + y \frac{\partial \phi}{\partial y} = m \phi$$

$$x \frac{\partial \phi}{\partial x} + y \frac{\partial \phi}{\partial y} = x(3x^2y/t + 2x^2y^2/t^3 + y^3/t^7) + y(x^3/t + 2x^2y/t^3 + 3y^2/t^7)$$

$$x \frac{\partial \phi}{\partial x} + y \frac{\partial \phi}{\partial y} = (3x^3y/t + 2x^3y^2/t^3 + xy^3/t^7) + (yx^3/t + 2x^2y^2/t^3 + 3y^3/t^7)$$

$$x \frac{\partial \phi}{\partial x} + y \frac{\partial \phi}{\partial y} = (4x^3y/t + 4x^3y^2/t^3 + 4xy^3/t^7) = 4 \phi$$

Problem 1.12

Determine a) $(\partial u/\partial x)_y$ and $(\partial u/\partial y)_x$ for the equation $u - x^2y + y^3u + yu^2 + 8x + 3 = 0$, and b) $(\partial u/\partial x)_{y,z}$, $(\partial u/\partial y)_{z,x}$ and $(\partial u/\partial z)_{x,y}$ for the equation $u^2xy + ux^2 + xy^2 + u^3 + uxyz = 0$.

Solution:

a) $u - x^2y + y^3u + yu^2 + 8x + 3 = 0$

Using total differentiation,

$$du - 2xy dx - x^2 dy + 3y^2 dy u + y^3 du + dyu^2 + 2u du y + 8dx = 0$$

Keep y constant and divide by dx

$$du/dx \{ 1 + y^3 + 2uy \} = 2xy - 8$$

$$\left(\frac{\partial u}{\partial x} \right)_y = \frac{2xy - 8}{y^3 + 2yu + 1}$$

Similarly keep x constant and divide by dy

$$du/dy \{ 1 + y^3 + 2uy \} x^2 + 3y^2 u + u^2 = 0$$

$$\left(\frac{\partial u}{\partial y} \right)_x = \frac{x^2 - 3y^2 u + u^2}{y^3 + 2yu + 1}$$

b) $u^2xy + ux^2 + xy^2 + u^3 + uxyz = 0$.

Using total differentiation

$$2uxydu + u^2 dx y + u^2 x dy + dux^2 + 2u x dx + dxy^2 + 2xy dy + 3u^2 du + duxyz + u dx yz + ux dy z + uxy dz = 0$$

Keep y and z constant; dy = 0

$$\left(\frac{\partial u}{\partial x} \right)_{y,z} = \frac{-[u^2y + 2ux + y^2 + uyz]}{3u^2 + x^2 + 2uxy + xyz}$$

Similarly keep x and z constant

$$\left(\frac{\partial u}{\partial y} \right)_{x,z} = \frac{-[u^2x + 2xy + uxz]}{3u^2 + x^2 + 2uxy + xyz}$$

Similarly keep y and x constant

$$\left(\frac{\partial u}{\partial z} \right)_{x,y} = \frac{-[uxy]}{3u^2 + x^2 + 2uxy + xyz}$$

Problem 1.13

Show whether the following equations are exact or inexact: (a) $du = 2y^2 dx + 3x^2 dy$? (b) $du = y dx + x dy$? (c) $du = 2xy dx + (x^2 + 1) dy$? (d) $du = (2x + y) dx + (x - 2y) dy$? (e) $du = (xy \cos(xy) + \sin(xy)) dx + (x^2 \cos(xy) + e^y) dy$? If exact write as "du" and if inexact write as "δu"

Solution :

$$a.) : du = 2y^2 dx + 3x^2 dy$$

$$N = 3x^2, \frac{\partial N}{\partial x} = 6x, M = 2y^2, \frac{\partial M}{\partial y} = 4y, 6x \neq 4y,$$

Ans.:inexact; write as $\delta u = 2y^2 dx + 3x^2 dy$ not du

$$b.) : du = y dx + x dy$$

$$\frac{dy}{dy} = 1, \frac{dx}{dx} = 1,$$

Ans.:exact

$$c.) : du = 2xy dx + (x^2 + 1) dy$$

$$\frac{dM}{dy} = 2x, \frac{dN}{dx} = \frac{d(x^2 + 1)}{dx} = 2x,$$

Ans.:exact

$$d.) : du = (2x + y) dx + (x - 2y) dy$$

$$\frac{d(2x + y)}{dy} = 1, \frac{d(x - 2y)}{dx} = 1,$$

Ans.:exact

$$e.) : \frac{d(xy \cos(xy) + \sin(xy))}{dy} = 2x \cos(xy) - x^2 y \sin(xy)$$

$$\frac{d(x^2 \cos(xy) + e^y)}{dx} = 2x \cos(xy) - x^2 y \sin(xy)$$

Ans.:exact

Alternate: since $\partial M / \partial y = x \cos xy + x^2 y \{(-\sin xy)\} + x \cos(xy)$, $\partial N / \partial x = 2x \cos xy + x^2 (-\sin xy)$
y

Problem 1.14

- a) Perform cyclic integrations for Problems 1.13 a and b and the path described by moving clockwise along the sides of a square whose vertices are (2, 2), (2, 1), (1, 1), (1, 2), (2, 2). {Figure problem P.1.14}
- b) What will be the results for anti-clockwise cycle ?

Solution:

- a) Since $2y^2 dx + 3x^2 dy$ is inexact, $\delta u = 2y^2 dx + 3x^2 dy$; the along AB (2,2) to (2,1), x is constant, $\Delta u_{AB} = 3 \cdot 2^2 \cdot \{1-2\} = -12$, along BC y is constant, $\Delta u_{BC} = 2 \cdot (1)^2 \cdot \{1-2\} = -2$, Similarly $\Delta u_{CD} = 3 \cdot (1)^2 \cdot (2-1) = 3$, $\Delta u_{DA} = 2 \cdot 2^2 \cdot (2-1) = 8$; thus

Cyclic integral : $-12 - 2 + 3 + 8 = -3$

- $du = y dx + x dy$. $\Delta u_{AB} = 1 \cdot \{1-2\} = -1$, $\Delta u_{BC} = (-1) \cdot \{1-2\} = -1$, Similarly $\Delta u_{CD} = 1 \cdot (2-1) = 1$, $\Delta u_{DA} = 1 \cdot (2-1) = 1$; thus Cyclic integral : $-1 - 1 + 1 + 1 = 0$;

- b) $\delta u = 2y^2 dx + 3x^2 dy$; along AD (2,2) to (1,2), y is constant, $\Delta u_{AD} = 2 \cdot 2^2 \cdot \{1-2\} = -8$, along DC, x is constant, $\Delta u_{DC} = 3 \cdot (1)^2 \cdot \{1-2\} = -3$, Similarly $\Delta u_{CB} = 2 \cdot (1)^2 \cdot (2-1) = 2$, $\Delta u_{BA} = 3 \cdot 2^2 \cdot (2-1) = 12$; thus

Cyclic integral : $-8 - 3 + 2 + 12 = 3$; this answer is opposite of clockwise cycle

For $du = y dx + x dy$, this is still zero for anti-clockwise cycle

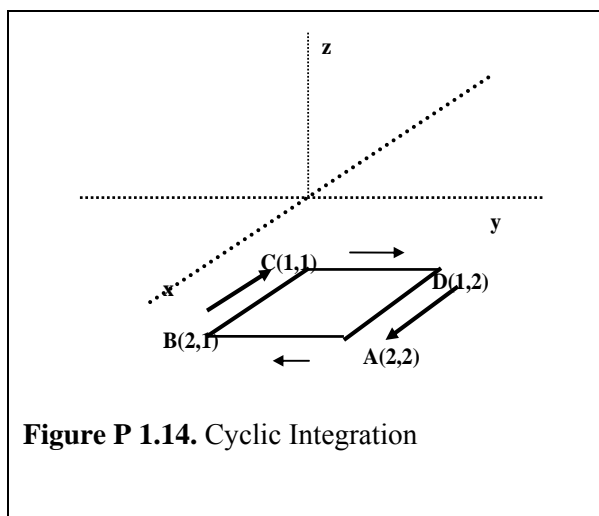


Figure P 1.14. Cyclic Integration

Problem 1.15

Minimize the distance between the point (1,0) to a parabola ($y^2 = x$) without using the LaGrange Multiplier method, and using the LaGrange multiplier method.

Solution:

Minimize the distance between points (A) and (B) where B is the point on the parabola.

$$d = [\{ (x-1)^2 + y^2 \}]^{1/2}$$

$$d^2 = u(x,y) = (x-1)^2 + y^2 \quad (A)$$

Minimize u subject to the condition and end point of the line must lie on the parabola.

$$y^2 = 4x \quad (B)$$

Procedure - A

Solve for y^2 from (B) and use in (A)

$$(x-1)^2 + 4x = u \quad (C)$$

The minimization of u requires that

$$du/dx = 0, \quad 4 + 2(x-1) = 0, \quad 2x + 2 = 0, \quad x = -1, \quad y^2 = -4$$

Using (D) in (B) we find that

$$y = \pm 2i$$

But parabola does not lie on this point. Instead of replacing y^2 with x in Eq. (A) we replace x in Eq. (A). Thus, from (B)

$$x = y^2 / 4$$

Use (E) in (A) to eliminate x

$$d^2 = \{y^2/4 - 1\}^2 + y^2 = u \quad (F)$$

Differentiating (F) with y ,

$$du/dy = 0$$

$$2 \{y^2/4 - 1\} \{2y/4\} + 2y = 0$$

Simplifying

$$y(y^2 + 4) = 0$$

Either $y^2 = -4$ or $y = 0$

We reject the first solution since it gives complex roots. Select the real solution $y = 0$. Then from Eq.(B), $x = 0$. The minimum distance is given as $AC = d = 1$ (from Eq.(A))

Procedure - B

Use Lagrange multiplier method.

$$\text{Define } F(x,y,\ell) = u(x,y) + \ell g(x,y) \quad (G)$$

$$\text{where } u(x,y) = (x-1)^2 + y^2 \quad (H)$$

$$g(x,y) = (y^2 - 4x) \quad (I)$$

But

$$\partial F / \partial x = 0, \quad \partial F / \partial y = 0 \quad (J)$$

Using (H) and (I) in (G) and then using (J)

$$\partial F / \partial x = 2(x-1) + \ell(-4) = 0 \quad (K)$$

$$\partial F / \partial y = 2y + 2\ell y = 0 \quad (L)$$

From eq.(B),

$$y^2 - 4x = 0 \quad (M)$$

Solve x , y , ℓ from Eqs. (K) to (M). From Eq. (L) $y = 0$ or $\ell = -1$

If $\ell = -1$, Eq. (K) implies that $x = -2$; then Eq. (M) will yield complete roots for y .

If $y = 0$, then $x = 0$ from Eq. (M). From Eq. (K), $\lambda = -\frac{I}{2}$

We lost some information in procedure (A) but Lagrange multiplier method (procedure B) yields complete map of solutions.

Microscopic Thermodynamics

Problem 1.16

Compute RMS, avg and MPS speeds in m/s and collision number (collisions/m³ s) and mean free paths (in Angstrom) of H₂ molecule at 298 K, 1000K, 3000 K

Solution:

Summary of formula Text p 897

$$V_{\text{rms}} = \{\overline{V^2}\}^{1/2} = (3k_B T/m)^{1/2} = (3\bar{R} T/M)^{1/2} \text{ where } V_{\text{rms}}^2 = V_x^2 + V_y^2 + V_z^2$$

$$V_{\text{rms}} = (3 * 8314 \text{ (J/kmole K)} * 1000 \text{ K} / 2.02 \text{ kg/kmole})^{1/2} = 3513 \text{ m/s}$$

$$V_{\text{avg}} = \{\bar{V}\} = \int V f(V) dV = (8/(3\pi))^{1/2} V_{\text{rms}} = (8 k_B T / (\pi m))^{1/2} = (8\bar{R} T / (M \pi))^{1/2}$$

$$V_{avg} = (8 \bar{R} T / M \pi)^{1/2} = (2 * 8314 * 1000 / 2.02)^{1/2} = 3237 \text{ m/s}$$

$$V_{mps} = (2 \bar{R} T / M)^{1/2} = 2869 \text{ m/s}$$

Bimolecular molecular Collision #

$$Z = \frac{2}{3} (3 \pi)^{1/2} \sigma^2 V_{avg} n'^2, \quad V_{avg} = \left(\frac{8 \bar{R} T}{M \pi} \right)^{1/2}$$

$$\sigma = 0.2827 \text{ nm}, \quad n' = n * N_{Avog}, \quad n = P / (\bar{R} T) = \{101 / (8.314 * 1000)\} = 0.0125 \text{ kmole/m}^3; \quad n' = 0.0125 * 6.023 * 10^{26} = 7.32 * 10^{24} \text{ molec/m}^3;$$

$$Z = \frac{2}{3} (3 * 3.1416)^{1/2} (0.2827 * 10^{-9})^2 * 3237 * (7.32 * 10^{24})^2 = 2.84 * 10^{34} \text{ collisions / (m}^3 \text{ s)}$$

$$\ell_{mean} = 1 / (2^{1/2} \pi n' \sigma^2), \quad \ell \approx 1 / n'^{1/3}, \quad n' = n * N_{Avog}, \quad n \text{ in kmol/m}^3;$$

See Table below for results

Subs	H2		
T, K	298	1000	3000
VRMS, m/s	1917.96	3513.43	6085.43
Vavg, m/s	1767.05	3236.98	5606.62
Vmps, m/s	1566.01	2868.70	4968.74
Collision#, #/ (s m ³)	1.743E+35	2.835E+34	5.455E+33
Mean free path, Angstrom	1158.54	3887.73	11663.20

Problem 1.17

If the number of molecules per unit volume (n') $\approx 1/\ell^3$ where ℓ is the average distance, determine the value of ℓ for the gases in your classroom at 25°C, 1 bar (assume the ideal gas law is applicable). a) Express your answer in μm and Angstrom ($1 \text{ \AA} = 10^{-10} \text{ m}$) units. Assume that your classroom is filled with pure oxygen. b) do you believe that the ideal gas law is applicable at this intermolecular distance (i.e., that the attractive force between adjacent molecules is negligible)? Assume that ℓ_0 corresponds to the liquid state of oxygen. The molal liquid volume of oxygen is given as $0.02804 \text{ m}^3/\text{kmol}$.

Solution:

a) $\bar{V} = \bar{R} T/P = 0.08314 \text{ (bar m}^3/\text{kmole K)} * 298 \text{ K} / 1 \text{ bar} = 24.77 \text{ m}^3/\text{kmole}$ or $n = 0.04036 \text{ kmole/m}^3$,

$$n' = 0.04036 \text{ kmole/m}^3 * 6.023 \times 10^{26} \text{ molecules/kmole} = 24.31 \times 10^{24} \text{ molecules/m}^3.$$

$$\ell = [1/24.31 \times 10^{24} \text{ 1/m}^3]^{1/3} = 3.45 \times 10^{-9} \text{ m or } 34.5 \text{ \AA}$$

b) For the liquid molar volume at 25 C;

$$n' = (1/0.02804) * 6.023 \times 10^{26} = 21.5 \times 10^{27}$$

$$\ell = [1/21.5 \times 10^{27} \text{ 1/m}^3]^{1/3} = 3.6 \times 10^{-10} \text{ m or } 3.6 \text{ \AA}$$

$\ell / \ell_0 = 34.5/3.6 = 9.6 \gg 3$ at which $\phi/\phi_{\max} = 0.01$ So approximately ideal gas law is applicable for Problem A.20. Rigorous proof will be given in Chapter 06

Problem 1.18

Starting from Maxwellian Distribution law,

$$f(V) = \left(\frac{\text{fraction of particles}}{m/s} \right) = \left(\frac{dn'_v}{n' dV} \right) = 4 \pi^{-1/2} \left\{ \frac{m}{2k_B T} \right\}^{3/2} V^2 \exp \left\{ -\frac{mV^2}{2k_B T} \right\}$$

Where n' , no of molecule per unit volume, nV' no of molecule sper unit velprove that

$$\left(\frac{n'_E}{n'} \right) = 2 \pi^{-1/2} \left[\left\{ \frac{E}{RT} \right\}^{1/2} \exp \left\{ -\frac{E}{RT} \right\} \right] + \left[1 - \text{erf} \left\{ \frac{E}{RT} \right\}^{1/2} \right]$$

where $E = e' N_{\text{Avog}} = M V^2/2$, M denotes the molecular weight (or the mass of 1 kmole), and $\bar{R} = k_B N_{\text{Avog}}$ is the universal gas constant,

Solution:

$$f_1(u) = \frac{d\{\text{fraction}(V)\}}{du}, \quad \frac{\text{fraction within } V \text{ to } V+dV}{(m/s)} = \frac{4}{\sqrt{\pi}} \left\{ \frac{1}{2} \frac{m}{k_B T} \right\}^{3/2} \exp \left\{ -\frac{1}{2} \frac{mV^2}{k_B T} \right\} V^2$$

$$(1/N') (dN'_v/dV) = \rho_v(V) = (4/\pi^{1/2}) \{m/(2k_B T)\}^{3/2} V^2 \exp[-(1/2) mV^2/(k_B T)]$$

Where N' , total no of molecules Integrate from 0 to V for all velocities.

$$e' = 1/2 (mV^2), \quad E = e' N_{\text{Avog}}, \quad E = (1/2) (MV^2); \quad V^2 = 2 E/M, \quad V = \{2 E/M\}^{1/2},$$

$$dV = (1/2) \{2/M\}^{1/2} dE/E^{1/2};$$

$$(1/n') dn'_E = (4/\pi^{1/2}) \{M/(2RT)\}^{3/2} (2 E/M) \exp[-E/(RT)] (1/2) \{2/M\}^{1/2} dE/E^{1/2}$$

$$= (1/\pi^{1/2}) (E/RT)^{1/2} \exp[-E/(RT)] 2 dE/(RT)$$

$$\text{Let } E/RT = x^2; \quad dE/RT = 2x dx$$

Fraction of molecules having energy between 0 and E

$$(1/n') dn'_E = (4/\pi^{1/2}) \int_0^x x^2 \exp[-x^2] dx$$

Integrating by parts,

$$(1/n') dn'_E = (2/\pi^{1/2}) [-x \exp(-x^2) + \int_0^x \exp[-x^2] dx]$$

$$\text{Erf}(x) = \{2/(\pi)^{1/2}\} \left[\int_0^x \exp\{-y^2\} dy \right]$$

$$(1/n') dn'_E = (2/\pi^{1/2}) [-x \exp(-x^2) + \{(\pi)^{1/2}/2\} \text{erf}(x)] = -(2/\pi^{1/2}) x \exp(-x^2) + \text{erf}(x) =$$

$$= -\{2/\pi^{1/2}\} [(E/RT)^{1/2}] \exp(-E/RT) + \text{erf}[(E/RT)^{1/2}]$$

Fraction between E and ∞

$$n'_E/n' = 1 - \text{erf} \left[\left(\frac{E}{RT} \right)^{1/2} \right] + \left\{ \frac{2}{\pi} \right\}^{1/2} \left[\left(\frac{E}{RT} \right)^{1/2} \right] \exp(-E/RT)$$

$$\left(\frac{n'_E}{n'} \right) = 2 \pi^{-1/2} \left[\left\{ \frac{E}{RT} \right\}^{1/2} \exp \left\{ -\frac{E}{RT} \right\} \right] + \left[1 - \text{erf} \left\{ \frac{E}{RT} \right\}^{1/2} \right]$$

Problem 1.19

Air sacs in lungs are called Alveoli from which O₂ enter into blood. The dia of each alveoli is 0.125 mm and O₂ % is 14 % (by mole %). At 37 C, 1 bar,

- what is the mass of O₂ in "g" in each Alveoli
- the number of **molecules** of O₂ in each alveoli
- the spacing between the molecules in nm

Solution

a) Volume = $\pi d^3/6 = 1.02265E-12 \text{ m}^3$

Mass of O₂ in alveoli = $p_{O_2} V M_{O_2}/(RT) = 0.14 \cdot 100 \cdot 1.023e-12 \cdot 32 / (8.314 \cdot 310) = 1.7776E-13 \text{ kg}$ or $1.7776E-10 \text{ g}$

b) $N_{O_2, \text{ kmole}} = m/M_{O_2} = 5.55501E-17 \text{ kmoles}$

$N_{O_2}' = N_{O_2} \cdot 6.023E26 = 3.46 \times 10^{10} \text{ Molecules}$

c) $n' = \{P/RT\} \cdot N_{avog} = 100 \cdot 6.023e26 / \{8.314 \cdot 310\} = 2.34E+25 \text{ molec/m}^3$

$n_{O_2}' = 2.34E+25 \cdot 0.14 = 3.28 E+24 \text{ molec/m}^3$

spacing between molecules, $\ell = 1/n'^{1/3} = 1.0e9 \cdot (1/2.34E+25)^{0.3333} = 3.5 \text{ nm}$

Remarks:

Note that there are other molecules like N₂, CO₂, within Alveoli; ℓ represents adjacent molecules

Problem 1.20

Plot the following vs ℓ/ℓ_0 for O₂ given the following

$$\phi(\ell)/|\phi_{\min}| = 4 \left(\left(\frac{\ell_0}{\ell} \right)^{12} - \left(\frac{\ell_0}{\ell} \right)^6 \right),$$

$$F(\ell)/|F_{\max}| = -[1/0.599] [-12 \left(\frac{\ell_0}{\ell} \right)^{13} + 6 \left(\frac{\ell_0}{\ell} \right)^7]$$

$$|F_{\max}| = 2.3964 \epsilon / \ell_0, \quad |\phi_{\min}| = \epsilon$$

a) $\phi(\ell)/|\phi_{\min}|$ vs ℓ/ℓ_0

b) $F(\ell)/|F_{\max}|$ vs ℓ/ℓ_0

c) Calculate ϕ_{\min} in J and $|F_{\max}|$ in Newtons per kmole, ℓ_{\min} in nm at $|\phi_{\min}|$ and ℓ_{\max} in nm at $|F_{\max}|$; assume that $\ell_0 = \sigma$

Note: $\ell_{\min}/\ell_0 = 2^{1/6} = 1.1225, \ell_{\max}/\ell_0 = 1.2445$

Solution:

a) $\phi(\ell)/|\phi_{\min}| = 4((\ell_0/\ell)^{12} - (\ell_0/\ell)^6)$, where $|\phi_{\min}| = \epsilon$; see Figure

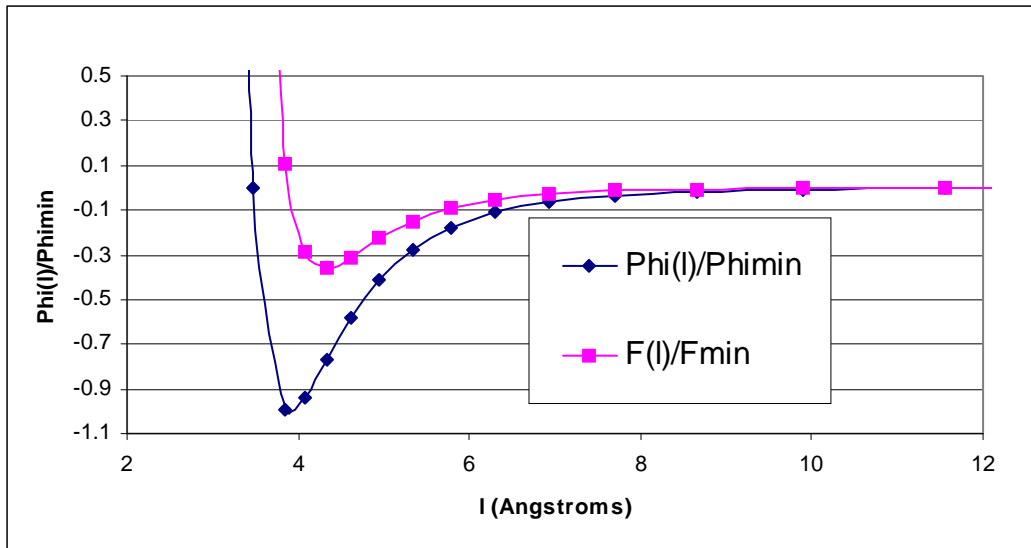


Fig. P 1.20

b) $F(\ell)/|F_{\max}| = -[1/0.599] [-12(\ell_0/\ell)^{13} + 6(\ell_0/\ell)^7]$; see figure

c) Calculate ϕ_{\min} in J and $|F_{\max}|$ in Newtons per kmole, ℓ_{\min} in nm at $|\phi_{\min}|$ and ℓ_{\max} in nm at $|F_{\max}|$; assume that $\ell_0 = \sigma = 0.347$ nm

from Table, $\epsilon/\kappa_B = 106.78$, $\epsilon = 106.7 * 1.38E-23$ J/molecule = 1.47×10^{-21} J/molecule

$|F_{\max}| = 2.3964 \epsilon / \ell_0$, $|F_{\max}| = 1.47e-21/0.347e-09 = 1.015 \times 10^{-11}$ N per molecule pair or

$$\{\ell\}_{\phi \min} / \ell_0 = 2^{1/6} = 1.1225; \{\ell\}_{\phi \min} = 1.1225 * 0.347 = 0.389 \text{ nm}$$

$$\ell_{\text{Fmax}} / \ell_0 = 1.2445, \ell_{\text{Fmax}} = 0.432 \text{ nm}$$

Review of Undergraduate Thermo

Problem 1.21

1 kg of Ar is contained in Section A at $P = 1 \text{ bar}$, $T = 100^\circ\text{C}$. This gas is in contact through a diathermal wall with another piston–cylinder section B assembly containing 1 kg partly liquid water (quality $x = 0.5$) and vapor at 100°C with a weight at top. As we compress the gas in Section A, the temperature tries to increase, but because of the contact with section B, T remains at 100°C . Answer the following True or False questions:

- The composite system consists of a pure substance.
- The composite system has two phases for H_2O and one single phase for Ar gas.
- The composite system is homogeneous.
- The total volume can not be calculated for the composite system.
- There is no heat transfer between Sections A and B.
- There is no work transfer between Sections A and B.
- There is work transfer from Section A to B.
- The quality in Section B decreases.

Solution:

- False, chem. composition varies
- true

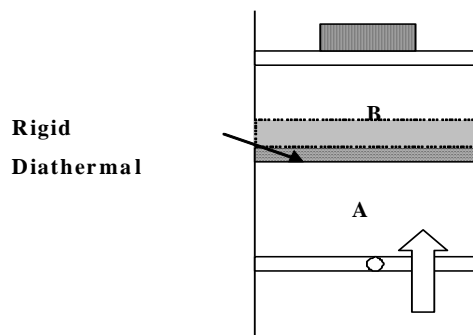


Figure Prob:1.21

- c) False since u, h, ρ vary within composite system
- d) False $V = V_A + V_B$
- e) False Ar when compressed transfers heat to B
- f) True
- g) Weight moved up or down in (B) when work is done on A
- h) False as we compress A

Problem 1.22

Natural gas has the following composition based on molal percentage: CH₄: 91.27, ethane: 3.78, N₂: 2.81, propane: 0.74, CO₂: 0.68, n-Butane: 0.15, i-Butane: 0.1, He: 0.08, i-pentane: 0.05, n-pentane: 0.04, H₂: 0.02, C-6 and heavier (assume the species molecular weight to be 72 kg kmol⁻¹): 0.26, Ar: 0.02. Determine the molecular weight, the methane composition based on weight percent, and the specific gravity of the gas at 25°C and 1 bar.

Solution:

Mol wt: $\{91.27 \cdot 16.05 + 3.78 \cdot (2 \cdot 12.01 + 6 \cdot 1.01) + \dots\} / 100 = 17.61$

Composition on mass %

Methane : $91.27 \cdot 16.05 = 1465$ kg

CH₄% on mass = $1465 \cdot 100 / (17.61 \cdot 100) = 83.16$ %

Input data to EXCEL program

	Mole %mass %			
Argon	0.02			
CH4	91.27	83.16010907		
C2H2	0	0		
C2H6	3.78	6.45478223		
C3H6	0	0		
C3H8	0.74	1.853022704		
C4H10-i	0.1	0.330055512		
C4H10-n	0.15	0.495083269		
C5H12-i	0.05	0.204851276		
C5H12-n	0.05	0.204851276		
CO	0	0		
CO2	0.68	1.698917321		
H2	0.02	0.002293471		
He	0.08			
N2	2.81	4.469782737		
O2	0	0		
other	0.26		Molec. wt	72

Output from Program

Total %99.99 98.87374886

Total	1761.52186		
Mol wt	17.61025557	kg/kmole	
STP vol	24.788191	m ³ /kmole	at 25 C, 1bar
Pressure	1	bar	
Mol wt	17.61025557	kg/kmole	
Density-Fuel	0.710429235	m ³ /kg	
Air density	1.169289934	m ³ /kg	
Sp. gravity-gas	0.607879033	dimensionles	
Density-Fuel	0.710429235	m ³ /kg	
Air density	1.169289934	m ³ /kg	
Sp. gravity-gas	0.607879033	dimensionles	

Problem 1.23

Salt water (sw) consists of 4000 ppm (1 ppm = $Y_k \cdot 10^6$ for liquids and solids; 1 ppm = $X_k \cdot 10^6$ for gases). Convert to mole fraction, $M_s = M_{NaCl} = 58.5$

Solution:

$$Y_k = X_k \cdot M_k / M_{mix}; \quad M_{mix} = M_{sw} = X_s M_s + X_w M_w = X_s M_s + (1 - X_s) M_w$$

$$Y_s = X_s \cdot M_s / [X_s M_s + (1 - X_s) M_w], \text{ solving}$$

$$X_s = M_w / [\{ (1/Y_s) - 1 \} M_s + M_w], \quad X_w = M_s / [\{ (1/Y_w) - 1 \} M_w + M_s],$$

$$X_s = 18.02 / [\{ (1/0.004) - 1 \} 58.5 + 18.02] = 0.001236 \text{ or } 0.1236 \%$$

Problem 1.24

- Ammonia gas mass flow rate: 34.16 kg/hr. Estimate standard (scientific) volume flow rate in m³
- Estimate Critical temperature, pressure, volumes, normal boiling point, heat of vaporization (hfg), triple point T and P, ϵ/k_B and σ using tables and using critical properties for NH₃
- ϵ/k_B in K and σ in nm using critical properties for R134A
- Saturation temperature, saturated liquid and vapor volumes for R134A at P= 10 bar
- Specific volume of R134A (or Freon 134a) at P= 10 bar and 50 C using tables and assuming ideal gas law

Solution:

(a) Using Table 0,

$$\dot{N} = \frac{34.16 \text{ (kg / hr)}}{(17.03 \text{ kg / m}^3)} = 2.006 \text{ kmole / hr}$$

Using STP volume, the volume flow rate is 2.006 (kmole/hr) * 24.5 (m³/kmole) = 49.15 m³/hr

(Table 6c may be used but it is at a pressure of 100 kPa while STP is at 25 C, 101 kPa)

Alternately using the ideal gas law at 25 C, 101.3 kPa,

$$v = \frac{\bar{R} \cdot T}{M \cdot P} = \frac{8.314 \left(\frac{\text{kPa} \cdot \text{m}^3}{\text{kmole} \cdot \text{K}} \right) \cdot 298.15 \text{ (K)}}{17.03 \left(\frac{\text{kg}}{\text{kmole}} \right) \cdot 101.3 \text{ (kPa)}} = 1.437 \text{ (m}^3 / \text{kg)}$$

$$\dot{v} = \dot{m} \cdot v = 34.16 \text{ (kg / hr)} \times 1.437 \text{ (m}^3 / \text{kg)} = 49.1 \text{ (m}^3 / \text{hr)}$$

(b) From Table 1,

$$T_c = 405.6 \text{ K}, P_c = 112.8 \text{ bar}, \bar{V}_c = 0.0725 \text{ m}^3/\text{kmole}, T_{BP} = 239.7 \text{ K},$$

$$h_{fg} = 1371.8 \text{ kJ/kg}$$

From Table 2,

$$T_{TP} = 195.4 \text{ K}, P_{TP} = 45.77 \text{ mmHg (or 0.0599605 bar)}$$

From Table 3,

$$\epsilon/k_B = 558.3 \text{ K (viscosity method)}, \sigma = 0.29 \text{ nm}$$

Using critical properties for NH₃,

$$\epsilon/k_B = 0.77 T_c = 0.77 \times 405.6 \text{ K} = 312.3 \text{ K}$$

$$\sigma = 0.841 \bar{V}_c^{1/3} \text{ m}^3/\text{kmol} = 0.841 \times (0.0725)^{1/3} = 0.35 \text{ nm}$$

Note : Virial method columns 5 and 6 of Table A.3 yield $\epsilon/k_B = 320 \text{ K}$ (not given in table)

$$(c) \epsilon/k_B = 0.77 T_c = 0.77 \times 374.2 \text{ K} = 288.1 \text{ K}$$

$$\sigma = 0.841 \bar{V}_c^{1/3} \text{ m}^3/\text{kmol} = 0.841 \times (0.198)^{1/3} = 0.49 \text{ nm}$$

$$(d) T_{sat} = 39.39 \text{ }^\circ\text{C}, v_f = 0.0008695 \text{ m}^3/\text{kg}, v_g = 0.0202 \text{ m}^3/\text{kg}$$

(e) From Table 5c for superheated gas,

$$v = 0.02171 \text{ m}^3/\text{kg}$$

Using the ideal gas law,

$$v = \frac{\bar{R} \cdot T}{M \cdot P} = \frac{8.314 \left(\frac{\text{kPa} \cdot \text{m}^3}{\text{kmole} \cdot \text{K}} \right) \cdot 323.15 \text{ (K)}}{102.04 \left(\frac{\text{kg}}{\text{kmole}} \right) \cdot 1000 \text{ (kPa)}} = 0.0263 \text{ (m}^3 \text{ / hr)}$$

Problem 1.25

- Average solar energy striking the surface of earth is about 1.360 W/m^2 . If water absorbs all this energy at 25°C , what is the estimated evaporation rate in $\text{kg/m}^2 \text{ s}$;
- If water covers the (2/3) of the earth's surface area (Mass of earth in kg 0.98×10^{24} , Diameter (km) 12756, Mean density (kg/m^3) :5520), what is the estimated evaporation rate in kg per s ?

Solution:

- hfg at $25^\circ\text{C} = 242.3$ (table A.4a) = 2442 kJ/kg
Evap. rate = $1.360 \text{ (kW/ m}^2\text{)}/2442 \text{ kJ/kg} = 5.569 \times 10^{-4} \text{ kg/ (m}^2 \text{ s)}$
- Earth's surface area: $\pi d^2 = \pi (1.2756 \times 10^4 \cdot 1000)^2 = 5.112 \times 10^{14} \text{ m}^2$;
Total flux on Earth's surface = $5.112 \times 10^{14} \text{ m}^2 \times 1.360 \text{ kW/m}^2 = 6.952 \times 10^{14} \text{ kW}$
Total flux on Earth's water surface = $(2/3) * 6.952 \times 10^{14} \text{ kW} = 4.635 \times 10^{14} \text{ kW}$
Evap. rate = $4.635 \times 10^{14} \text{ kW}/2442 \text{ kJ/kg} = 1.898 \times 10^{11} \text{ kg/s}$

Problem 1.26

A helium-filled scientific balloon is to be designed just to be in the earth's atmosphere at an altitude of 40,000 m with a payload of 4,000 kg. The total mass of balloon includes all masses including payload except mass of the helium gas. The ambience is at $P = 300 \text{ Pa}$ and $T = -32^\circ\text{C}$, determine

- V, the volume of the balloon in cubic meters and***
- m, the mass of the helium in kg.***

Solution:

a) Upward Buoyancy force = weight of displaced fluid = $V \cdot \rho_{\text{air}}$ = downward force = Payload + He mass
 $V \cdot \rho_{\text{air}} = \text{downward force} = \text{Payload} + V \cdot \rho_{\text{He}}$

$$V \cdot \{\rho_{\text{air}} - \rho_{\text{He}}\} = \text{Payload} = 4000$$

Neglecting ρ_{He} since $\rho_{\text{He}} < \rho_{\text{air}}$,

$$\rho_{\text{air}} = P / (R_{\text{air}} T) = 0.3 / \{0.287 \cdot 241\} = 0.00434 \text{ kg/m}^3$$

$$V \cdot \rho_{\text{air}} = \text{Payload} = 4000 \text{ kg}$$

Neglecting ρ_{He} since $\rho_{\text{He}} < \rho_{\text{air}}$,

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$$V = 4000 \text{ kg} / 0.00434 \text{ (kg/m}^3\text{)} = 922,000 \text{ m}^3.$$

b) Mass of He = $V \cdot \rho_{\text{He}}$, assuming P of he is slightly above ambient pressure,
 $\rho_{\text{He}} = P / (R_{\text{He}} T) = 0.3 / \{(8.314/4) \cdot 241\} = 0.000599 \text{ kg/m}^3$

$$V \cdot \rho_{\text{He}} = 921659 \cdot 0.000599 = 552.3 \text{ kg}$$

Remarks: He mass is 552 kg < 4000 kg; more exact solution involves the following

$$V \cdot \{\rho_{\text{air}} - \rho_{\text{He}}\} = 4000$$

$$\rho_{\text{air}} = P / (R_{\text{air}} T) = 0.3 / \{0.287 \cdot 241\} = 0.00434 \text{ kg/m}^3$$

$$V \cdot \{P / (R_{\text{air}} T) - P / (R_{\text{He}} T)\} = V \cdot \{P / (\bar{R} T)\} \{M_{\text{air}} - M_{\text{He}}\} = \text{Payload}$$

$$V \cdot \{P M_{\text{air}} / (\bar{R} T)\} = \{\text{Payload} / \rho_{\text{air}}\} / \{1 - M_{\text{He}} / M_{\text{air}}\} = \{4000 / 0.00434\} / (1 - 4 / 28.97) = 1,069,000 \text{ m}^3$$