Solutions to Problem Set 1

1. ethane in a bulb which bursts at what temperature?

Equation	Basis for the equation	Eq. #
$n = 5\ g / 30\ g\ mol^{-1}$	ethane C_2H_6 molar mass = 2(12) + 6(1) = 30 g mol^{-1}	1
$pV = nRT$ 10 atm (1.0 L) = (5/30)(0.0820578 L atm mol^{-1} K^{-1}) T Solve for T T = 731.2 K or 458 °C	Ideal gas law. bulb will exceed 10 atm above 458 °C	2

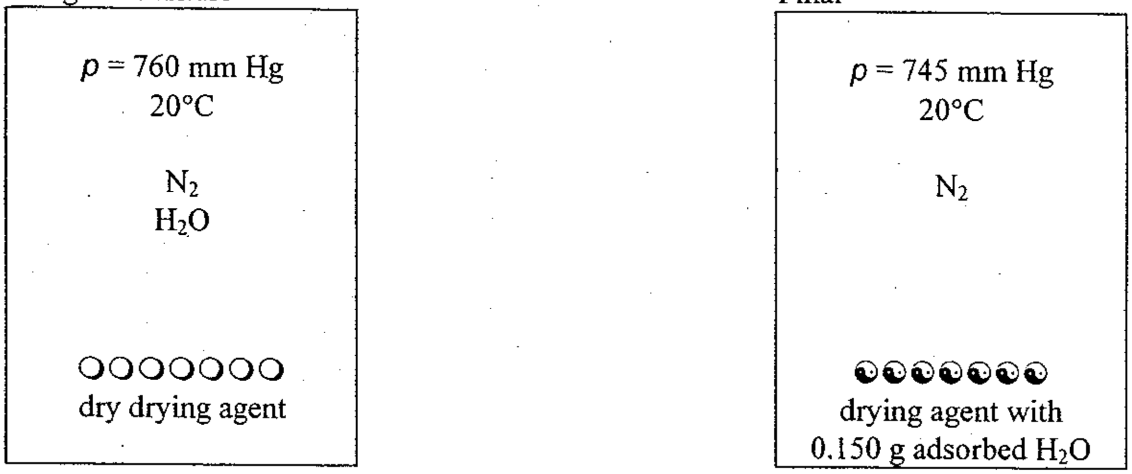
2. coefficients for an ideal gas

Equation	Basis for the equation	Eq. #
$\alpha = (1/V)(\partial V/\partial T)_p$ $\beta = -(1/V)(\partial V/\partial p)_T$	Given definition of coefficient of thermal expansion Given definition of coefficient of compressibility	1 2
$pV = nRT$ $V = nRT/p$ $(1/V) = p/nRT$	Ideal gas law	3 4 5
$(\partial V/\partial T)_p = (nR/p)$ $\alpha = (1/V)(\partial V/\partial T)_p = [p/nRT]\bullet (nR/p)$ $\alpha = 1/T$ **Q.E.D.**	Differentiation of Eq 4 Using Eq 5 and Eq 6	6
$(\partial V/\partial p)_T = -nRTp^{-2}$ $\beta = - (1/V)(\partial V/\partial p)_T$ $= - [p/nRT]\bullet(-nRTp^{-2})$ $\beta = + 1/p$ **Q.E.D.**	Differentiation of Eq 4 Using Eq 5 and 7	7

Problem 3.

Draw a picture

Original mixture Final



Question: (a) mole percent N_2= ? (b) V = ?

Principles and Definitions:

Definition of partial pressure: $p_{N2} = x_{N2}p$

Dalton's law of partial pressures:

$p_{N2} + p_{H2O} = p$ $\qquad\qquad$ $p_{N2} = p$

Assume the gases behave ideally: $pV = nRT$

For an ideal gas the partial pressure of a gas in a mixture of gases is the pressure that would be exerted by the gas if it had been alone by itself in the same volume and temperature.

Solution:

In the same volume V= unknown and same T = (20+273.15) K, $p_{N2} = p$ =745 mm Hg.
Therefore, p_{N2} =745 mm Hg in the original mixture (and p_{H2O} = 760-745 = 15 mm Hg).
From the definition of partial pressure:
{ $p_{N2} = x_{N2}p$ } applies in the original mixture, where p_{N2} =745 mm Hg and p = 760 mm Hg, from which equation we find $x_{N2} = p_{N2}/p$ =745/760 = 0.980

(a): 100× x_{N2} = 98% **Answer**

(b) Mass of water vapor in original mixture = increase in weight of the drying agent = 0.150 g H_2O. Assume water vapor behaves ideally in the original mixture:
p_{H2O} = 15 mm Hg, which is the pressure 0.150 g H_2O would exert if by itself in the volume V and temperature T = 293.15 K. Substitute these data into

$V = nRT/p$ to obtain V = (0.150 g/ 18.0 g mol^{-1})×8.20578×10^{-2} L atm K^{-1} mol^{-1}×293.15 K ÷(15 mm Hg× 1 atm/760 mm Hg)

= 10.2 L **Answer**

Not asked for, but we can also find the amount of N_2:

(1) We can use the ideal gas law in the final picture:

$$n = pV/RT = 745 \text{ mm Hg} \times (1 \text{ atm}/760 \text{ mm Hg}) \times 10.2 \text{ L}$$
$$\div \{8.20578\times10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1} \times 293.15 \text{ K}\}$$
$$= 0.414 \text{ mol } N_2$$

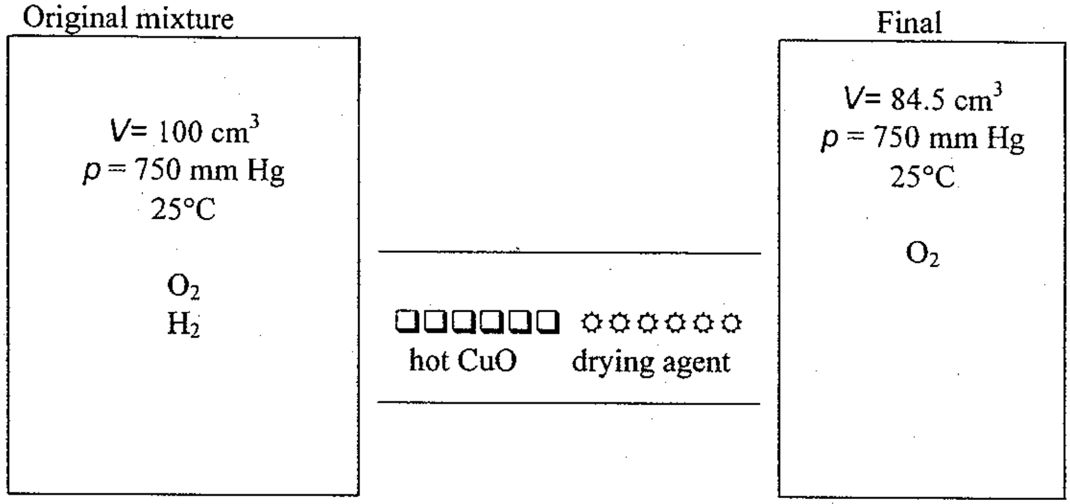
or (2) we can use the definition of mole fraction: $x_{N2} = 0.98 = n_{N2} / [\, n_{N2} + n_{H2O}]$

$$= n_{N2} / [\, n_{N2} + (0.150/18.0)]$$

3. A mixture of nitrogen and water vapor is admitted to a flask which contains a solid drying agent. Immediately after admission, the pressure in the flask is 760 mm. After standing some hours, the pressure reaches a steady value of 745 mm. (a) Calculate the composition, in mole percent, of the original mixture. (b) If the experiment is done at 20°C and the drying agent increase in weight by 0.150 g what is the volume of the flask? (The volume occupied by the drying agent may be ignored.)

Problem 4.

Draw a picture



Question:

In original mixture, x_{O2} = ? x_{H2} = ?

Principles and Definitions:

Chemical reactions:

$O_2 + CuO \rightarrow$ no reaction

$H_2 + CuO \rightarrow Cu + H_2O$ — amount of Cu formed is stoichiometric - based on moles H_2 reacted.

$\frac{1}{2}O_2 + Cu \rightarrow CuO$ — amount of O_2 removed is stoichiometric - based on moles Cu present, which in turn, is the same as moles H_2 reacted.

Definition of mole fraction: $x_{O2} = n_{O2} / (n_{O2} + n_{H2})$

Assume ideal gas behavior:

$pV = nRT$

Solution:

Let n = original no. of moles of gas = $n_{O2} + n_{H2}$

$n = pV/RT$ = 750 mm Hg × (1 atm/760 mm Hg) × 100 cm^3 L × (1 L/10^3 cm^3)

÷ {8.20578×10^{-2} L atm K^{-1} mol^{-1} × (25+273.15) K}

= 4.034×10^{-3} moles gas

$x_{H2} + x_{O2} = 1$

moles O_2 in original = x_{O2} (4.034×10^{-3} moles)

moles H_2 in original = x_{H2} (4.034×10^{-3} moles)

After reaction, no. of moles of O_2 gas = pV/RT

= 750 mm Hg × (1 atm/760 mm Hg) × 84.5 cm^3 L× (1 L/10^3 cm^3)

÷ {8.20578×10^{-2} L atm K^{-1} mol^{-1} × (25+273.15) K}

= 3.408×10^{-3} moles O_2 gas are left

Let y = moles of H_2 reacted $\qquad H_2 + CuO \rightarrow Cu + H_2O \qquad (1)$

$$\begin{array}{llll} H_2 & + CuO & \rightarrow Cu & + H_2O \\ y & y & y & y \text{ moles} \end{array} \qquad (1)$$

This amount of Cu then reacts :

$$\begin{array}{lll} \tfrac{1}{2}O_2 & + Cu & \rightarrow CuO \\ \tfrac{1}{2}y & y & y \end{array} \qquad \text{using up } \tfrac{1}{2}y \text{ moles of } O_2. \qquad (2)$$

From reaction (1), moles of $H_2 = n_{H2} = x_{H2}\,(4.034\times10^{-3}\text{ moles}) = y$

or $x_{H2} = y\,/\,(4.034\times10^{-3}\text{ moles})$

Because of reaction (2), moles of O_2 left $= x_{O2}\,(4.034\times10^{-3}\text{ moles}) - \tfrac{1}{2}y = 3.408\times10^{-3}$ moles

or $x_{O2} = [3.408\times10^{-3} + \tfrac{1}{2}y]\,/\,(4.034\times10^{-3})$

Since $x_{H2} + x_{O2} = 1$ $\qquad y\,/\,(4.034\times10^{-3}\text{ moles}) + [3.408\times10^{-3} + \tfrac{1}{2}y]\,/\,(4.034\times10^{-3}) = 1$

or $\qquad (3/2)\,y = (4.034 - 3.408)\times10^{-3}$

$y = 4.173\times10^{-4}$ moles

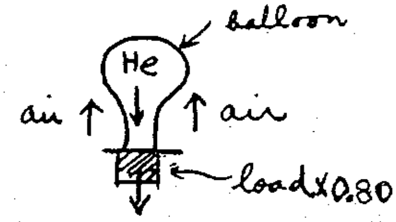
Substitute into $x_{H2} = y\,/\,(4.034\times10^{-3}\text{ moles})$ to get $x_{H2} = 0.103$ $\qquad$ Answers

$\therefore x_{O2} = (1 - x_{H2}) = 0.897$

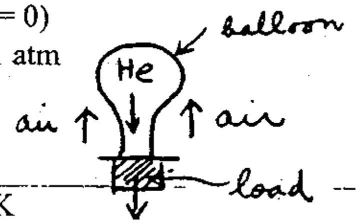
4. A mixture of oxygen and hydrogen is analyzed by passing it over hot copper oxide and through a drying tube. Hydrogen reduces the CuO to metallic Cu. Oxygen then reoxidizes the copper back to CuO. 100 cm^3 of the mixture measured at 25°C and 750 mm yields 84.5 cm^3 of dry oxygen measured at 25°C and 750 mm after passage over CuO and the drying agent. What is the original composition of the mixture? {Hint: First write balanced chemical equations for the reactions.}

Problem 5.

Draw a picture



At ground level ($z = 0$)
Atmosphere : $p = 1$ atm



$V = 10^4\ m^3$ He
$T = (20 + 273.15)$ K
mass of empty balloon = 1.3×10^6 g
Total mass = $m_{balloon} + m_{load} + m_{He}$

At $z = h = ?$
$p = ?$ atm

$V = 10^4\ m^3$ He
$T = (20 + 273.15)$ K
mass of empty balloon = 1.3×10^6 g
Total mass= $m_{balloon} + 0.80(m_{load}) + m_{He}$

Question:

$h = ?$

Principles and Definitions:

1. Archimedes principle : At equilibrium, the surrounding fluid (air, in this case) supports a body (balloon + load it is carrying) whose weight is equal to the weight of the displaced fluid.
This means:
at height $z = h$ equilibrium is reached when mass of displaced air = $m_{balloon} + 0.80\ (m_{load}) + m_{He}$
at ground level $z = 0$, equilibrium is reached when mass of displaced air = $m_{balloon} + m_{load} + m_{He}$
2. Barometric formula: $p/p_0 = \rho/\rho_0 = \exp[-Mgh/RT]$
3. Assume ideal gas behavior for both air and He: $pV = nRT$ or
units : $J \equiv kg\ m^2\ s^{-2}$
Assume that we can neglect the volume of air displaced by the load in comparison to the volume of the balloon.

Solution:

At ground level, the mass of displaced air = $\rho_0 V$ At h, the mass of displaced air = ρV
The equilibrium conditions are:

$$m_{balloon} + m_{load} + m_{He} = \rho_0 V \quad (1) \quad \text{and} \quad m_{balloon} + 0.80(m_{load}) + m_{He} = \rho V \quad (2)$$

Eq. (2) ÷Eq. (1): $\rho/\rho_0 = [\, m_{balloon} + 0.80(m_{load}) + m_{He}]/[\, m_{balloon} + m_{load} + m_{He}]$ (3)

$$m_{He} = M_{He}(pV/RT)$$
$$= 4.0\ g\ mol^{-1}\times1\ atm\times10^4\ m^3\times(10^3\ L / 1\ m^3)$$
$$\div[\,8.20578\times10^{-2}\ L\ atm\ K^{-1}\ mol^{-1}\times293.15\ K] \quad =1.663\times10^6\ g$$

$$\rho_0 V = m_{air}$$
$$= 28.8\ g\ mol^{-1}\times1\ atm\times10^4\ m^3\times(10^3\ L / 1\ m^3)$$
$$\div[\,8.20578\times10^{-2}\ L\ atm\ K^{-1}\ mol^{-1}\times293.15\ K] \quad =1.1972\times10^7\ g$$

From eq. (1), we obtain

$$\therefore m_{load} = 1.1972\times10^7\ g - [\,1.3\times10^6\ g + 1.663\times10^6\ g\,] = 9.01\times10^6\ g$$

Substitute this into eq. (3),

$$\rho/\rho_0 = [1.3\times10^6 + 1.663\times10^6 + 0.80\times9.01\times10^6\,]/[\,1.3\times10^6 + 1.663\times10^6 + 9.01\times10^6] = 0.85$$
$$\rho/\rho_0 = 0.85 = \exp[-Mgh/RT]$$
$$= \exp[28.8\ g\ mol^{-1}\times1\ kg/10^3\ g\times9.80665\ m\ s^{-2}\times h\ m / 8.31451\ J\ K^{-1}\ mol^{-1}\times293.15\ K]$$
$$0.85 = \exp[1.159\times10^{-4}\,h] \quad \text{or } 1.159\times10^{-4}\,h = \ln(0.85), \quad h = 1.402\times10^3\ m$$

Answer

Approximate method: If $m_{balloon} + m_{He} << m_{load}$ then, the equilibrium conditions are:

$$m_{load} \approx \rho_0 V \qquad\qquad 0.80(m_{load}) \approx \rho V$$

$$\rho/\rho_0 \approx 0.80 = \exp[-Mgh/RT]$$
$$= \exp[28.8 \text{ g mol}^{-1} \times 1 \text{ kg}/10^3 \text{ g} \times 9.80665 \text{ m s}^{-2} \times h \text{ m} /8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \times 293.15 \text{ K}]$$

$0.80 \approx \exp[1.159\times10^{-4} h]$ or $1.159\times10^{-4} h \approx \ln(0.80)$, $\therefore h \approx 1.926\times10^3$ m

5. A balloon having a capacity of 10,000 m^3 is filled with helium at 20°C and 1 atm pressure. If the balloon is loaded with 80% of the load that it can lift at ground level, at what height will the balloon come to rest? Assume that the volume of the balloon is constant, the atmosphere isothermal, 20°C; the molecular weight of air is 28.8 and the ground level pressure is 1 atm. The mass of the balloon is 1.3×10^6 g.

6. Composition of the atmosphere as function of height above ground level

Equation	Basis for the equation	Eq. #
$p_i / p_{i0} = \exp [-M_i g\ z/RT]$ joule = kg $m^2\ s^{-2}$ use M in kg mol^{-1} and z in m or equivalently, use M in g mol^{-1} and z in km with $g = 9.8\ m\ s^{-2}$ so that Mgz is in J mol^{-1} thus use R = 8.31451 J $mol^{-1}\ K^{-1}$	Relation of partial pressure of a gas at height z relative to its partial pressure at ground level depends on molar mass of gas, as derived in lecture notes part 1 RT has units of energy, has to have same units as Mgz Use $g = 9.8\ m\ s^{-2}$	1
For N_2, molar mass = 2(14) = 28 g mol^{-1} $p_{N2\ 0}$ = 0.7809 (1 atm) = 0.7809 atm $p_{N2} / p_{N2\ 0}$ $= \exp [-28\ g\ mol^{-1} \bullet z \bullet 9.8\ m\ s^{-2} /(8.31451\ J\ mol^{-1}\ K^{-1} 298\ K]$ $= \exp [-28\ g\ mol^{-1} \bullet z\ km \bullet 0.003955]$	At ground level p_{tot} = 1 atm, T = 298 K p_i = mole fraction$\bullet$ p_{tot}	2 3
p_{i0} = mole fraction $\bullet$1 atm At z km $p_i = p_{i0} \exp[[-M\ g\ mol^{-1} \bullet z\ km \bullet 0.003955]$ p_{tot} at z km = sum over p_i Using this p_{tot} we can find the mole fractions at z km by mole fraction = p_i / p_{tot} All **answers** are in the table below.	How to fill the table This is the p_{i0} we will use for all calculations at different heights z. Note that in the earth's atmosphere T is different at different heights above ground level, but we will ignore this and use T = 298 K Note that the mol % of heavier gases are going down, whereas the mol % of lighter gases (He, Ne) are going up	4 5 6 7 8

Gas	mole % at grd level	p_{i0} atm	molar mass	p_i atm at 50 km	mole % at 50 km	p_i atm at 100 km	mole % at 100 km
N_2	78.09	0.7809	28	0.003075	89.01	1.211×10^{-5}	87.70
O_2	20.93	0.2093	32	0.000374	10.82	6.67×10^{-7}	4.83
Ar	0.93	0.0093	39.95	3.44×10^{-6}	0.0996	1.28×10^{-9}	0.009
CO_2	0.03	0.0003	44	4.99×10^{-8}	0.0015	8.31×10^{-12}	6×10^{-5}
Ne	0.0018	1.8×10^{-5}	20.18	3.33×10^{-7}	0.0098	6.15×10^{-9}	0.044
He	0.0005	5×10^{-6}	4.003	2.27×10^{-6}	0.0657	1.028×10^{-6}	7.44
p_{tot}		1 atm		0.003455		1.381×10^{-5}	

7. (a) Total number of molecules

Equation	Basis for the equation	Eq. #
$p_i / p_{i0} = \exp[-M_i g\, z/RT]$	Using the barometric formula	1
Let A = area of earth's surface Assume p_{i0} for the gas throughout $z = 0$ up to $z = RT/Mg$	Given	2
This means number density of gas, is constant = N_{i0} molecules L^{-1}, throughout the volume, the volume $V = A(RT/M_i g)$	$V = A\bullet z$	3
Total number of molecules, N_i molecules= N_{i0} molecules $L^{-1}\bullet V$ L $N_i = N_{i0}\, ART/M_i g$ **Q.E.D.**	Using V from Eq 3	4
On the other hand, total number of molecules in the atmosphere can be obtained by integrating from $z = 0$ to ∞ Let dN_i = number density in the slice between z and z+dz $dN_i = AN_{i0}\exp[-M_i g\, z/RT]\, dz$	Use the barometirc formula in Eq 1 for how number density drops off with height	5
$N_i = \int dN_i$ $= \int_0^\infty AN_{i0}\exp[-M_i g\, z/RT]dz$	Integrate over all these dN_i	6
$= AN_{i0}\exp[-M_i g\, z/RT]/(-M_i g/RT) \Big\vert_0^\infty$ $= \{-AN_{i0}RT/M_i g\} \bullet \exp[-M_i g\, z/RT] \Big\vert_0^\infty$ $= \{-AN_{i0}RT/M_i g\} \bullet [0-1]$		7
$N_i = AN_{i0}RT/M_i g$ **Q.E.D.**	This is the same total number of molecules as for a uniform partial pressure at ground level through a height $RT/M_i g$ and no molecules above this height. (That is, Eq 8 is the same as Eq 4)	8

7. (b) Total mass of earth's atmosphere

Equation	Basis for the equation	Eq. #
$N_i = (ART/g)(N_{i0}/M_i)$ is the total number of molecules of type *i* in the atmosphere. mass of *i* in the atmosphere $= (N_i / N_{Avo})M_i$	Derived in 7(a) above	1 2
m_{tot}= all mass $= (1/N_{Avo})\ \Sigma_i N_i M_i$ $= (1/N_{Avo})\ \Sigma_i (ART/g)N_{i0}$ $= (A/g)RT\ \Sigma_i N_{i0}/N_{Avo}$ $RT\ \Sigma_i N_{i0}/N_{Avo}$ gives total pressure at ground level, that is, p_0. Total mass of the atmosphere is then $m_{tot} = (A/g)p_0$ **Q.E.D.**	Summing up over all *i* and Using Eq 2 Using N_i from Eq 1 Rearranging $\Sigma_i N_{i0}/N_{Avo}$ is mol L^{-1} at ground level Using ideal gas law $p = RT(n/V)$ Substituting p_0 into Eq 4	3 4 5
OR ELSE $F = (\Sigma_i N_i M_i)\bullet g = m_{tot}\bullet g$ also $F = p_0A$ $m_{tot}\bullet g = p_0A$ $m_{tot} = p_0A/g$ **Q.E.D.**	Fundamental equations for Force	

7. (c) Total mass of earth's atmosphere in grams

Equation	Basis for the equation	Eq. #
$m_{tot} = (A/g)p_0$	Derived in part **7 (b)**	1
$r = 6.37\times10^8$ cm	Given radius of earth	2
$A = 4\pi r^2 = 4(3.14159)(6.37\times10^8)^2$ $= 509.9\times10^{16}$ cm^2	surface area of a sphere	3
$g = 980$ cm s^{-2}	Acceleration of gravity constant	4
$p_0 = 1$ atm = 101325 Pa = 101325 kg m^{-1} s^{-2}	1 Pa is kg m^{-1} s^{-2}	5
$m_{tot} = (A/g)p_0 = 509.9\times10^{16}$ cm^2 /980 cm s^{-2} •101325 kg m^{-1} s^{-2} •10^{-2} m/cm $m_{tot} = 527.2\times10^{16}$ kg **Answer**		

8. Ar from Julius Caesar's last breath

Equation	Basis for the equation	Eq. #
last breath = 500 cm^3 at 300 K 1 atm last breath $n_{tot} = \frac{(0.500\ L)(1\ atm)}{(0.0820578)\ 300\ K}$ n_{tot} = 0.02031 mol 1 mole % Ar : 0.0002031 mol Ar	Given Assuming ideal gas behavior	1 2
0.0002031 mol Ar distributed throughout earth's atmosphere = 0.0002031mol •6.022×10^{23} atoms mol^{-1} = 1.22×10^{20} Ar atoms	N_{Avo}	3
At z = RT/M_{Ar} g a uniform distribution of gas throughout the volume will have the equivalent Ar content as entire atmosphere z = (8.31451 kg $m^{-1}s^{-2}$ m^3 K^{-1} mol^{-1}) •(300 K)/0.03995 kg mol^{-1} 9.80 m s^{-2} z = 6371 m	We proved this in problem **7 (a)** 1 Pa is kg m^{-1} s^{-2} Atomic mass of Ar = 0.03995 kg mol^{-1} g = 9.80 m s^{-2}	4
Volume = A•z A = 509.9×10^{16} cm^2 z = 6371×10^2 cm Volume = 3.248573 $\times10^{24}$ cm^3 has 1.22 $\times10^{20}$ Ar atoms	From **7 (c**) we found surface area of the earth	5
To get at least one Ar atom we need to inhale at least 3.249×10^{24} cm^3 /1.22 $\times10^{20}$ = 2.663×10^4 cm^3 One inhalation is 500 cm^3 2.663×10^4 cm^3 / 500 cm^3 = 53 inhalations **Answer**	Given	6