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) $2.7\text{x}10^{13}$
b) $3.3\ \text{x}10^{12}$
c) $6.02\ \text{x}10^{26}$
d) None of above within 10 %

Solution:

Volume 1.022e-12 m3; PV = N RT, N = 3.97e-14 , n = 2.38e13 molecues or 3.33e12 molecules of O2

Problem 1.4

This differential sum $3\ x^2dy + 2\ y^2\ dx$ 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:

Sat temp at sea level: 100 C; given T< Tsat; however at Tsat = 91.76 C; hence it will boil

Problem 1.6

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

a) $\overline{u}_d < \overline{u}_m$ since diatomic species has higher molecular weight compared to monatomic gas
b) $\overline{u}_d > \overline{u}_m$ since diatomic species has lower molecular weight
c) $\overline{u}_d > \overline{u}_m$ since monatomic species has vibrational and rotational energies in addition to translational energies.
d) $\overline{u}_d > \overline{u}_m$ since diatomic species has vibrational and rotational energies in addition to translational energies.
e) 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

a) 2.172
b) 1.673
c) 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 (m3), 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

a) extensive
b) intensive
c) neither of above since insufficient information is given.

Solution:

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

<u>Mathematical background</u>

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 K , $\bar{R} = 0.08314$ bar m^3/kmole, and $\bar{v} = 0.245$ m^3 kmol^{-1}, assuming that $\bar{a} = 142.64$ bar m^6 K$^{1/2}$ kmol^{-2} and $\bar{b} = 0.0211$ m^3 kmol^{-1}.

Solution:

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

P = P (v, T) (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)

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

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

From (A)

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

And

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

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

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

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

$0 = \{- RT/(v-b)^2 + [a/ \{T^{1/2}] [2v +b] / \{v^2(v+b)^2\}\quad dv_P + [R/(v-b) + [a/ \{2\ T^{132}\ v(v+b)\}\ ]\ dT_P$ (F)

From (F)

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

b) T = 873 K, v = 0.245 m^3 /kmole, a = 142.64 baes m3 K1/2/kmole 2 b = 0.0305 m3/kmole

dv_P/dT_P = [0.08314 bar m^3 /kmole K /(0.245-0.0211) + 142.64/ {2 $873^{3/2}$ 0.245(0.245+0.0211)}] /[{ 0.08314 * 873 /$(0.245-0.0211)^2$ - [142.64/ {$873^{1/2}$] [2*0.245+0.0211]/ [0.245^2 $(0.245+0.0211)^2$]} = (0.3713-0.0424)/(1447.8+579.8) = 0.000477 m^3/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): $xy^3\,dx + 3\,x^2y^2dy$, and $2e^xydy + e^xy^2dx$ 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)

$$xy^3\,dx + 3\,x^2y^2\,dy \qquad \textit{Eq. } (1)$$

$$2\,e^xy\,dy + e^xy^2\,dx \qquad \textit{Eq. } (2)$$

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

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

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

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

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

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

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

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

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

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

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

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

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):

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

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

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

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

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

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

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

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

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

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

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

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:

$$M(x,y) = e^x y^2 \tag{M}$$

$$N(x,y) = 2\, e^x y \tag{N}$$

Taking the following differentials:

$$\frac{\partial M}{\partial y} = 2e^x y \tag{O}$$

$$\frac{\partial N}{\partial x} = e^x y^2 \tag{P}$$

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

$$Z = e^x y^2 + f(x) \tag{Q}$$

Differentiating (O) 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 $\phi = x^3 y/t + x^2y^2/t^3 + x\, y^3/t^7$. 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:

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

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

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

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

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

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

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

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,

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

Keep y constant and divide by dx

$du/dx\ \{\ 1+ y^3 + 2\,u\,y) = 2\,xy - 8$

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

Similarly keep x constant and divide by dy

$du/dy\ \{\ 1-+y^3 + 2\,u\,y)\ x^2 + 3\,y^2\,u + u^2 = 0$

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

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

Using total differentiation

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

Keep y and z constant; dy =0

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

Similarly keep x and z constant

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

Similarly keep y and x constant

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

Problem 1.13

Show whether the following equations are exact or inexact: (a) du = 2 y^2 dx+3 x^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 :

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

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

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

$$b.):du = ydx + xdy$$

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

$$Ans.:exact$$

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

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

$$Ans.:exact$$

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

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

$$Ans.:exact$$

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

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

$$Ans.:exact$$

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

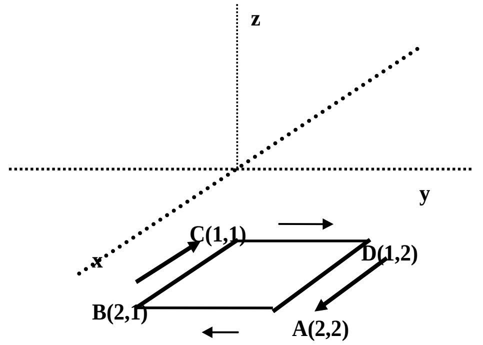

Figure P 1.14. Cyclic Integration

Solution:

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

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

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

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

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.

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

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

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

$$y^2 = 4\,x \qquad (B)$$

Procedure - A

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

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

The minimization of u requires that

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

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

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

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))

<u>Procedure - B</u>

Use Legrange multiplier method.

Define $F(x,y,\ell) = u(x,y) + \ell\, g(x,y)$ (G)

where $u(x,y) = (x-1)^2 + y^2$ (H)

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

But

$$\partial F/\partial x = 0, \; \partial F/\partial y = 0 \qquad \text{(J)}$$

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

$$\partial F/\partial x = 2(x-1) + \ell(-4) = 0 \qquad \text{(K)}$$

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

From eq.(B),

$y^2 - 4x = 0$ (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), $\lambda = -\frac{1}{2}$

We lost some information in procedure (A) but Legrange 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 (icolisons/m3 s) and mean free paths (in Angstrom) of H_2 molecule at 298 K, 1000K, 3000 K

Solution:

Summary of formula Text p 897

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

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

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

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

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

Bimolecular molecular Collision #

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

σ=0.2827 nm, n' n * NAvog, n= $P/(\bar{R}T)$ = {101/(8.314*1000)}=0.0125 kmole/m^3; n'=0.0125x6.023x10^{26} = 7.32x10^{24} molec/m3;

$$Z = \frac{2}{3}(3*3.1416)^{1/2}(0.2827x10^{-9})^2\, x3237x\left(7.32x10^{24}\right)^2 = 2.84x10^{34}\ \text{collisions}/(m3\ s)$$

$\ell_{mean} = 1/(2^{1/2}\pi n'\sigma^2)$, $\ell \approx 1/n'^{1/3}$, n' = n * N_{Avog}, n 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 m3)	**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') ≈ $1/\ell^3$ where ℓ is the average distance, determine the value of ℓ for the gases in your classroom at 25ºC, 1 bar (assume the ideal gas law is applicable). a) Express your answer in μm and Angstrom (1 A = 10^{-10} 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 m^3/kmol.

Solution:

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

n' = 0.04036 kmole/m^3 * 6.023x10^{26} molecules/kmole = 24.31X10 ^{24} molecules/m^3.

ℓ= [1/24.31 x 10^{24} 1/m^3]$^{1/3}$= 3.45x10^{-09} m or 34.5 A

b) For the liquid molar volume at 25 C;

n' = (1/0.02804)* 6.023x10 ^{26} =21.5x10 ^{27}

ℓ= [1/21.5x10^{27} 1/m^3]$^{1/3}$= 3.6x10^{-10} m or 3.6 A

ℓ/ℓ_0= 34.5/3.6 = 9.6 >> 3 at which ϕ/ϕ_{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,

$$f(V)=\left(\frac{\textit{fraction of particles}}{m/s}\right)=\left(\frac{dn'_V}{n'dV}\right)=4\,\pi^{-1/2}\left\{\frac{m}{2k_BT}\right\}^{3/2}V^2\exp\left\{-\frac{mV^2}{2k_BT}\right\}$$

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

$$\left(\frac{n'_E}{n'}\right)=2\,\pi^{-1/2}\left[\left\{\frac{E}{\bar{R}T}\right\}^{1/2}\exp\left\{-\frac{E}{\bar{R}T}\right\}\right]+\left[1-erf\left\{\frac{E}{\bar{R}T}\right\}^{1/2}\right]$$

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

Solution:

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

$(1/N')(dN'_V/dV) = \rho_v(V) = (4/\pi^{1/2})\,\{m/(2k_BT)\}^{3/2}\,V^2\exp[-(1/2)\,mV^2/(k_BT)]\}$

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

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

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

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

Let $E/RT = x^2$; $dE/RT = 2x\,dx$

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,

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

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

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

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

Fraction between E and ∞

$n'_E/n' = 1 - \mathrm{erf}\,[(E/RT)^{½}] + \{2/\pi^{1/2}\}\ [(E/RT)^{½}]\exp(-E/RT)$

$$\left(\frac{n'_E}{n'}\right) = 2\,\pi^{-1/2}\left[\left\{\frac{E}{\bar{R}T}\right\}^{1/2} \exp\left\{-\frac{E}{\bar{R}T}\right\}\right] + \left[1 - erf\,\left\{\frac{E}{\bar{R}T}\right\}^{1/2}\right]$$

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,

a) what is the mass of O2 in "g" in each Alveoli
b) the number of **<u>molecules</u>** of O2 in each alveoli
c) the spacing between the molecules in nm

Solution

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

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

b) N_{O2}, kmole = m/MO2 = 5.55501E-17 kmoles

N_{O2}' = N_{O2}* 6.023E26 = 3.46xe10 Molecules

c) n'= {P/RT} * Navog = 100*6.023e26/{8.314*310} = 2.34E+25 molec/m^3

n_{O2}'= 2.34E+25*0.14= 3.28 E+24 molec/m^3

spacing between molecules, $\ell = 1/n'^{1/3}$ = 1.0e9 * (1/2.34E+25) ^0.3333= 3.5 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 O_2 given the following

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

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

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

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 $|\phi_{min}| = \varepsilon$; see Figure

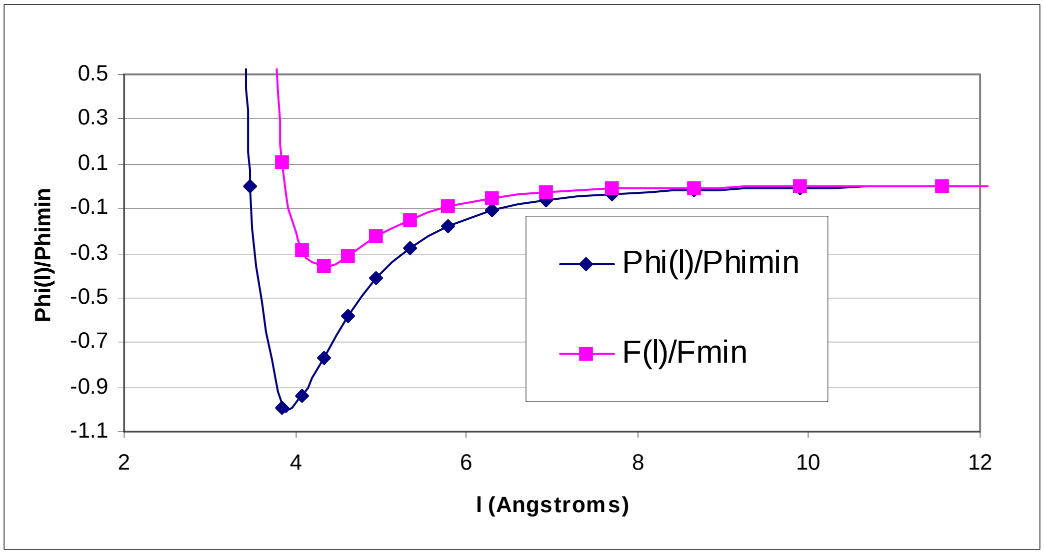

Fig. P 1.20

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, $\varepsilon/\kappa_B = 106.78$, $\varepsilon = 106.7*1.38E-23$ J/molecule = 1.47x10-21 J/molecule

$|F_{max}| = 2.3964\, \varepsilon/\ell_0$, $|F_{max}| = 1.47e-21/0.347e-09 = 1.015\times10^{-11}$ N per molecule pair or

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

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

Review of Undergraduate Thermo

Problem 1.21

1 kg of Ar is contained in Section A at P = 1 bar, T = 100ºC. 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 100ºC 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 100ºC. Answer the following True or False questions:

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

Solution:

a) False, chem. composition varies
b) true

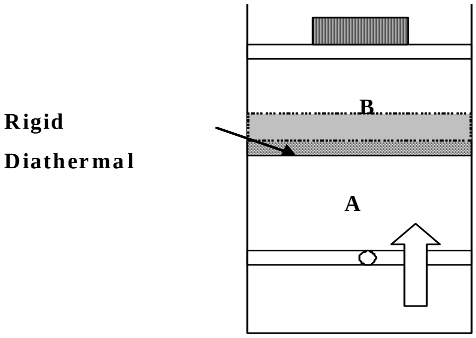

Figure Prob:1.21

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: CH_4: 91.27, ethane: 3.78, N_2: 2.81, propane: 0.74, CO_2: 0.68, n–Butane: 0.15, i–Butane: 0.1, He: 0.08, i–pentane: 0.05, n–pentane: 0.04, H_2: 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* 16.05+ 3.78* (2*12.01+6*1.01)+….}/100 = 17.61
Composition on mass %
Methane : 91.27* 16.05= 1465 kg
CH4% on mass = 1465*100 /(17.61*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*10^6 for liquids and solids; 1 ppm = X_k*10^6 for gases). Convert to mole fraction , $M_s=M_{NaCl}=$ 58.5

Solution:

$Y_k = X_k*M_k/M_{mix}$; $M_{mix} = M_{sw} = X_s M_s + X_w M_w = X_s M_s + (1-X_s) M_w$
$Y_s = X_s*M_s/[X_s M_s + (1-X_s) M_w]$, solving
$X_s = M_w/[\{(1/Y_s\}-1)M_s + M_w]$, $X_w = M_s/[\{(1/Y_w\}-1)M_w + M_s]$,

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

Problem 1.24

a) Ammonia gas mass flow rate: 34.16 kg/hr. Estimate standard (scientific) volume flow rate in m^3
b) 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
c) ε/k_B in K and σ in nm using critical properties for R134A
d) Saturation temperature, saturated liquid and vapor volumes for R134 A at P= 10 bar
e) 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,

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

Using STP volume, the volume flow rate is 2.006 (kmole/hr)*24.5 (m^3/kmole) = 49.15 m^3/hr

(Table 6c may be sued 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,

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

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

(b) From Table 1,

Tc = 405.6 K, Pc = 112.8 bar, $\bar{V}_C$ = 0.0725 m^3/kmole, T_{BP} = 239.7 K,

h_{fg} = 1371.8 kJ/kg

From Table 2,

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

From Table 3,

ε/k_B = 558.3 K (viscosity method) , σ = 0.29 nm

Using critical properties for NH3,

ε/k_B = 0.77 Tc = 0.77 x 405.6 K = 312.3 K

σ = 0.841 $\bar{V}_C^{\ 1/3}$ m^3/kmol = 0.841 x $(0.0725)^{1/3}$ = 0.35 nm

Note : Virial method columns 5 and 6 of Table A.3 yield ε/k_B = 320 K (not given in table)

(c) ε/k_B = 0.77 Tc = 0.77 x 374.2 K = 288.1 K
σ = 0.841 $\bar{V}_C^{\ 1/3}$ m^3/kmol = 0.841 x $(0.198)^{1/3}$ = 0.49 nm

(d) Tsat = 39.39 °C, v_f = 0.0008695 m^3/kg, v_g = 0.0202 m^3/kg

(e) From Table 5c for superheated gas,
v = 0.02171 m^3/kg

Using the ideal gas law,

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

Problem 1.25

a) Average solar energy striking the surface of earth is about 1.360 W/m^2. If water absorbs all this energy at 25C, what is the estimated evaporation rate in kg/m^2 s;
b) 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:

a) hfg at 25 C = 242.3 (table A.4a) = 2442 kJ/kg

Evap. rate = 1.360(kW/ m^2)/2442kJ/kg= 5.569×10^{-4} kg/ (m^2 s)

b)Earth's surface area:$\pi d^2 = \pi * (1.2756 \times 10^4 * 1000)^2 = 5.112 \times 10^{14}$ m^2;

Total flux on Earth's surface = 5.112×10^{14} $m^2 \times 1.360$ kW/m^2=6.952×10^{14} kW

Total flux on Earth's water surface = (2/3) * 6.952×10^{14} kW=4.635×10^{14} kW

Evap. rate = 4.635×10^{14} kW/2442kJ/kg= 1.898×10^{11} 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 o 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 Pa and T = –32 °C, determine

a) V, the volume of the balloon in cubic meters and
b) m, the mass of the helium in kg.

Solution:

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

$V*\rho_{air}$= downward force=Payload+ $V*\rho_{He}$

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

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

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

$V*\rho_{air}$ = Payload= 4000 kg

Neglecting ρ_{He} since $\rho_{He}<\rho_{air}$, V=4000 kg/0.00434(kg/m3) = 922,000 m^3.

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

V*ρ_{He}= 921659*0.000599=552.3 kg

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

V*{ρ_{air-} ρ_{He}} = 4000

ρ_{air}=P/(R_{air}T) =0.3/{0.287*241} = 0.00434 kg/m^3

V*{ P/(R_{air}T)- P/(R_{He}T)} = V*{P/($\overline{R}$ T)}{ M_{air}-M_{He}} = Payload

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