Review of Basic Chemistry and Physics Related to Atmospheric Pollution Research

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Physics

Common Physical Characteristics of Gases

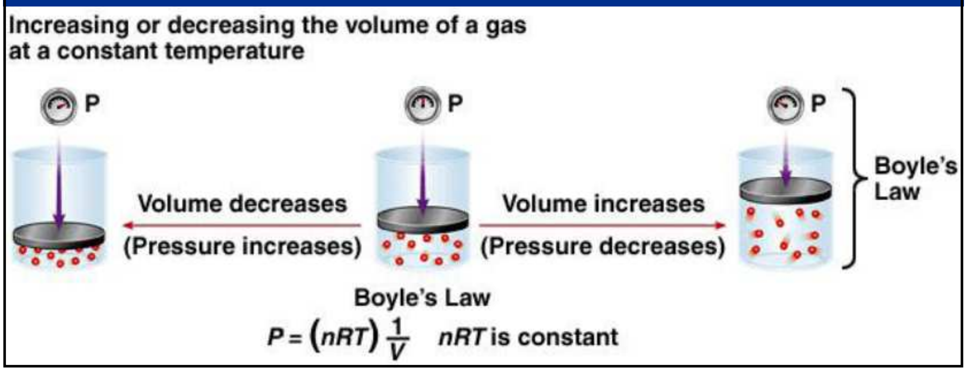
- 氣體密度低：Gases have much lower densities than liquids and solids (~2 g/L vs. 2 g/mL).
- 氣體可以壓縮：Gases are the most compressible of the states of matter.
- 氣體可以均勻混和：Gases will mix evenly and completely when confined to the same container.
- 氣體在容器中均勻分布：Gases assumes the volume and shape of their containers.
- 氣體對器壁產生均勻壓力

The Gas Laws

- 下列定律連結氣體的P(pressure)、V(volume)、T(temperature)、n(moles or amount)等四項性質
- Boyle's Law: The pressure-volume relationship
- Charles's Law: The temperature-volume relationship
- Gay-Lussac's Law: The temperature-pressure relationship
- Combined Gas Law
- Avogadro's Law: The volume-amount relationship
- The Ideal Gas Equation
- Henry's Law
- Raoult's Law

Boyle's Law(波以耳定律)

- Boyle's Law: the pressure of a fixed amount of gas maintained at constant temperature is inversely proportional to the volume of the gas.
- 定量氣體在定溫時，其體積與壓力間呈反比關係。
- $P \propto 1/V$ (at constant n and T)



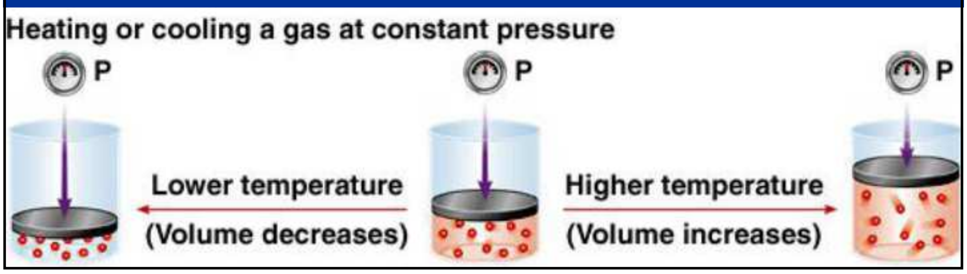
Boyle's Law

At constant temperature, for a fixed amount of gas:

- $P \times V = k$, k is a constant
- $P_1 \times V_1 = P_2 \times V_2$
- $V_2 = V_1 \times (P_1/P_2)$

Charles's Law(查理定律)

- Charles's Law: the volume of a fixed amount of gas maintained at constant pressure is proportional to the absolute temperature of the gas.
- 定量氣體在定壓下，其體積與溫度間呈正比關係。
- $V \propto T$ (at constant n and P)

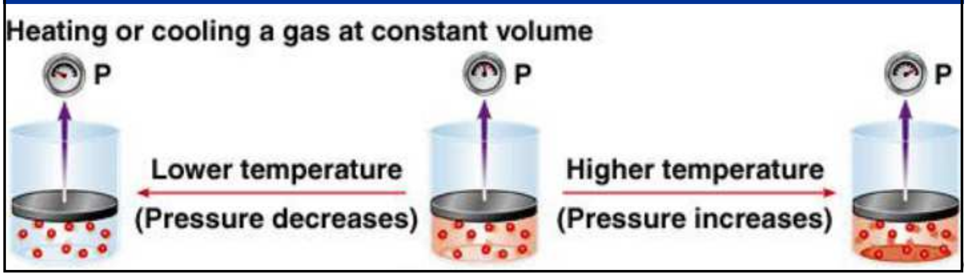


Charles's Law(查理定律)

- At constant pressure, for a fixed amount of gas:
  - $V = k \times T$ or $V/T = k$, k is a constant
  - $V_1/T_1 = V_2/T_2$

Gay-Lussac's Law(給呂薩克定律)

- Gay-Lussac's Law: the pressure of a fixed amount of gas maintained at constant volume is proportional to the absolute temperature of the gas.
- 定量氣體在固定體積時，其壓力與溫度間呈正比關係。
- $P \propto T$ (at constant n and V)



Gay-Lussac's Law(給呂薩克定律)

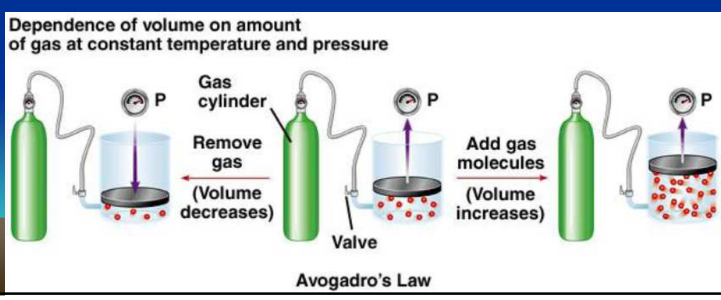
- At constant pressure, for a fixed amount of gas:
  - $P = k \times T$ or $P/T = k$, k is a constant
  - $P_1/T_1 = P_2/T_2$

Combined Gas Law(聯合氣體定律)

- Combined Gas Law: For a fixed amount of gas, Boyle's Law, Charles's Law, and Gay-Lussac's Law can be combined in the following form:
- $P \times V = k \times T$ or $(P \times V)/T = k$, k is a constant
- $(P_1 \times V_1)/T_1 = (P_2 \times V_2)/T_2$

Avogadro's Law(亞佛加厥定律)

- Avogadro's Law: At constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas presented.
- 在定溫定壓下，氣體體積與莫耳數成正比。
- $V \propto n$ (at constant P and T)



Avogadro's Law(亞佛加厥定律)

- At constant pressure and temperature:
  - $V = k \times n$, k is a constant
  - $V_1/n_1 = V_2/n_2$

Ideal Gas Law(理想氣體定律)

- Boyle's Law:
  - $V \propto 1/P$ (at constant n and T)
- Charles's Law:
  - $V \propto T$ (at constant n and P)
- Avogadro's Law:
  - $V \propto n$ (at constant P and T)
- Combine the above expressions, we get
  - $V \propto (n \times T)/P$

Ideal Gas Law

- $V = R \times ((n \times T)/P)$, R is the universal gas constant
- Ideal gas law: $P \times V = n \times R \times T$
- R = 0.082 L•atm•mol^{-1}•K^{-1}

R with different units	
8.31451	J K^{-1} mol^{-1}
8.20578 x 10^{-2}	L atm K^{-1} mol^{-1}
8.31451 x 10^{-2}	L bar K^{-1} mol^{-1}
8.31451	Pa m^3 K^{-1} mol^{-1}
62.364	L Torr K^{-1} mol^{-1}
1.98722	cal K^{-1} mol^{-1}

Ideal Gas Law

$$P \times V = n \times R \times T$$

- Ideal gas law describes the relationship among the four variable (P, V, T, and n) of ideal gas.
- The molecules of an ideal gas do not attract or repel one another, and their volume is negligible.

Example 5.5 Sulfur hexafluoride (SF_6) is a colorless, odorless, very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 69.5°C.

Reasoning and Solution This problem provides information about the number of moles, volume, and temperature of a gas, but no change in any of the quantities occurs. Therefore, to calculate the pressure we can use the ideal gas equation, which can be rearranged to give

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

$$= \frac{(1.82\ \text{mol})(0.0821\ \text{L}\cdot\text{atm/K}\cdot\text{mol})(69.5 + 273)\ \text{K}}{5.43\ \text{L}}$$

$$= 9.42\ \text{atm}$$

Ideal Gas Law

- Standard temperature and pressure (STP): 0°C (or 273 K) and 1 atm
- At STP, 1 mole of any gas has a volume of 22.4 L.

Example 5.6 Calculate the volume (in liters) occupied by 7.40 g of NH_3 at STP.

Reasoning and Solution Recognizing that 1 mole of an ideal gas occupies 22.41 L at STP, we write

$$V = 7.40\ \text{g NH}_3 \times \frac{1\ \text{mol NH}_3}{17.03\ \text{g NH}_3} \times \frac{22.41\ \text{L}}{1\ \text{mol NH}_3}$$

$$= 9.74\ \text{L}$$

Ideal Gas Law

- $(P_1 \times V_1)/(n_1 \times T_1) = (P_2 \times V_2)/(n_2 \times T_2)$

Example 5.7 A small bubble rises from the bottom of a lake, where the temperature and pressure are 8°C and 6.4 atm, to the water's surface, where the temperature is 25°C and pressure is 1.0 atm. Calculate the final volume (in mL) of the bubble if its initial volume was 2.1 mL.

Reasoning and Solution Note that this problem involves the change of temperature, pressure, and volume, but not the number of moles of a gas. Thus we can use Equation (5.8) to calculate the final volume. We start by writing

Initial conditions	Final conditions
$P_1 = 6.4$ atm	$P_2 = 1.0$ atm
$V_1 = 2.1$ mL	$V_2 = ?$
$T_1 = (8 + 273)$ K $= 281$ K	$T_2 = (25 + 273)$ K $= 298$ K

The amount of the gas in the bubble remains constant, so that $n_1 = n_2$. To calculate the final volume, V_2, we rearrange Equation (5.8) as follows:

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

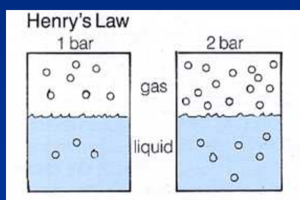
$$= 2.1\ \text{mL} \times \frac{6.4\ \text{atm}}{1.0\ \text{atm}} \times \frac{298\ \text{K}}{281\ \text{K}}$$

$$= 14\ \text{mL}$$

Thus, the bubble's volume increases from 2.1 mL to 14 mL because of the decrease in water pressure and the increase in temperature.

Henry's Law(亨利定律)

- Henry's Law: At constant temperature, the mass of any gas that will dissolve in a given volume of a liquid is directly proportional to the pressure that the gas exerts above the liquid.
- 在定溫下，某氣體溶解於某溶劑中的體積莫耳濃度和該溶液達成平衡的氣體分壓成正比。



- $P_{gas} = K_H \times C_{eq}$ or $C_{eq} = K'_H \times P_{gas}$
  - where P_{gas} is partial pressure of the gas above liquid in equilibrium,
  - $C_{eq.}$ is the equilibrium concentration of gas dissolved in liquid
  - K_H (or K'_H) is the Henry's law constant for gas at given temperature; varies with temperature

EXAMPLE 2-13 The concentration of carbon dioxide in water at 20°C is 1.00×10^{-5} M. The Henry's constant for carbon dioxide dissolution in water is 3.91×10^{-2} M atm^{-1} at 20°C. What is the partial pressure of CO_2 in the air?

Solution With Henry's law given in units of molar per atmosphere ($M \cdot atm^{-1}$), we must write the proportionality equation as

$$C_{CO_2} = K'_H P_{CO_2}$$

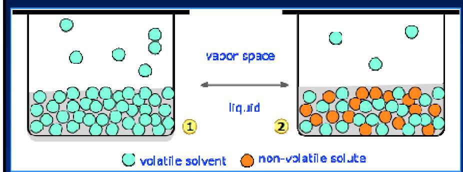
or

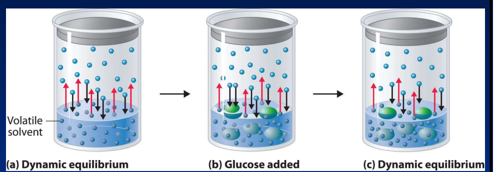
$$P_{CO_2} = \frac{C_{CO_2}}{K'_H}$$

Thus,

$$P_{CO_2} = \frac{(1.00 \times 10^{-5}\ M)}{3.91 \times 10^{-2}\ M \cdot atm^{-1}} = 2.56 \times 10^{-4}\ atm$$

Raoult's Law(拉午耳定律)





- If a solute is non-volatile, the vapor pressure of its solution is always less that that of the pure solvent.
- Raoult's Law: The partial pressure of a solvent over a solution (P_i) is given by the vapor pressure of the pure solvent (P^o) times the mole fraction of the solvent in the solution (X_i).
- 描述溶液的蒸氣壓與其濃度的關係。溶液的組成決定了溶液的蒸汽壓。根據拉午耳定律，溶質為非揮發性非電解質的稀薄溶液，其蒸氣壓和溶劑的莫耳分率成正比。
- $P_i = X_i \times P^o$

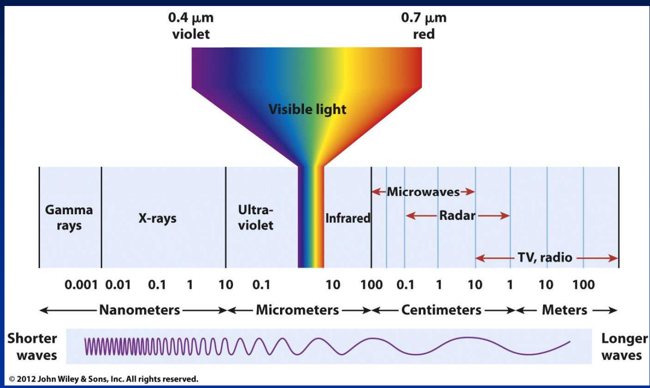
Atmospheric Radiation

- Radiation is the emission or propagation of energy in the form of a photon or an electromagnetic wave.
- Radiation is emitted by all bodies in the universe that have a temperature above absolute zero (0 K = -273.15 °C).
- A blackbody is a body that absorbs all radiation incident upon it.

Atmospheric Radiation

- Almost all the energy balance for the earth is determined by solar heating. Additionally, many reactions are influenced by solar energy.
- $C = \lambda \times \nu$, where C is the speed of light (3×10^8 m/s), λ is wavelength, ν is frequency.
- Energy of a photon = $E = h \times \nu = h \times (C/\lambda)$, where h is Planck's constant = 6.6×10^{-34} J·s
- Radiation with shorter wavelength (or higher frequency) has higher energy.

Radiation Spectrum



- Gamma radiation: 10^{-8} to 10^{-4} µm; X radiation: 10^{-4} to 10^{-2} µm; Ultraviolet (UV): 0.01 to 0.40 µm; Visible light: 0.40 to 0.75 µm; Infrared (IR): 0.75 to 1000 µm.
- UV-A: 0.32 to 0.40 µm; UV-B: 0.28 to 0.32µm; UV-C: 0.10 to 0.28 µm.

Typical Wavelengths, Frequencies, Wave numbers, and Energies of Various Regions of the Electromagnetic Spectrum

Name	Typical Wavelength or Range of Wavelengths (nm)	Typical Range of Frequencies ν (s^{-1})	Typical Range of Wavenumbers ω (cm^{-1})	Typical Range of Energies (kJ $einstein^{-1}$)[a]
Radiowave	$\sim 10^8$–10^{13}	$\sim 3 \times 10^4$ –3×10^9	10^{-6}–0.1	$\sim 10^{-3}$–10^{-8}
Microwave	$\sim 10^7$–10^8	$\sim 3 \times 10^9$ –3×10^{10}	0.1–1	$\sim 10^{-2}$–10^{-3}
Far infrared	$\sim 10^5$–10^7	$\sim 3 \times 10^{10}$–3×10^{12}	1–100	$\sim 10^{-2}$–1
Near infrared	$\sim 10^3$–10^5	$\sim 3 \times 10^{12}$–3×10^{14}	10^2–10^4	~ 1–10^2
Visible				
Red	700	4.3×10^{14}	1.4×10^4	1.7×10^2
Orange	620	4.8×10^{14}	1.6×10^4	1.9×10^2
Yellow	580	5.2×10^{14}	1.7×10^4	2.1×10^2
Green	530	5.7×10^{14}	1.9×10^4	2.3×10^2
Blue	470	6.4×10^{14}	2.1×10^4	2.5×10^2
Violet	420	7.1×10^{14}	2.4×10^4	2.8×10^2
Near ultraviolet	400–200	$(7.5\text{–}15.0) \times 10^{14}$	$(2.5\text{–}5) \times 10^4$	$(3.0\text{–}6.0) \times 10^2$
Vacuum ultraviolet	~200–50	$(1.5\text{–}6.0) \times 10^{15}$	$(5\text{–}20) \times 10^4$	$\sim(6.0\text{–}24) \times 10^2$
X ray	~50–0.1	$\sim(0.6\text{–}300) \times 10^{16}$	$(0.2\text{–}100) \times 10^6$	$\sim 10^3$–10^6
γ ray	$\leqslant 0.1$	-3×10^{18}	$\geqslant 10^8$	$> 10^6$

[a] For kcal $einstein^{-1}$, divide by 4.184 (1 cal = 4.184 J).

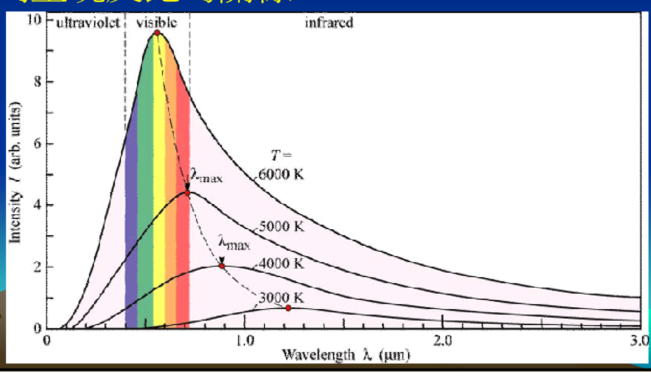
Wavelength and Energy of Typical Atmospheric Radiation

Name	Typical Wavelength or Range of Wavelengths, nm	Typical Range of Energies, kJ mol^{-1}
Visible		
Red	700	170
Orange	620	190
Yellow	580	210
Green	530	230
Blue	470	250
Violet	420	280
Near ultraviolet	400–200	300–600
Vacuum ultraviolet	200–50	600–2400

- Compare with bond energies of molecules, e.g.:
  - In the ozone molecule, the O—O_2 bond energy is about 105 kJ mol^{-1}
  - In NO_2, the O—NO bond energy is about 300 kJ mol^{-1}

Wien's Displacement Law

- Wien's displacement law: The wavelength of peak intensity of emission of a blackbody is inversely proportional to the absolute temperature of the body.
- 黑體的溫度與所產生的電磁輻射中能量最大的波長之間呈現反比的關係。



Wien's Displacement Law

- λ_{max} = 2897/T, where λ_{max} is the wavelength of peak blackbody emission (in µm), T is the absolute temperature of the body (in K).

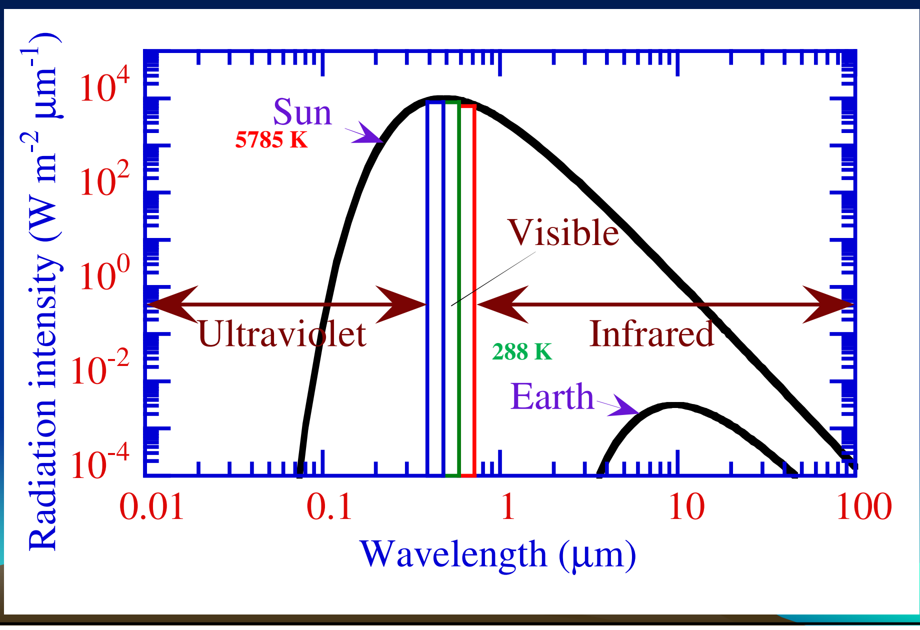
Example 2.1

Calculate the peak wavelength of blackbody radiative emission for both the sun and the Earth.

Solution

The effective temperature of the sun's photosphere is 5,785 K. Thus, from Equation 2.1, the peak wavelength of the sun's emissions is about 0.5 µm. The average surface temperature of the Earth is 288 K, giving the Earth a peak emission wavelength of about 10 µm.

Emission Spectra of the Sun and Earth



Total Radiation from a Blackbody

- Stefan-Boltzmann Law: $E = \sigma \times T^4$, where E is the radiation intensity (W/m^2), σ is the Stefan-Boltzmann constant (5.67×10^{-8} $W\bullet m^{-2}\bullet K^{-4}$), T is the absolute temperature of the blackbody (K).

Total Radiation from a Blackbody

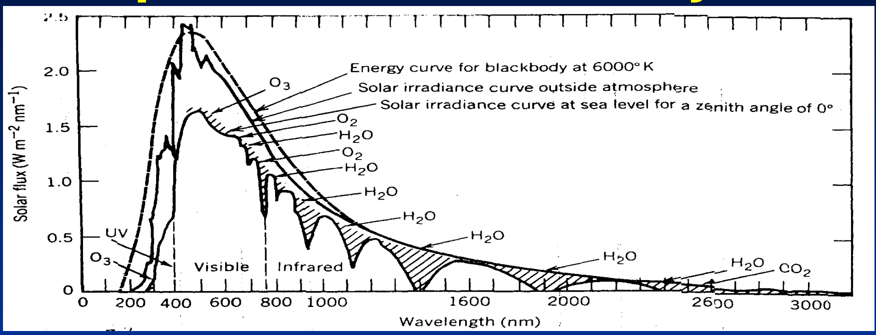
Example 2.2

How does doubling the Kelvin temperature of a blackbody change the intensity of radiative emission of the body? What is the ratio of intensity of the sun's radiation compared with that of the Earth's?

Solution

From Equation 2.2, the doubling of the Kelvin temperature of a body increases its intensity of radiative emission by a factor of 16. The temperature of the sun's photosphere (5,785 K) is about twenty times that of the Earth (288 K). Assuming both are blackbodies ($\varepsilon = 1$), the intensity of the sun's radiation (63.5 million W m^{-2}) is 163,000 times that of the Earth's (390 W m^{-2}).

Absorption of Radiation by Gases



- The most significant absorbing gases in the atmosphere are O_2, O_3, H_2O, and CO_2.
- Absorption by O_2 and O_3 is responsible for removal of practically all the incident radiation with wavelengths shorter than 290 nm.
- H_2O and CO_2 absorb much of the long-wave radiation.
- However, atmospheric absorption is not strong from 300 to about 800 nm, forming a "window" in the spectrum.

Chemistry

Chemical Reactions

- Gas-phase chemical reactions are conveniently divided into
  - Photolysis reactions
    - Unimolecular
    - Initiated when solar radiation strikes a molecule and breaks it down into two or more products
  - Chemical kinetic reactions
    - Usually bimolecular
    - Including thermal decomposition, isomerization, and standard collision reactions

Chemical Reactions

Unimolecular photolysis reaction (1.1)

$\dot{N}O_2(g) + h\nu \longrightarrow \dot{N}O(g) + \cdot\dot{O}(g)$ $\lambda < 420$ nm

Nitrogen dioxide → Nitric oxide, Atomic oxygen

Bimolecular thermal decomposition reaction (1.2)

$N_2O_5(g) + M \longrightarrow \dot{N}O_2(g) + \dot{N}O_3(g) + M$

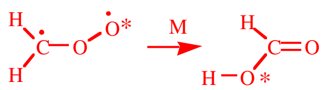
Dinitrogen pentoxide → Nitrogen dioxide, Nitrate radical

-- also written as (1.3)

$N_2O_5(g) \xrightarrow{M} \dot{N}O_2(g) + \dot{N}O_3(g)$ (M: Remain itself)

Dinitrogen pentoxide → Nitrogen dioxide, Nitrate radical

Isomerization reaction: no change in composition (1.4)



Excited Criegee biradical → Excited formic acid

M: any molecule, O_2 or N_2

Chemical Reactions

Bimolecular collision reaction (1.5)

$$\underset{\text{Methane}}{CH_4(g)} + \underset{\text{Hydroxyl radical}}{\dot{O}H(g)} \longrightarrow \underset{\text{Methyl radical}}{\dot{C}H_3(g)} + \underset{\text{Water vapor}}{H_2O(g}$$

Reversible termolecular combination reaction (1.6)

$$\underset{\text{Nitrogen dioxide}}{\dot{N}O_2\,(g)} + \underset{\text{Nitrate radical}}{\dot{N}O_3\,(g)} + M \rightleftharpoons \underset{\text{Dinitrogen pentoxide}}{N_2O_5\,(g)} + N$$

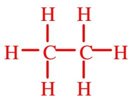
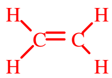
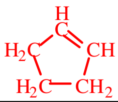
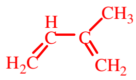
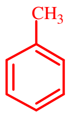
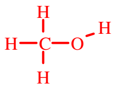
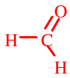
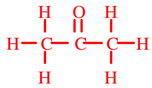
Derived from a pair of bimolecular reactions

A+B<=>AB*   AB*+M<=>AB+M

Organic Chemistry

- The organic chemistry can be regarded as the chemistry of compounds of the element carbon.
- All organic compounds contain carbon atoms, and with a few exceptions, hydrogen atoms. Oxygen, nitrogen, the halogens, sulfur, phosphorous, silicon and a few other elements may be present.
- All organic compounds can be thought of as derived from hydrocarbons.
- Hydrocarbons contain bonds.

Structures of Organic Compounds

Alkane	Alkene	Cycloalkene	Hemiterpene
Ethane $C_2H_6(g)$ 	Ethene $C_2H_4(g)$ 	Cyclopentene $C_5H_8(g)$ 	Isoprene $C_5H_8(g)$ 
Aromatic	**Alcohol**	**Aldehyde**	**Ketone**
Toluene $C_6H_5CH_3(g)$ 	Methanol $CH_3OH(g)$ 	Formaldehyde $HCHO(g)$ 	Acetone $CH_3COCH_3(g)$ 

(a) Alkanes (paraffins)；烷

C_nH_{2n+2}

ex. CH_4 methane

CH_3-CH_3 ethane

CH_3-CH_2-CH_3 propane

CH_3-CH_2-CH_2-CH_3 n-butane

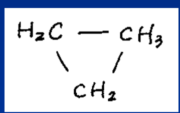
表 2.2 直鏈烷類的命名

碳數 (n)	名稱	化學式 (C_nH_{2n+2})	碳數 (n)	名稱	化學式 (C_nH_{2n+2})
1	甲烷（Methane）	CH_4	9	壬烷（Nonane）	C_9H_{20}
2	乙烷（Ethane）	C_2H_6	10	癸烷（Decane）	$C_{10}H_{22}$
3	丙烷（Propane）	C_3H_8	11	十一烷（Undecane）	$C_{11}H_{24}$
4	丁烷（Butane）	C_4H_{10}	12	十二烷（Dodecane）	$C_{12}H_{26}$
5	戊烷（Pentane）	C_5H_{12}	13	十三烷（Tridecane）	$C_{13}H_{28}$
6	己烷（Hexane）	C_6H_{14}	20	二十烷（Icosane）	$C_{20}H_{42}$
7	庚烷（Heptane）	C_7H_{16}	21	二十一烷（Henicosane）	$C_{21}H_{44}$
8		C_8H_{18}	30		$C_{30}H_{62}$

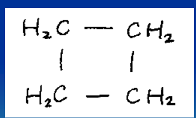
Cycloalkanes；環烷

C_nH_{2n}

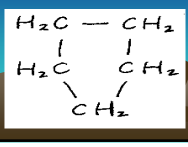
Cyclopropane



Cyclobutane



Cyclopentane



Alkyl radicals: R；烷基

CH_3 methyl

CH_3CH_2 ethyl

$CH_3CH_2\ CH_2$ n-propyl

$CH_3\ CH_2\ CH_2\ CH_2$ n-butyl

(b) Alkenes (olefins) ；烯

C_nH_{2n}

ex $CH_2= CH_2$ ethene(ethylene)

$CH_3CH= CH_2$ propene(propylene)

$CH_3CH_2CH= CH_2$ 1-butene

$CH_3CH= CHCH_3$ 2-butene

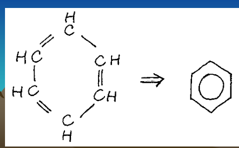
(c) Alkynes ；炔

C_nH_{2n-2}

ex. $HC \equiv CH$ acetylene

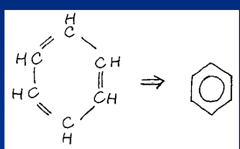
(d) Aromatics ；芳香烴

ex. benzene ；苯

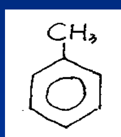


BTEX (Benzene, Toluene, Ethylbenzene, and Xylene) are the most soluble of the major gasoline compounds and, therefore, are common indicators of gasoline contamination.

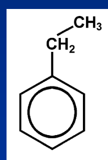
Bezene
苯



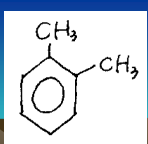
Toluene
甲苯



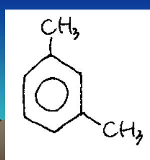
Ethylbezene
乙苯



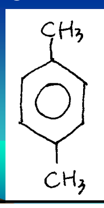
Orthoxylene
鄰二甲苯



Metaxylene
間二甲苯

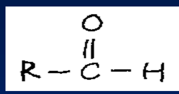


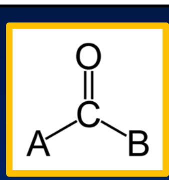
Paraxylene
對二甲苯



(e) Aldehydes (one or more oxygen atoms)；醛

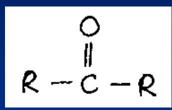
ex. HCHO formaldehyde
CH_3 CHO acetaldehyde

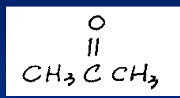




Compounds containing a carbonyl group (C=O)

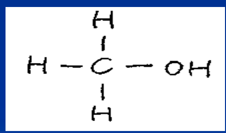
(f) ketones ；酮



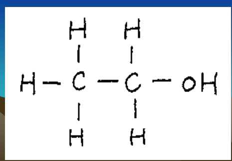


Acetone

(e) Alcohol ；醇
R-O-H



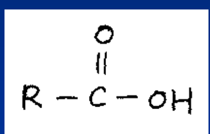
Methyl alcohol (methanol)



Ethyl alcohol (ethanol)

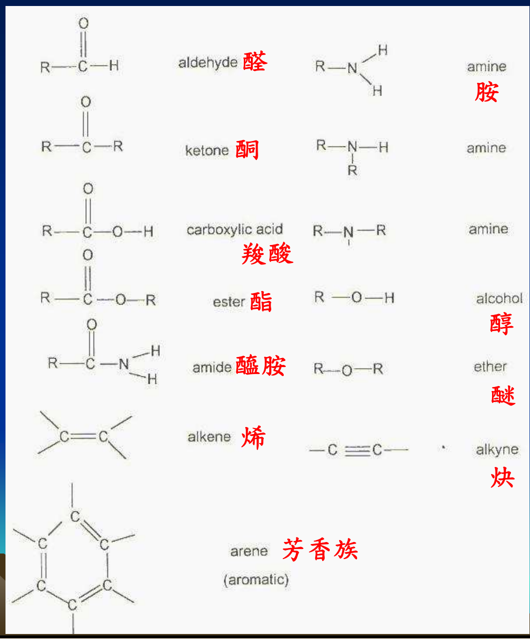
(g) Ether；醚
R-O-R
CH_3OCH_3 dimethyl ether 二甲醚，簡稱甲醚

(h) Carboxylic acid；羧酸



HCOOH formic acid

Functional Groups



Definitions

- Non-methane hydrocarbons (NMHCs): all the hydrocarbons, except methane.
- Oxygenated hydrocarbons: when oxygenated functional groups are added to hydrocarbons.
- Reactive organic gases (ROGs): NMHCs plus oxygenated hydrocarbons.
- Total organic gases: ROGs plus methane.
- Volatile organic compounds (VOCs): organic compounds with low boiling points that, therefore, readily evaporate.
- Carbonyls (羰基，C=O): aldehydes plus ketones.
- Non-methane organic carbon (NMOC): NMHCs plus carbonyls.

Residence time (physical) or Lifetime (chemical)

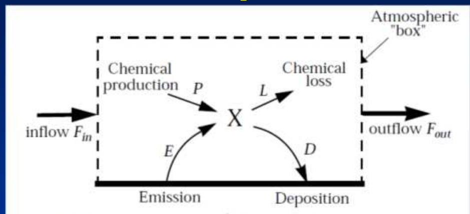


Figure 3-1 One-box model for an atmospheric species X

At steady-state, the residence time (τ) of X in the box is defined as the average time that a molecule of X remains in the box.

In the atmosphere, τ is the amount of X in the atmosphere divided by the rate at which X is removed from the atmosphere.

$$\tau = \frac{m}{F_{out} + L + D} \quad \text{or} \quad \tau = \frac{M}{F}$$

Exercise 2.2. Ammonia (NH_3), nitrous oxide (N_2O) and methane (CH_4) comprise 1×10^{-8}, 3×10^{-5}, and 7×10^{-5}% by mass of the Earth's atmosphere, respectively. If the effluxes of these chemicals from the atmosphere are 5×10^{10}, 1×10^{10}, and 4×10^{11} kg a^{-1}, respectively, what are the residence times of NH_3, N_2O, and CH_4 in the atmosphere? (Mass of the Earth's atmosphere = 5×10^{18} kg.)

Solution. From Eq. (2.4) the residence time is given by

$$\tau = \frac{M}{F}$$

where M is the quantity of chemical in the atmosphere, and F the efflux. For NH_3,

$$M = \frac{1 \times 10^{-8}}{100}(5 \times 10^{18})\ \text{kg}$$

and $F = 5 \times 10^{10}$ kg a^{-1}, therefore, $\tau_{NH_3} = 0.01$ a = 4 days. For N_2O,

$$M = \frac{(3 \times 10^{-5})}{100} \times (5 \times 10^{18})\ \text{kg}$$

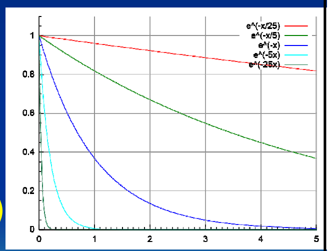
and $F = 1 \times 10^{10}$ kg a^{-1}, therefore, $\tau_{N_2O} = 150$ a. For CH_4,

$$M = \frac{(7 \times 10^{-5})(5 \times 10^{18})}{100}\ \text{kg}$$

and $F = 4 \times 10^{11}$ kg a^{-1}, therefore, $\tau_{CH_4} = 9$ a.

Residence time (physical) or Lifetime (chemical)

- If the rate of loss of a chemical is proportional to its amount present:
- $d[C]/dt = -k \times [C]$, where [C] is the concentration of the chemical, t is time, k is a reaction rate constant.
- $[C]_t = [C]_0 \times e^{-kt}$, where $[C]_0$ is the initial concentration, $[C]_t$ is the concentration at time t.
- Residence time $\tau = M/F = [C]/(-d[C]/dt) = [C]/(k \times [C]) = 1/k$
- Residence time is independent of the initial concentration of the chemical.



Overall Chemical Lifetime

- The overall chemical lifetime of a species is determined by calculating the lifetime of the species against loss due to each individual chemical reaction or other loss process that it is involved in.

$$\tau_A = \frac{1}{\frac{1}{\tau_{A1}} + \frac{1}{\tau_{A2}} + \cdots \frac{1}{\tau_{An}}}$$

Table 2.1. *Residence times of some atmospheric gases*[a] *(in many cases only very rough estimates are possible)*

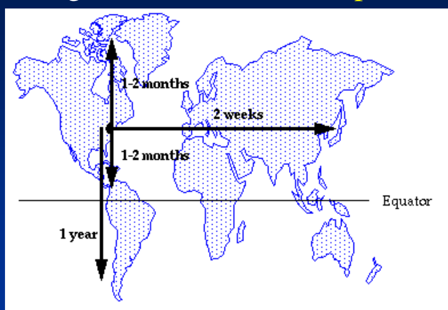
Gas	Residence Time
Nitrogen (N_2)	1.6×10^7 a
Helium (He)	10^6 a
Oxygen (O_2)	3,000–10,000 a
Carbon dioxide (CO_2)	3–4 a
Nitrous oxide (N_2O)	150 a
Methane (CH_4)	9 a
CFC-12 (CF_2Cl_2)	>80 a
CFC-11 ($CFCl_3$)	~80 a
Hydrogen (H_2)	4–8 a
Methyl chloride (CH_3Cl)	2–3 a
Carbonyl sulfide (COS)	~2 a
Ozone (O_3)	100 days
Carbon disulfide (CS_2)	40 days
Carbon monoxide (CO)	~60 days
Water vapor[b]	~10 days
Formaldehyde (CH_2O)	5–10 days
Sulfur dioxide (SO_2)	1 day
Ammonia + Ammonium (NH_3 + NH_4^+)	2–10 days
Nitrogen dioxide (NO_2)	0.5–2 days
Nitrogen oxide (NO)	0.5–2 days
Hydrogen chloride (HCl)	4 days
Hydrogen sulfide (H_2S)	1–5 days
Hydrogen peroxide (H_2O_2)	1 day
Dimethyl sulfide (CH_3SCH_3)	0.7 days

[a] The residence time (or lifetime) is defined as the amount of the chemical in the atmosphere divided by the rate at which the chemical is removed from the atmosphere. This time scale characterizes the rate of adjustment of the atmospheric concentration of the chemical if the emission rate is changed suddenly.

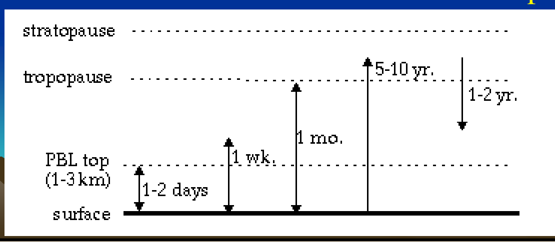
[b] The residence time of liquid water in clouds is ~6 h.

Time Scales of Atmospheric Transport

Typical time scales for global horizontal transport in the troposphere



Characteristic time scales for vertical transport



Residence Time and Spatiotemporal Variability of Chemicals

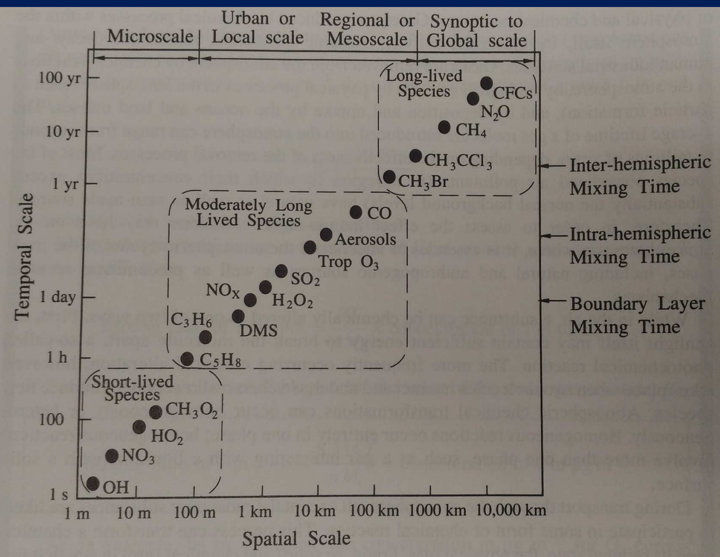


FIGURE 1.4 Spatial and temporal scales of variability for atmospheric constituents.

Units of Concentration of Atmospheric Composition

SI prefixes

Factor	Name	Symbol	Factor	Name	Symbol
10^{1}	deca	da	10^{-1}	deci	d
10^{2}	hecto	h	10^{-2}	centi	c
10^{3}	kilo	k	10^{-3}	milli	m
10^{6}	mega	M	10^{-6}	micro	µ
10^{9}	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a
10^{21}	zetta	Z	10^{-21}	zepto	z
10^{24}	yotta	Y	10^{-24}	yocto	y

Units of Concentration of Atmospheric Composition

- Need units for chemicals in gas phase, liquid phase and solid phase.

Units of Concentration of Atmospheric Composition

- For gas phase:
  - Mixing ratio
  - Partial pressure
  - Number density
  - Mass concentration

Units of Concentration: Gas Phase

Mixing ratio (C_x): defined as the number of moles of X per mole of air. Remains constant when pressure, temperature or air density changes.

- %
- ppm(v) – parts per million
- ppb(v) – parts per billion
- ppt(v) – parts per trillion
- (v) means by volume

to express the number of pollutants in a

million (10^6)
billion (10^9)
trillion (10^{12}) molecules of air

	Volume mixing ratio	
Gas	(percent)	(ppmv)
Nitrogen (N_2)	78.08	780,800
Oxygen (O_2)	20.95	209,500
Argon (Ar)	0.93	9,300
Neon (Ne)	0.0015	15
Helium (He)	0.0005	5
Krypton (Kr)	0.0001	1
Xenon (Xe)	0.000005	0.05

Gas Phase

Partial pressure (P_x): defined as the pressure that would be exerted by the molecules of X if all the other gases were removed from the mixture of gases.

- The partial pressure and mixing ratio of a gas X are related by Dalton's law:
- $P_x = C_x \times P$, where P is the total atmospheric pressure

Units of Concentration: Gas Phase

Number density (n_x): defined as the number of molecules of X per unit volume of air. Commonly expressed in units of molecules cm^{-3}.

- For example, global average concentration of OH radical is $\sim 5 \times 10^5$ molecules cm^{-3}
- At STP (1 atm and 0°C), the volume of 1 mole of air is 22.4 L = 22400 cm^3. 1 mole of air has 6.02×10^{23} molecules.
- Number density of air (n_a) at STP = $(6.02 \times 10^{23})/22400 = 2.69 \times 10^{19}$ molecules cm^{-3}

Gas Phase

- The number density and mixing ratio of a gas X are related by the number density of air:
- $n_x = C_x \times n_a$
- At any pressure and temperature:
- $n_a = (A_v \times n)/V$ and $n = PV/RT$, where A_v is Avogadro's number
- $\therefore\ n_a = A_v P/RT$
- Therefore, $n_x = C_x \times (A_v P/RT)$
- We can see from the above equation that n_x is not conserved when P or T changes.

Gas Phase

Mass concentration (ρ_x): defined as the mass of gas X per unit volume of air. Commonly expressed in units of mg m^{-3}, µg m^{-3}, or ng m^{-3}.

- The mass concentration and number density of a gas X are related by the molecular weight of X (M_x, g/mol):
- $\rho_x = (n_x/A_v) \times M_x$

Units of Concentration: Solution

- Molarity: defined as the number of moles of the solute in 1 L of the solution (mol L^{-1}, or M).
- Mixing ratio by weight: such as ppm, ppb, or ppt
- Mass concentration: defined as the mass of the solute in 1 L of the solution, such as mg L^{-1} or μg L^{-1}

Units of Concentration: Solid Phase

Commonly expressed in units of mass concentration, such as mg m^{-3} or μg m^{-3}.

TSP (Total suspended particulates) ~ 60 μg m^{-3}

Example:中壢空品站