Mass and volume flow of gases

Ideal gas equation:

$$\boxed{nRT = PV} \quad \text{or} \quad \boxed{NkT = PV}$$

n	=	number of moles		
R	=	ideal gas constant = $k\,N_A$	=	8.316 J/(mol K)
T	=	absolute temperature		
P	=	pressure		
V	=	volume		
N_A	=	Avogadro's constant	=	6.022×10^{23} mol^{-1}
k	=	Boltzmann's constant	=	1.381×10^{-23} J/K
N	=	number of gas atoms or gas molecules	=	$n \times N_A$

Definition of standard ("s") or normal ("n") conditions:

P_s = 1013 mbar, T_s = 273 K (U.S.)
P_s = 1013 mbar, T_s = 293 K (Europe)

Molar volume:

The *molar volume* is the volume occupied by one mole of ideal gas at standard temperature and pressure (STP). Its value is:

$$\boxed{22.4 \text{ liters / mol}}$$

Ideal gas dynamics:

$$\boxed{\frac{\mathrm{d}n}{\mathrm{d}t} RT = P \frac{\mathrm{d}V}{\mathrm{d}t}}$$

Thus, *molar flow rate* $\Phi_M = \mathrm{d}n/\mathrm{d}t$ is directly proportional to *volume flow rate* $\Phi_V = \mathrm{d}V/\mathrm{d}t$

Units at standard conditions:

unit $[\Phi_V]$ = sccm or slm
unit $[\Phi_M]$ = mol/min

Note: Since the mass density of an ideal gas can be calculated using the static ideal gas equation and the molar mass m_m, the volume flow Φ_V can be related to a mass flow Φ_m measured in g/min. Often the mass flow at standard conditions is just given in units of the volume flow, i.e., sccm, slm, or scfm.

Partial pressure:

Assume that two gases are mixed. Each gas contributes to the total pressure of the gas mixture. Under equilibrium conditions, the sum of all partial pressures is equal to the total pressure of the gas mixture.

Assume that a gas A and gas B are mixed. Assume that the partial pressure of A is P_A and the partial pressure of gas B is P_B. The total pressure is $P_{total} = P_A + P_B$. The molar ratio of the two gases is given by the ratio of the partial pressures. The molar content of gas A in a mixture of gas A and gas B with a total volume of V is given by $P_A / (P_A + P_B) \times V \times 44.6$ mmol/liter.

We can write the following equations:

Molar fraction = Partial pressure / Total pressure
Molar content per liter = Partial pressure / Total pressure × 44.6 mmol/liter
Molar content = Partial pressure / Total pressure × Volume of mixture × 44.6 mmol/liter

For further studies, see ***John Dalton's law of partial pressures***: The pressure of a gas in a mixture is equal to the pressure it would exert if it occupied the same volume alone at the same temperature. This is because gas molecules are so far apart that they don't interfere with each other. A consequence of this is that the total pressure of a gas mixture at equilibrium is equal to the sum of partial pressures of all gases in the mixture.

The vapor pressure in thermal equilibrium is a characteristic of a substance and depends, in addition to the chemistry of the substance, only on the temperature. The partial pressure of a liquid in equilibrium with a gaseous environment is equal to the liquid's vapor pressure. The partial pressure of a liquid does not depend on the chemistry of the gaseous environment. The vapor pressure can be calculated for different materials or is tabulated. The vapor pressure typically has the Arrhenius dependence:

$$P = P_0 \, \mathrm{e}^{-E\mathrm{a} / kT}$$

Exercises:

1. Calculate the molar volume of an ideal gas at standard conditions ($T = 273$ K, $P = 1013$ mbar).
   $V_\mathrm{m} = RT / P = 22.4$ l/mol

2. What is the molar concentration of an ideal gas?
   $C_\mathrm{m} = 1/V_\mathrm{m} = 1/22.4$ mol/l = 44.6 mmol/l

3. What is the mass density of nitrogen at standard conditions?
   N_2 molar weight: $m_\mathrm{m} = 2 \times 14$ g/mol
   N_2 standard density: $\rho_\mathrm{s} = 28 \text{ g/mol} \times (22.4 \text{ l/mol})^{-1} = 1.25 \text{ g/l} = 1.25 \text{ mg/cm}^{-3}$

4. Which real gases behave almost like an ideal gas, which don't?
   The following gases behave almost like ideal gases: He, Ne, Ar, and N2
   The following do less so: CO_2, NH_3, and CH_4

5. What is the mass flow rate and the molar flow rate of N_2 with volume flow rate of 10 sccm?
   10 cm^3 of N_2 has the mass 28 g / 22.4 liter × 10 cm^3 = 12.5 mg
   The mass flow rate is 12.5 mg/min
   12.5 mg of N_2 are 1 mol / 28 g × 12.5 mg = 0.446 mmol
   Thus the molar flow of 10 sccm N_2 is 0.446 mmol/min

6. What is the mass flow rate and the molar flow rate of NH_3 with volume flow of rate1500 sccm?
   1500 cm^3 of NH_3 weigh 17 g / 22.4 liter × 1500 cm^3 = 1.14 g
   The mass flow rate is 1.14 g/min
   1.14 g of NH_3 are 1 mol / 17 g × 1.14 g = 67.1 mmol
   Thus the molar flow of 1500 sccm NH_3 is 67.1 mmol/min

7. What is the mass of NH_3 consumed during 1 hr of growth at a mass flow rate of 1500 sccm?
   From previous exercise: Molar flow rate of 1500 sccm NH_3 is 67.1 mmol/min.
   Consumed in 1 hr: 67.1 mmol/min × 60 min = 4.03 mol
   Mass consumed in 1 hr = 68.5 g

8. What is the mass of TMGa consumed during 1 hr of growth at a mass flow rate of 15 sccm using H_2 as carrier gas?
   15 cm^3 of pure TMGa gas at 0° C and 1013 mbar weigh 114.7 g / 20.87 liter × 15 cm^3 = 0.0768g.
   Thus the mass flow rate corresponding to 15 sccm of pure TMGa gas is 0.0768g/min.
   The partial pressure of TMGa gas over liquid TMGa at 0° C is 98 mbar
   Therefore the mass of TMGa consumed is 0.0768g/min × 60 min × 98 mbar / 1013 mbar = 0.45 g

9. What is the mass of TEGa consumed during 1 hr of growth at a mass flow rate of 150 sccm using N_2 as a carrier gas?
   150 cm^3 of pure TEGa gas weigh 156.7 g / 22.4 liter × 150 cm^3 = 1.05 g.
   Thus the mass flow rate corresponding to 150 sccm of pure TEGa gas is 1.05 g/min.
   The partial pressure of TEGa over liquid TEGa at 17° C is 5.28 mbar
   Therefore the mass of TEGa consumed is 1.05 g/min × 60 min × 5.28 mbar / 1013 mbar = 0.33 g

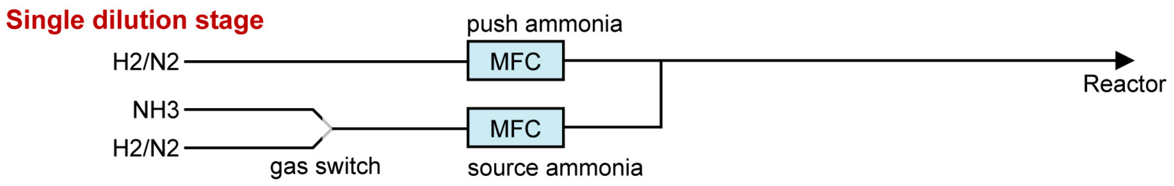
10. What are the units of

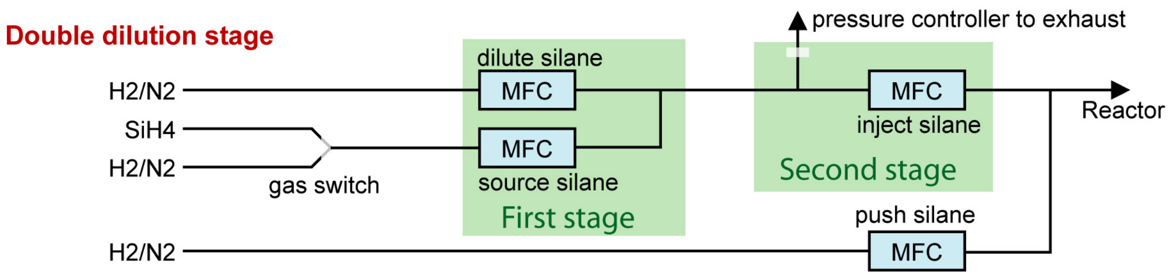
Molar volume	liter
Molar flow rate	mol / min
Molar concentration	mol / liter
Molar concentration flow rate	mol / (liter min)
Volume flow rate	liter / min
Mass flow rate	g / min (frequently also given in sccm which is, strictly speaking, incorrect)

11. Note that some MFCs are calibrated for H_2 (calibration for other gases such as air, N_2, Ar is possible as well). What is the true flow of N_2 and NH_3 when these gases are flowing through an H_2-calibrated MFC with a flow rate of 10 sccm?
    The MFC manufacturer (Bronkhorst Corporation) makes the following statement on this point: If the MFC calibration gas is different from the process gas, the true flow of the process gas can be obtained using the conversion factors c (e.g., $c_{\mathrm{N2}} = 1$, $c_{\mathrm{NH3}} = 0.73$ if H_2 was used for calibration). Therefore the actual flow rate of N_2 through an H_2-calibrated MFC at 10 sccm would be 10 sccm, the actual flow rate of NH_3 through an H_2-calibrated MFC at 10 sccm would be 7.3 sccm.

Single and double dilution stages

Consider the following gas flow schematics typical for MOCVD (MFC = mass flow controller):





Exercises:

1. What is the purpose of the "push silane" gas?
   The flow rate of the "inject silane" MFC can be very small (at low doping concentrations). The volume flow rate of the "push silane" gas is a constant to provide a reasonable gas-flow velocity to the reactor.

2. Does the "push ammonia" MFC in the single dilution stage change the molar flow of ammonia arriving in the reactor?
   No, the push flow does not change the NH_3 molar flow into reactor.

3. Would a very high "push ammonia" MFC in the single dilution stage change the molar flow of ammonia arriving in the reactor?
   No, the push flow does not change the NH_3 molar flow into reactor.

4. What is the purpose of the exhaust line in the double-dilution stage?
   The exhaust line is used to release excess silane/carrier gas flow which exceeds the mass flow of the second-stage MFC.

5. What are the typical operating ranges of MFCs?
   5 – 500 sccm, depending on the type of MFC.

6. Why is it advisable to **not** reduce an MFC flow rate to values < 5 sccm?
   At very low flow the accuracy decreases.

7. Using a minimum and maximum volume flow rate of an MFC to be 5 sccm and 500 sccm, respectively, give the dynamic range of a single- and double dilution stage.
   Dynamic range of single-dilution stage is 2 orders of magnitude.
   Dynamic range of double-dilution stage is 4 orders of magnitude.

Nomenclature of MOCVD gases

Name	Example	Explanation
Source	TMGa source	The Source Gas provides the precursor.
Source push	TMGa push	The Source Push Gas is chosen so that the sum of MO Source and MO push give 500 sccm. This keeps the reactor gas flow coming from an MO Source constant. The Source Push strongly dilutes the MO source so that condensation is avoided.
Run MO		The Run MO gas increases the degree of dilution of MO precursors thereby reducing the risk of condensation, parasitic chemical reactions, and provides a more rapid transport of MO precursors to the reactor.
Push MO		The Push MO gas is combined with the Run MO Gas shortly before the reactor and allows one to control the injection velocity into the reactor. The Push MO gas increases the degree of dilution of MO precursors thereby reducing the risk of condensation and parasitic chemical reactions.

Exercises:

1. What is the typical flow of the “MO run”? Why is this flow chosen that way?
   500 sccm – it is chosen that way based on experience. The flow dynamic also plays a role.

2. What is the typical flow of the “MO push”? Why is this flow chosen that way?
   500 sccm – it is chosen that way based on experience. The flow dynamic also plays a role.

Appendix: Pressure units

The following information is from UK's National Measurement Laboratory: The SI unit of pressure is the *Pascal*, symbol *Pa*, the special name given to a pressure of one Newton per square meter (N/m^2). The relationships between the Pascal and some other pressure units are shown in the table but note that not all are, or can be, expressed exactly. Note also that the term *standard atmosphere* is not a pressure unit(5).

Unit	Symbol	No. of Pascals
Bar	bar	1×10^5 Pa (exactly)
millibar(1)	mbar	100 Pa (exactly)
Hectopascal(1)	hPa	100 Pa (exactly)
Conventional millimeter of mercury(2,3)	mmHg	133.322... Pa
Conventional inch of mercury(2,3)	inHg	3 386.39... Pa
Torr(4)	Torr	101325 / 760 Pa (exactly)
Pound-force per square inch	lbf/in^2	6 894.76... Pa

Notes:

1. Following the 8th Congress of the World Meteorological Organization, from 1 January 1986 the term *hectopascal* (hPa) is preferred to the numerically identical *millibar* (mbar) for meteorological purposes. This choice was made, despite the fact that *hecto* (x 100) is not a preferred multiple in the SI system, to avoid having to change the numerical values on barometer scales.
2. The *conventional millimeter of mercury* (mmHg) and the *conventional inch of mercury* (in Hg) are defined in terms of the pressure generated by a mercury column of unit length and of assigned density 13595.1 kg/m^3 at 0 °C under standard gravity of 9.80665 m/s^2 (see note 3 and BS 2520: 1983 *Barometer conventions, their application and use*).
3. The so-called 'manometic' pressure unit definitions such as *millimeters of mercury* and *inches of mercury* depend on an assumed liquid density and acceleration due to gravity, assumptions which inherently limit knowledge of their relationship with the Pascal. In order to encourage the demise of non-SI units, whose definitions are becoming inadequate for the most precise measurement of pressure, there is international effort to exclude them from conversion tables or, in the meantime, restrict the precision of newly published conversion factors. It is strongly recommended that, wherever possible, all new applications of pressure measurement use the Pascal, with multiples or sub-multiples as appropriate to the magnitude of the pressure values.
4. The *Torr* is defined as exactly 101325/760 Pa - the '760' coming from the original and arbitrary definition of *standard atmosphere*. Its value differs from the conventional millimeter of mercury by about 1 part in 7 million (see BS 2520: 1983 *Barometer conventions, their application and use*).
5. The definition of *standard atmosphere* (atm) is 101 325.0 Pa exactly. It is still occasionally used in defining a reference environment – e.g. for specifying gas density - but it is not a pressure unit and should not be used to express pressure values. The large number of significant figures used to define it and its far-from-round-number appearance sometimes leads to the erroneous assumption that it is the measured average pressure on the surface of the earth. It is not and such a measurement could not realistically be made. (Consider how many locations would be used and over what timescale? Changing either of these parameters would change the result.)