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1.1 THE ATMOSPHERE AND AIR POLLUTANTS

1.1.1 ATMOSPHERIC DATA

1.1-1A AVERAGE COMPOSITION OF DRY AIR

For most applications the following accepted values for the average composition of the atmosphere are adequate. These values are for sea level or any land elevation. Proportions remain essentially constant to 50 000 ft altitude.

Gas	Molecular weight	Percentage by volume, mol fraction	Percentage by weight
Nitrogen	N ₂ = 28.016	78.09	75.55
Oxygen	O ₂ = 32.000	20.95	23.13
Argon	Ar = 39.944	0.93	1.27
Carbon dioxide	CO ₂ = 44.010	0.03	0.05
		100.00	100.00

For many purposes the percentages 79% N₂–21% O₂ by volume and 77% N₂–23% O₂ by weight are sufficiently accurate, the argon being considered as nitrogen with an adjustment of molecular weight to 28.16.

Other gases in the atmosphere constitute less than 0.003% (actually 27.99 parts per million by volume), as given in the following table.

1.1-1B MINOR CONSTITUENTS OF DRY AIR

Gas	Molecular weight	Parts per million	
		By volume	By weight
Neon	Ne = 20.183	18.	12.9
Helium	He = 4.003	5.2	0.74
Methane	CH ₄ = 16.04	2.2	1.3
Krypton	Kr = 83.8	1.	3.0
Nitrous oxide	N ₂ O = 44.01	1.	1.6
Hydrogen	H ₂ = 2.0160	0.5	0.03
Xenon	Xe = 131.3	0.08	0.37
Ozone	O ₃ = 48.000	0.01	0.02
Radon	Rn = 222.	(0.06 × 10 ⁻¹²)	

Minor constituents may also include dust, pollen, bacteria, spores, smoke particles, SO₂, H₂S, hydrocarbons, and larger amounts of CO₂ and ozone, depending on weather, volcanic activity, local industrial activity, and concentration of human, animal, and vehicle population. In certain enclosed spaces the minor constituents will vary considerably with industrial operations and with occupancy by humans, plants, or animals.

The above data do not include water vapor, which is an important constituent in all normal atmospheres.

Source: *Handbook of Tables for Applied Engineering Science*, R.E. Bolz and G. L. Tuve, Eds., The Chemical Rubber Co., Cleveland, O., 1970, p. 533.

1.1.2 AIR POLLUTANT PROPERTIES

Air pollution is the presence in the ambient air of one or more contaminants, which can be naturally occurring or man-made. The quantities, characteristics, and duration of these contaminants are, or may tend to be, injurious to human, plant, and animal life or may interfere with the enjoyment of life or use of property.

1.1-2 CLASSIFICATION OF AIR POLLUTANTS

Major classes	Subclasses	Typical members
Inorganic gases	Oxides of nitrogen (NO_x) Oxides of sulfur (SO_x) Other inorganics	Nitrogen dioxide, nitric oxide Sulfur dioxide, sulfuric acid Ammonia, carbon monoxide, chlorine, hydrogen fluoride, hydrogen sulfide, ozone
Organic gases	Hydrocarbons Aldehydes, ketones Other organics	Benzene, butadiene, butene, ethylene, isooctane, methane Acetone, formaldehyde Acids, alcohols, chlorinated hydrocarbons, peroxyacyl nitrates, polynuclear aromatics
Aerosols	Solid particulate matter Liquid particulates	Dusts, smoke Fumes, oil mists, polymeric reaction-products

Source: *Environmental Biology*, P.L. Altman and D.S. Dittmer, Eds., Federation of American Societies for Experimental Biology, Bethesda, Md., 1966. With permission.



1.1-3 Characteristics of particles and particle dispersoids.

1.1-4 MOBILITIES OF ATMOSPHERIC IONS

Type of ions	Average mobility, cm ² /volt sec	Approximate diameter, μ m
Small +	1.4 ^a , 1.1 ^b	0.001–0.005
Small –	1.9 ^a , 1.2 ^b	0.001–0.005
Intermediate	0.05	0.005–0.015
Large	0.000 4	0.015–0.10
Fog droplets	$0.5 \times 10^{-6} n^c$	2–70

^aIn dry air.^bIn moist air.^cWith n charges.

GENERAL REFERENCES

1. H. Neuberger, "Introduction to Physical Meteorology," Pennsylvania State University Press, University Park, Pa., 1951.
2. V.A. Gordiyeff, *Arch. Ind. Health*, 14:471, 1956.

1.1-5 PROPERTIES OF SOME TYPICAL AEROSOLS

Type of dispersal system	Size range of particles diameter, μ m	Terminal velocity (cm/sec) due to gravity settling in air, 20°C and 1 atm
Raindrops	5 000–500	Turbulent motion $v_t = k_1 pD$ for particles down to about 1 000 μ m
Natural mist	500–40	p = particle density
Natural fog	40–1.0	D = particle diameter, μ m
Dust		
Foundry sand	2 000–200	
Ground limestone, fertilizers	800–30	Intermediate region for particles between 1 000–100 μ m
Sand tailings from flotation	400–20	$v_i = k_2 p^{2/3} D$
Pulverized coal	400–10	Stokes' law for streamline region, applicable to particles from 100–1.0 μ m
Ground sulfide ore for flotation	200–4	$v_s = KpD^2/n$
Foundry shake-out dust	200–1	
Cement	150–10	n = coefficient of viscosity of air, poises
Fly ash	80–3	$v_s = k_3 pD^2$
Silica dust in silicosis	10–0.5	
Pigments	8–1.0	
Pollens	60–20	
Plant spores	30–10	
Bacteria	15–1.0	

1.1-5 PROPERTIES OF SOME TYPICAL AEROSOLS (continued)

Type of dispersal system	Size range of particles diameter, μm	Terminal velocity (cm/sec) due to gravity settling in air, 20°C and 1 atm										
Fumes and Mist												
Metallurgical fumes	100–0.1	Cunningham's correction for particles in range 1.0–0.10 μm										
H ₂ SO ₄ concentrator mist	10–1.0											
Alkali fume	2–0.1	$v_c = v_s \left(\frac{1 + 1.72 l}{D} \right)$										
SO ₃ mist	3–0.5	l = mean free path of gas molecules, μm										
NH ₄ Cl fume	2–0.1											
Zinc oxide fume	0.3–0.03	$v_c = v_s \left(\frac{1 + 0.172}{D} \right)$ in air										
Smokes												
Oil smoke	1.0–0.03	Velocity due to Brownian. Motion exceeds velocity of gravity settling for particles less than 0.1 μm										
Rosin smoke	1.0–0.01											
Tobacco smoke	0.15–0.01											
Carbon smoke	0.2–0.01	Einstein equation										
Normal impurities in quiet atmosphere	1.0–0.01	$x = k_4 t/D$ x = average displacement in cm of spherical particle in air in time, t sec										
		<table><tr><th>Spheres</th><th>Irregular shape</th></tr><tr><td>$k_1 = 24$</td><td>16</td></tr><tr><td>$k_2 = 0.41$</td><td>0.26</td></tr><tr><td>$k_3 = 0.0030$</td><td>0.002</td></tr><tr><td>$k_4 = 0.00068$</td><td>—</td></tr></table>	Spheres	Irregular shape	$k_1 = 24$	16	$k_2 = 0.41$	0.26	$k_3 = 0.0030$	0.002	$k_4 = 0.00068$	—
Spheres	Irregular shape											
$k_1 = 24$	16											
$k_2 = 0.41$	0.26											
$k_3 = 0.0030$	0.002											
$k_4 = 0.00068$	—											

Sources: C.E. Miller, "Pointers on Selecting Equipment for Industrial Gas Cleaning," *Chem. Metallurg. Eng.*, 45:132, 1938; and L. Silverman, "What Process Wastes Cause Air Pollution?" *Chem. Eng.*, 5(58):132, 1951.

1.1-6 AIRBORNE PARTICLE SHAPES

Shape	Examples
Spherical	Smoke, pollen, fly ash
Irregular	Mineral
Cubical	Cinder
Flakes	Mineral, epidermis
Fibrous	Lint, plant fiber
Condensation flocs	Carbon, smoke, fume
Loose flocs	Magnesium oxide
Platelet	Mica
Solids of revolution	
Ellipse	
Short right circular cylinder	Asbestos
Needles	Talc
Chains	Carbon black, smokes

GENERAL REFERENCES

1. *Air Pollution Manual*, Part II, Control Equipment, American Industrial Hygiene Association Detroit, Mich., 1968.
2. K.T. Whitby *et al.*, *Heat, Piping, Air Cond.*, 29:185, 1957.

1.1-7 PARTICLE DENSITIES
FOR AGGLOMERATES

Material	Floc density, g/cc	Normal density, g/cc
Aluminum oxide	1.18	3.70
Antimony trioxide	0.63	5.57
Arsenic trioxide	0.91	3.7
Cadmium oxide	0.51	6.5
Lead monoxide	0.62	9.36
Magnesium oxide	0.35	3.65
Mercury	1.70	13.6
Silver	0.94	10.5
Stannic oxide	0.25	6.71

REFERENCE

1. G.R. Whytlaw and H.H. Patterson, *Smoke*, Edward Arnold and Co., London, England, 1932.

1.1-8 FREE NONVOLATILE FATTY ACIDS AS DETERMINED IN PARTICULATE MATTER OF AIR POLLUTANT SAMPLES^a

	Sampled in Detroit, Mich., on freeway-interchange, October–November 1963		Sampled in New York, N.Y., at high-traffic city location, February 1964	
	Per cent in acidic portion ^b	μg per 1 000 m ³ air	Per cent in acidic portion ^b	μg per 1 000 m ³ air
Saturated Acids				
Lauric	0.29	13.7	0.43	39.4
Myristic	0.47	17.5	0.53	48.6
Palmitic	3.10	146.8	2.40	220.0
Stearic	2.42	113.7	1.50	137.5
Behenic	1.31	61.6	1.30	119.2
Unsaturated Acids				
Oleic	0.68	32.2	1.34	122.8
Linolenic	0.56	26.5	Trace	Trace

^aValues represent averages from three analyses.

^bAs defined in separation scheme for organic particulate matter, E.L. Wynder and D. Hoffmann, *J. Air Pollut. Contr. Assn.*, 15:155, 1965.

Source: D. Hoffman and E.L. Wynder, in *Air Pollution*, A.C. Stern, Ed., Vol. 2, Academic Press, New York, N.Y., 1968, p. 221. With permission.

1.1-9 CHEMICAL ANALYSIS AND PHYSICAL PROPERTIES OF FLY ASH

Per Cent by Weight as Collected Dried

Constituent	Utilities	Industrials
Carbon, as C	0.37–36.2	2.4–64
Iron, Fe ₂ O ₃ or Fe ₃ O ₄	2.0–26.8	10.6–43.6
Magnesium, as MgO	0.06–4.77	0.10–1.49
Calcium, as CaO	0.12–14.73	1.92–11.8
Aluminum, as Al ₂ O ₃	9.81–58.4	10.0–21.0
Sulfur, as SO ₃	0.12–24.33	0.66–28.0
Titanium, as TiO ₂	0.50–2.8	0.22–3.81
Carbonate, as CO ₃	0.05–2.6	0.05
Silica, as SiO ₂	17.3–63.6	25.0–46.0
Phosphorus, as P ₂ O ₅	0.07–47.2	0.05–1.93
Undetermined	0.08–18.9	—
Other Tests		
Hydrogen ion concentration, pH	4.7–11.7	6.3–12
Apparent specific gravity	0.8–3.0	0.77–1.45
Retained on 325-mesh screen (44 μm), %	8–95	29–84
Through 325-mesh screen (44 μm), %	5–92	16–71
Fusion temperature of ash, °F	1 910–3 000	1 980–2 900

REFERENCE

1. *Air Pollution Abatement Manual*, Manufacturing Chemists' Association, Inc. Washington, D.C.

1.1-10 MINERAL ASSEMBLAGES IN ATMOSPHERIC DUSTS

SYMBOLS:

- | | |
|---------------|-------------|
| 1—Talc | 4—Mica |
| 2—Quartz | 5—Amphibole |
| 3—Plagioclase | 6—Chlorite |

Sample	Location	Collection date	Solid phase concentration, mg/l	Mineral found
Rain	San Diego, Calif. 32°50' N 117°16' W	7 Nov. 1966	1.9	1, 2, 3
		7 Nov. 1966		1, 2, 3, 4, 5
		5 Dec. 1966		1, 2, 3, 4, 5, 6
		13 March 1967	2.5	1, 2, 3, 4, 5
		13 March 1967	0.4	2, 3
Atmospheric dust	San Diego, Calif.	17 Nov. 1966		1, 2, 3, 4, 5, 6
		15 Feb. 1967		1?, 2, 3, 4, 5, 6
		16 Feb. 1967		2, 3, 4
		17 Feb. 1967		2, 3, 4, 5
		21 Feb. 1967		2, 3, 4, 5
		22 Feb. 1967		2, 3, 4, 5
		23 Feb. 1967		1, 2, 3, 4, 5
		24 Feb. 1967		2, 3, 4
		27 Feb. 1967		1, 2, 3, 4, 5
		28 Feb. 1967		1, 2, 3, 4, 5
		6 March 1967		2, 3, 4, 5?
		7 March 1967		1, 2, 3, 4, 5, 6
		8 March 1967		1, 2, 3, 4, 5, 6
		9 March 1967		2, 3, 4, 5
	Scotts Bluff, Neb. 41°52' N 103°40' W	28 April 1966		1, 2, 3, 4
		28 April 1966		1, 2, 3, 4
		10 May 1966		1, 2, 3, 4
	Minicoy Island, India 8°20' N 73°01' E	1963		1, 2, 3, 4, 6
		1965		1, 2, 3, 4, 6
Dust storm	Bagdad, Iraq 33°20' N 44°26' E	17 Feb. 1966		1?, 2, 3, 4, 6
Glacier ^a	Yukon 60°45' N 139°30' W	1967	0.8	1, 2, 3, 4, 5, 6
		1961	0.5	1?, 2, 3, 4, 5, 6
		1955	0.5	1?, 2, 3, 4, 5, 6
		1947	0.3	2, 3, 4, 6
		1936	0.5	1?, 2, 3, 4, 6
	Orizaba, Mexico 19°01' N 97°15' W	1962-64	89	1, 2, 3, 4, 5, 6
		1957-62	734	1, 2, 3, 4, 5, 6
		1952-57	17	1, 2, 3, 5, 6
		1942-47	19	1, 2, 3, 4, 5
		1937-42	49	1, 2, 3, 4, 5, 6
	Popocatepetl, Mexico 19°01' N 98°37' W	1960-67	302	1, 2, 3, 4, 5
		1949-53	38	1, 2?, 3
		1943-46	159	1, 2, 3, 4, 5

1.1-10 MINERAL ASSEMBLAGES IN ATMOSPHERIC DUSTS (continued)

Sample	Location	Collection date	Solid phase concentration, mg/l	Mineral found
Glacier (continued)	Washington 47° 52' N 123° 36' W	1967	1.8	1, 2, 3, 4, 5, 6
		1962	1.9	1, 2, 3, 4, 5, 6
		1950	2.4	1, 2, 3, 4, 5, 6
		1940	1.8	1, 2, 3, 4, 5, 6
		1932	9.9	2, 3, 4, 5, 6
		1925	3.7	2, 3, 4, 5, 6
		1916	10.1	2, 3, 4, 5, 6
	Palomar 33° 24' N 116° 53' W	1965	2.2	1, 2, 3, 4, 5, 6
			1.4	1, 2, 3, 4, 5, 6
Snow samples	Julian 33° 04' N 116° 36' W	1965	2.9	1, 2, 3, 4, 5, 6
	Mount Rainier 46° 51' N 121° 45' W	1965	30	1, 2, 3, 4, 6
	Canadian Rockies 52° 55' N 118° 10' W	1967	2.7	2, 3, 4, 5, 6

^aFor the glacial materials the collection date is the time of accumulation of the strata sampled.

Source: Reprinted with permission from H. Griffin, *Environ. Sci. Technol.*, 1(11):925, November 1967. Copyright 1967, American Chemical Society.

1.1-11 NATURAL CHARGES ON REPRESENTATIVE PARTICLE DISPERSOIDS

Dispersoid	Method of dispersal	Charge distribution, %			Specific charge, esu/g	
		Positive	Negative	Neutral	Positive	Negative
Raw cement mix	Agitation in air stream	35	35	30	0.7×10^4	0.7×10^4
Gypsum dust (Schumacher Plant, L.A.)	Grinding, drying in flash dryer	44	50	6	1.6	1.6
		40	50	10	0.2	0.4
Copper smelter dust (Tooele, Utah)						
Fly ash (Stateline, Chicago)		31	26	43	1.9	2.1
Fly ash (Rochester Electric)		40	44	16	4.8	4.2
Gypsum dust (U.S. Gypsum, Phila., Pa.)	Grinding and drying in rotary kiln				0.2	0.2
Lead fume (Tooele, Utah)	Dwight-Lloyd sintering machine	25	25	50	0.003	0.003
Laboratory oil fume	Condensation from vapor	0	0	100	0	0

REFERENCE

1. H.J. White, "Report on Electrical Characteristics of Industrial Dispersoids," Unpublished report, Research Corporation, 1941.

1.1-12 MOST COMMON
AEROALLERGENIC FUNGI^{1,2}

<i>Alternaria</i>	<i>Hormodendrum</i>
<i>Aspergillus</i>	<i>Macrosporium</i>
<i>Botrytis</i>	<i>Penicillium</i>
<i>Cladosporium</i>	<i>Phoma</i>
<i>Curvularia</i>	<i>Pullularia</i>
<i>Epicoccum</i>	<i>Spondylocadium</i>
<i>Fusarium</i>	<i>Stemphyllum</i>
<i>Helminthosporium</i>	

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1. R.H. Criepe, R.A. Teufel, and C.S. Miller, "Fungicidal Agents in the Treatment of Allergy to Molds," *J. Allergy*, 29:258, 1968.
2. M.C. Harris and N. Shure, *Sensitivity Chest Diseases*, F.A. Davis Company, Philadelphia, Pa., 1964.

1.1-13 RATE CONSTANTS FOR ATOMIC OXYGEN
AND ATMOSPHERIC POLLUTANTS

Reaction	Rate constant at 300°K	Reference
$O + O_3 + M \rightarrow O_3 + M$	$1.5 \times 10^8 \text{ l}^2 \text{ mol}^{-2} \text{ sec}^{-1}$	1-4
$O + NO_2 \rightarrow NO + O_2$	$5.3 \times 10^9 \text{ l mol}^{-1} \text{ sec}^{-1}$	5
$O + NO_2 + M \rightarrow NO_3 + M$	$4.2 \times 10^{10} \text{ l}^2 \text{ mol}^{-2} \text{ sec}^{-1}$	5
$O + NO + M \rightarrow NO_2 + M$	$2.3 \times 10^{10} \text{ l}^2 \text{ mol}^{-2} \text{ sec}^{-1}$	5
$O + SO_2 + O_2 \rightarrow SO_3 + O_2$	$2.7 \times 10^9 \text{ l}^2 \text{ mol}^{-2} \text{ sec}^{-1}$	6

Source: Reprinted with permission from A.P. Altshuller and J.P. Bufalini, "Photochemical Aspects of Air Pollution: A Review," *Environ. Sci. Technol.*, 5(1):39, 1971. Copyright 1971, American Chemical Society.

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5. E.A. Schuck, E.R. Stephens, and R.R. Schrock, presented at the 59th Annual Meeting of Air Pollution Control Association, San Francisco, Calif., June 20-24, 1966.
6. M.F.R. Mulcahy, J.R. Steven, and J.C. Ward, *J. Phys. Chem.*, 71:2124, 1967.