

2 Introduction to the Physics of Gases

In physical textbooks and especially in thermodynamic textbooks there are more or less detailed explanations with the most important equations. For a more in-depth study the monograph from (Atkins 2006) is recommended as detailed as well as the German handbook from (Messer Griesheim 1989) and the monograph from (Hering et al. 1999).

2.1 The Ideal Gas

Since it has been possible to examine gases using physical methods two questions have always been of interest:

- How do the pressure p and the volume V of an enclosed quantity of gas behave at a constant temperature T (isothermal state change)?
- How does the volume of a gas behave at changing temperatures but constant pressure (isobaric state change)?

The answers can be found in Boyle-Mariotte's Law (17th century) according to the equation.

$$p \cdot V = \text{constant} = k \quad (2.1-1)$$

with k as a constant and in Gay-Lussac's Law (around 1800)

$$V_{T_1} = V_{T_0} \cdot (1 + \alpha \cdot \Delta T_{1-0}) \quad (2.1-2)$$

with a constant p for the states 0 and 1, and with the temperature difference $\Delta T_{1-0} = T_1 - T_0$ and α as the (spatial) expansion coefficient of gas. α was determined by experiment and is found to be in a borderline case $p \rightarrow 0$ as $1/(273.15)$ K. A gas with this borderline case is described as ideal.

All known gases show no ideal behaviour, rather, they are so called "real gases". The above mentioned Eqs. for the ideal gas can be used, if the temperatures are clearly above the melting point or the triple point and/or the pressure or the differences in pressure are small. The monoatomic He as the lightest inert gas comes closest to this ideal behaviour which is why it is used in gas thermometers.

The analogous equation (2.1-2) also applies to the behaviour of pressure at a constant geometric volume (isometric state change).

$$p_{T_1} = p_{T_0} (1 + \alpha \cdot \Delta T_{1-0}) \quad (2.1-3)$$

Example E2.1-1: Calculating pressure with varying temperature.

At 15°C the pressure of the gas cylinder is determined to 198 bar gauge-pressure, thus the absolute pressure is 199 bar. A temperature of 35°C is expected, consequently $\Delta T = 20^\circ\text{C}$. By approximation

$$p_{T35} = 199 \left(1 + \frac{1}{273.15} 20 \right) = 213.6 [\text{bar}]$$

The equations (2.1-2 and -3) assume a very simple form when V_{T_0} is equal to V_0 for 0°C. Taking $\alpha = (273.15 \text{ K})^{-1} = (T_{\text{stand}})^{-1}$ into consideration one obtain

$$V_1 = V_0 \frac{T_1}{T_{\text{stand}}} \quad \text{and} \quad p_1 = p_0 \frac{T_1}{T_{\text{stand}}} \quad (2.1-4)$$

with T in K or more generally

$$\frac{V}{T} = k_1 \quad \text{and} \quad \frac{p}{T} = k_2 \quad (2.1-5)$$

2.1.1 State Equations

The combination of Boyle-Mariotte's Law and Gay-Lussac's Law produces the state equation for the ideal gas.

$$\frac{p \cdot V}{T} = k \quad (2.1-1)$$

where k indicates a specific constant in each case. With a fixed but arbitrary mass M of an ideal gas for two states 1 and 2 and the standard condition this equation is therefore valid.

$$\frac{p_1 \cdot V_1}{T_1} = \frac{p_2 \cdot V_2}{T_2} = \frac{p_{\text{stand}} \cdot V_{T-\text{stand}}}{T_{\text{stand}}} \quad (2.1.1-2)$$

with $V_{T-\text{stand}}$ the volumes for V_1 and V_2 under standard conditions. By introducing the experimentally measured density of the real gas G at standard conditions $\varphi_{G,\text{STP}}$ and the specific gas constant R_G a simplification is obtained.

$$V_{G,T-\text{stand}} = \frac{M_G}{\varphi_{G,\text{STP}}} = V_{G,\text{STP}} \quad (2.1.1-3)$$

$$\frac{p \cdot V}{T} = \frac{M_G \cdot p_{\text{stand}}}{T_{\text{stand}} \cdot \varphi_{G,\text{STP}}} \quad (2.1.1-4)$$

$$R_G = \frac{p_{G,\text{stand}}}{T_{\text{stand}} \cdot \varphi_{G,\text{STP}}} \quad (2.1.1-5)$$

$$p \cdot V = M \cdot R_G \cdot T \quad (2.1.1-6)$$

Example E2.1.1-1: Calculating R_G for Ar (R_{Ar}) with a density $\varphi_{Ar,STP} = 1,784 \text{ kg} \cdot \text{m}^{-3}$.

$$R_{Ar} = \frac{101325}{273.15 \cdot 1.784} = 207.9 \left[\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \right]$$

From the equations (2.1-10 and -11) one can derive a formula to calculate the density when R_G is known.

$$\varphi_{G,T,p} = \frac{M_G}{V_G} = \frac{p}{T \cdot R_G} \quad (2.1.1-7)$$

Example E2.1.1-2: Calculating the density φ_{Ar} at 15°C ($=288.15 \text{ K}$) and 1 bar ($=10^5 \text{ Pa}$) using R_{Ar} from Example E2.1.1-1.

$$\varphi_{Ar} = \frac{10^5}{288.15 \cdot 207.9} = 1.669 \left[\text{kg} \cdot \text{m}^{-3} \right]$$

If it is necessary to start from a different point than $\varphi_{G,STP}$ one can use a formula which can also be derived from the equation (2.1.1-2). This also applies in idealized conditions, i.e. for small pressure and temperature differences.

$$\varphi_{G,T2,p2} = \varphi_{G,T1,p1} \frac{p_2 \cdot T_1}{p_1 \cdot T_2} \quad (2.1.1-8)$$

The specific gas constant can also be formed for mixtures. The basis is Dalton's Law (1807): The pressure p of an ideal gas mixture consists of the sum of the partial pressure p_i of the n individual gases.

$$p = \sum_{i=1}^n p_i \quad (2.1.1-9)$$

Thus one obtains the equation (2.1.1-6) for the individual gas i and the number n

$$p_i \cdot V = M_i \cdot R_i \cdot T \quad \text{and} \quad p \cdot V = \sum_{i=1}^n (M_i \cdot R_i) \cdot T$$

The specific gas constant R_{1-n} can be represented as

$$R_{1-n} = \frac{\sum_{i=1}^n M_i \cdot R_i}{\sum_{i=1}^n M_i} \quad \text{and} \quad M = \sum_{i=1}^n M_i$$

$$p \cdot V = M \cdot R_{1-n} \cdot T \quad (2.1.1-10)$$

The gases can be compared with each other using the molar volume. According to Avogadro's Principle (1811) different gases contain the identical number of molecules at the same pressure and the same temperature and the same volume.

The molar volume $V_{G,Mol}$ is the volume that the molar mass $M_{G,Mol}$ of a gas adopts. The molar volume of an ideal gas at standard conditions is the V_{STP} from paragraph 1.2.3.

With v as the number of moles in the mass M_G of the gas G , partly also referred to as fractions one obtains

$$M_G = v \cdot M_{G,Mol} \quad (2.1.1-11)$$

$\varphi_{G,STP}$ from equation (2.1.1-3) can be expressed through $V_{G,Mol,STP}$ at standard condition as

$$\varphi_{G,stand} = \frac{M_{G,Mol}}{V_{G,Mol,STP}} \quad (2.1.1-12)$$

The $\varphi_{G,Mol}$ is usually referred to as molar density (at standard condition). However the $V_{G,Mol,STP}$ for an ideal gas is the V_{STP} from chapter 1.2.3. Thus one can introduce a universal molar gas constant R_{Mol} . It is combined with the specific gas constant *via* the molar masses.

$$R_{Mol} = \frac{P_{stand}}{T_{stand} \cdot V_{STP}} = M_{G,Mol} \cdot R_G \quad (2.1.1-13)$$

$$= 8.31441 \left[\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \right] = 8.31441 \cdot 10^{-2} \left[\text{bar} \cdot \text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{K}^{-1} \right]$$

From the equation (2.1.1-6) $p \cdot V = M \cdot R_G \cdot T$ and the equations (2.1.1-11) as well as (2.1.1-13) follows the Clapeyronish State Equation (mid. 19th century).

$$p \cdot V = v \cdot R_{Mol} \cdot T \quad (2.1.1-14)$$

For 1 v , i.e. 1 mole, the following equation is valid

$$p \cdot V_{Mol} = R_{Mol} \cdot T \quad (2.1.1-15)$$

Thus a new equation for the density is aquired.

Omitting the index G and introducing the molar density φ_{Mol} one obtains

$$\varphi_{G,T,p} = \frac{M}{V} = \frac{p \cdot M_{Mol}}{R_{Mol} \cdot T} \quad (2.1.1-16)$$

$$\varphi_{Mol} = \frac{1}{V_{Mol}} = \frac{p}{R_{Mol} \cdot T} \quad (2.1.1-17)$$

The Boltzmann constant $k_{Boltzmann}$ (around 1900) is used for state equations. Here R_{Mol} is reduced to a single molecule (or atom in the case of the noble gases). The molar volume contains $6.0221367 \cdot 10^{23}$ particles. This number is referred to as Avogadro or Loschmidish Number.

$$k_{Boltzmann} = \frac{R_{Mol}}{k_{Avogadro}} \quad (2.1.1-18)$$

$k_{\text{Boltzmann}}$ is $1.380658 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$. Thus instead of the equation (2.1.1-15) we obtain

$$p \cdot V_{\text{Mol}} = k_{\text{Boltzmann}} \cdot k_{\text{Avogadro}} \cdot T \quad (2.1.1-19)$$

This equation is valid for one mole. Therefore the counterpart for the equation (2.1.1-14) with the number of particles n_{particle} in volume V is the equation

$$p \cdot V = k_{\text{Boltzmann}} \cdot n_{\text{particle}} \cdot T \quad (2.1.1-20)$$

$$n_{\text{particle}} = v \cdot k_{\text{Avogadro}} \quad (2.1.1-21)$$

2.1.2 Kinetic Gas Theory

Two concepts are associated with the ideal gas and form the basis of the kinetic gas theory:

- Molecules are so small that their own volume is negligible in comparison with the dimension of the container.
- No forces act between the molecules except those of the completely elastic collisions with each other.

Amongst other things the kinetic gas theory provides us with the equation for the average velocity v_m of a molecule or an atom using the root mean square statistical method. It is therefore called the RMS value.

$$v_{m,G} = \sqrt{\frac{3 \cdot R_{\text{Mol}} \cdot T}{M_{G,\text{Mol}}}} \quad (2.1.2-1)$$

As there is a dependency of the gas G on the molar mass the velocity is referred to as $v_{m,G}$.

Example E2.1.2-1: Calculating the molecular velocity of hydrogen and sulphur hexafluoride at a room temperature of 20°C.

The specifications are $M_{\text{H}_2,\text{Mol}} = 2.0 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$, $M_{\text{SF}_6,\text{Mol}} = 146.05 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$, $T = 293.15 \text{ K}$. The $R_{\text{Mol}} = 0.0831441 \text{ bar} \cdot \text{m}^{-3} \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$ from the equation 2.1.1-13 needs to be adjusted: $1 \text{ bar} = 10^5 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$, $1 \text{ kmol} = 10^3 \text{ mol}$, $R_{\text{Mol}} = 8.31441 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

$$v_{m,\text{H}_2} = \sqrt{\frac{3 \cdot 8.31441 \cdot 293.15}{2.016 \cdot 10^{-3}}} = 1904.5 \text{ [m} \cdot \text{s}^{-1}\text{]}$$

$$v_{m,\text{SF}_6} = \sqrt{\frac{3 \cdot 8.31441 \cdot 293.15}{146.05 \cdot 10^{-3}}} = 223.8 \text{ [m} \cdot \text{s}^{-1}\text{]}$$

The average velocity which has been introduced here $v_{m,G}$ is only one of several common ways of determining the average value. It is important to mention Maxwell distribution and probability distribution when determining the average value.

$$v_{m,G,\text{Maxwell}} = \sqrt{\frac{8}{3 \cdot \pi}} v_{m,G} = 0.9212 \cdot v_{m,G} \quad (2.1.2-2)$$

$$v_{m,G,\text{probability}} = \sqrt{\frac{2}{3}} v_{m,G} = 0.8165 \cdot v_{m,G} \quad (2.1.2-3)$$

The diffusion which will be dealt with in chapter 2.2.3 is directly proportional to $v_{m,\text{Maxwell}}$. Therefore there may be significant differences in the reaction times of chemical syntheses, adsorption and catalysis depending on the mass of the gases.

The kinetic gas theory provides us with another important factor: The mean free path of a molecule or an atom which was first introduced by Clausius in 1858. It is the path which a molecule travels between two collisions. We refer to the average value as s_{particle} .

$$s_{\text{particle}} = \frac{k_{\text{Boltzmann}} \cdot T}{\sqrt{2} \cdot \pi \cdot p \cdot d^2} = \frac{R_{\text{Mol}} \cdot T}{\sqrt{2} \cdot \pi \cdot p \cdot d^2 \cdot k_{\text{Avogadro}}} \quad (2.1.2-4)$$

with the diameter d of the particle.

2.1.3 Enthalpy

From thermodynamics we introduce the properties of state quantities U for the internal thermodynamic energy of a system and H as enthalpy, both are measured in Joules J . The enthalpy is the sum of the internal energy and the product $p \cdot V$ meaning the work which is done by a gas, e.g. when it drives a piston.

$$H = U + p \cdot V \quad (2.1.3-1)$$

We need this equation to calculate the heat capacity. This is defined as the heat quantity which is needed to heat a specific quantity of a material by 1 K. If 1 kg is used we talk about the specific heat capacity. If we refer to one mole then it is the molar heat capacity. The equation symbol is the lower case c . Now we need to differentiate between the c_v at constant volume and the c_p at constant pressure.

If we have a container with rigid walls (constant V) and heat the gas in it, then p increases and thus also the internal energy U . c_v is therefore defined as the differential quotient of U with respect to the temperature

$$c_v = \left(\frac{dU}{dT} \right)_v \quad (2.1.3-2)$$

This only applies to the ideal gas (which is not intended to be proven here!)

$$c_v = \left(\frac{dU}{dT} \right)_v = \left(\frac{dU}{dT} \right)_p$$

Looking at a container with a moving piston an increase in temperature will lead to an increase in volume with the pressure remaining the same. The increase

in volume, however, necessitates further derivation. Thus we must use enthalpy for the definition of c_p .

$$c_p = \left(\frac{dH}{dT} \right)_p \quad (2.1.3-3)$$

We ascertain the difference and put $pV = \nu R_{\text{Mol}} T$ into the equation (2.1.3-1) and differentiate according to T

$$\begin{aligned} c_p - c_v &= \left(\frac{dH}{dT} \right)_p - \left(\frac{dU}{dT} \right)_v = \left(\frac{dH}{dT} \right)_p - \left(\frac{dU}{dT} \right)_p \\ &= \left(\frac{dH}{dT} \right)_p - \left(\frac{dU}{dT} \right)_p + \nu \cdot R_{\text{Mol}} \\ c_p - c_v &= \nu \cdot R_{\text{Mol}} \end{aligned}$$

and with reference to moles

$$c_{p,\text{Mol}} - c_{v,\text{Mol}} = R_{\text{Mol}} \quad (2.1.3-4)$$

This is the known equation for the difference of the heat capacities which can also be calculated individually from the kinetic gas theory. For a monoatomic ideal gas which has three degrees of freedom as to translation of its atoms (vibration in three directions without rotation) the following applies:

$$c_{p,\text{Mol}} = \frac{5}{2} R_{\text{Mol}} \quad \text{and} \quad c_{v,\text{Mol}} = \frac{3}{2} R_{\text{Mol}}$$

The heat capacities of ideal gases do not depend on temperature, thus they only give an approximation of the correct values for real gases. For diatomic gases like N_2 and O_2 $c_{p,\text{Mol}} = (7/2) \cdot R_{\text{Mol}}$ and $c_{v,\text{Mol}} = (5/2) \cdot R_{\text{Mol}}$ apply. For molecules like H_2O with three degrees of freedom in translation and rotation they are $c_{p,\text{Mol}} = (8/2) \cdot R_{\text{Mol}}$ and $c_{v,\text{Mol}} = (6/2) \cdot R_{\text{Mol}}$. The proportion ε of both heat capacities will be required in chapter 2.2.3 for the adiabatic expansion:

$$\varepsilon = \frac{c_{p,\text{Mol}}}{c_{v,\text{Mol}}} \quad (2.1.3-5)$$

ε equals $5/3$ for a monatomic and $7/5$ for a diatomic ideal gas.

2.2 The Real Gas

The real gas is differentiated from the ideal gas because the forces between the molecules or atoms as well as their own volume cannot be neglected. This causes a number of consequences.

The gases can be liquefied under suitable conditions and also transformed into solid phase. Therefore the critical point with T_{Cri} and p_{Cri} and density φ_{Cri} is

important. However when $T > T_{\text{Cri}}$, one cannot achieve liquefaction even at high pressure. At the triple point all three thermodynamic phases exist simultaneously, illustrated in P2.2-1 explains this.

The vapour-pressure curve separates the gaseous from the liquid phase, the sublimation curve separates the gaseous from the solid, and the melting-pressure curve separates the liquid from the solid. Thus these curves are called phase separation curves. The melting point T_{mp} is obtained from the intersection point of the isobars at $p_{\text{stand}} = 1.01325$ bars with the vapour-pressure curve.

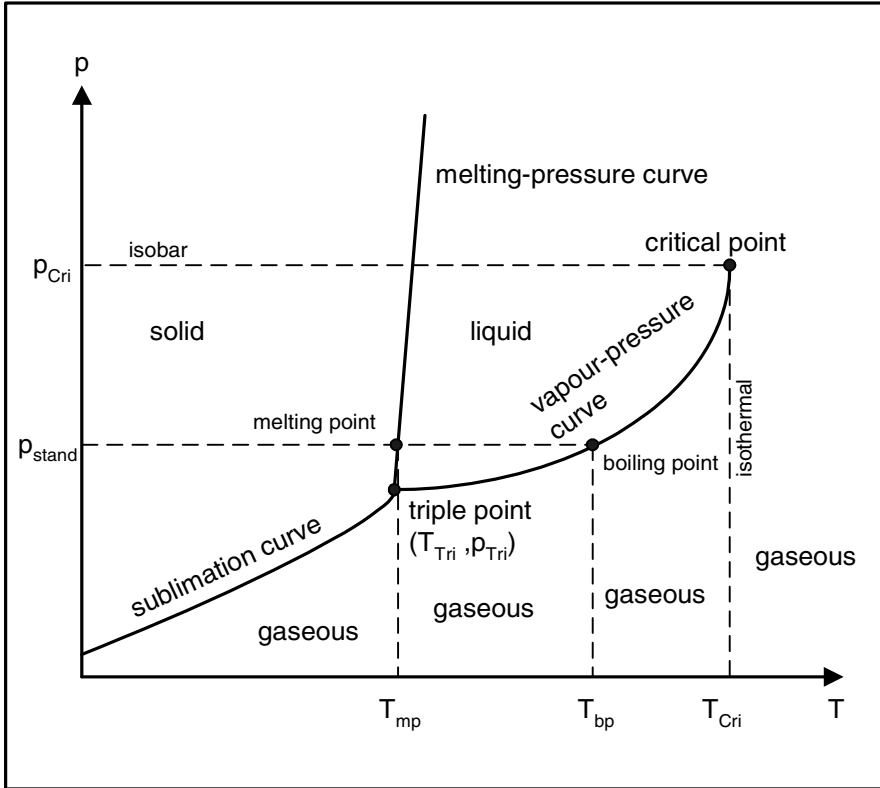


Illustration P2.2-1: T, p – diagram of the real gas in schematic depiction.

In order to obtain the melting point at p_{stand} we must differentiate between two cases.

- The pressure p_{Tri} at the triple point is below p_{stand} as shown in P2.2.1. Thus the melting point at the intersection curve of the isobars p_{stand} with the melting pressure curve, this results in the melting point T_{mp} which is always close to the triple temperature T_{Tri} . This is also adverted to gases which boil at a low temperature He, N_2 , H_2 , O_2 or Ar, a typical example is Xe with $p_{\text{Tri}} = 0.8167$ bar $< p_{\text{stand}}$.

- If $p_{\text{Tri}} > p_{\text{stand}}$, then the sublimation point is the one at the intersection point of the isobars p_{stand} with the sublimation curve, thus we can give a sublimation temperature T_{Subl} which is close to the triple temperature. A typical example is CO_2 with $p_{\text{Tri}} = 5.185$ bar. These relationships imply that the release of CO_2 causes the formation of some carbon dioxide snow. In order to avoid this e.g. when mixing it with other gases attention must be paid to the fact that the expansion pressure is not smaller than p_{Tri} (5.2 bar abs. for CO_2) or that the expansion takes place isothermally.

2.2.1 Equations of State

In his dissertation in 1873 Van der Waals introduced an equation which reflects the liquefaction of real gases qualitatively and corrects the ideal gas equation quantitatively. With reference to mole this equation is

$$\left(p + \frac{a}{V_{\text{G,Mol}}^2} \right) (V_{\text{G,Mol}} - b) = R_{\text{Mol}} T \quad (2.2.1-1)$$

For $a = 0$ and $b = 0$ one obtains the state equation of the ideal gas. The correcting factor $a/(V_{\text{G,Mol}})^2$ is referred to as the internal pressure and takes into consideration the intermolecular attraction force. The constant b stands for the molecules' own volume. The following table expresses the experimentally ascertained numerical values for a and b for some selected gases. The larger these values become the greater is the deviation from the ideal behaviour.

Table T2.2.1-1: Numerical values of the constants in van der Waals' equation.

Gas	a in $10^3 [\text{N} \cdot \text{m}^4 \cdot \text{kmol}^{-2}]$	b in $10^{-2} [\text{m}^3 \cdot \text{kmol}^{-1}]$
He	3.47	2.38
H_2	24.86	2.67
Air	136	3.66
CH_4	230	4.31
CO_2	366	4.28
C_3H_8	937	9.03
C_4H_{10}	1389	11.64

There are a large number of additional state equations which are built up similarly. Thus we achieve a good approximation especially in the boundary area to liquefaction. For the calculation and use of such data please refer to the previous work of (Baumer 1983) and especially the comprehensive work of (Poling et al. 2001). The dependence of the intermolecular forces can be represented with a compression factor Z (Atkins 2006). An ideal gas has $Z = 1$. If $Z > 1$ then the gas is compressed more heavily than an ideal gas. Z is also referred to as a real gas factor, there is a dependency on pressure and temperature.

$$Z_{p,T} = \frac{P \cdot V_{\text{Mol}}}{R \cdot T} \quad (2.2.1-2)$$

$$Z_{p,T} = \frac{V_{\text{real}}}{V_{\text{ideal}}} \quad (2.2.1-3)$$

For $Z_{p,T} < 1$ the real molar volume is smaller than the ideal. This means that in a pressurised container there is more gas than would be expected according to the ideal equation. With $Z_{p,T} > 1$ it is vice versa. The dependency of Z on p and T can be so extreme that for a gas both $Z_{p,T} < 1$ and $Z_{p,T} > 1$ are possible. For N_2 $Z = 0.9752$ for $p = 120$ bar and $T = -10^\circ\text{C}$, and $Z = 1.0711$ for $p = 200$ bar and $T = +50^\circ\text{C}$. $Z_{p,T}$ is represented as a polynomial of the pressure p . The polynomial is an infinite mathematical series according to increasing powers of p .

$$Z_{p,T} = 1 + \beta \cdot p + \gamma \cdot p^2 + \dots \quad (2.2.1-4)$$

with the β , γ , ... as virial coefficients dependent on temperature which has to be determined experimentally. The word virial is derived from the Latin vis = power, plural vires/virium and is intended to draw attention to the intermolecular forces. For reasons of simplification the first virial coefficient was set = 1, in most cases the series is terminated after the first power of p . As well as the development of powers of p it is also possible to obtain polynomials for the molar density and the molar volume with different virial coefficients. The second virial coefficients are easily transferable with each other. Using equation (2.1.1-16) we obtain

$$p = \varphi_{\text{Mol}} \cdot R_{\text{Mol}} \cdot T = \frac{R_{\text{Mol}} \cdot T}{V_{\text{Mol}}} \quad (2.2.1-5)$$

$$Z_{p,T} = 1 + \beta^* \cdot \varphi_{\text{Mol}} + \gamma^* \cdot \varphi_{\text{Mol}}^2 + \dots \quad (2.2.1-6)$$

With

$$\beta^* = \beta \cdot R_{\text{Mol}} \cdot T \quad (2.2.1-7)$$

$$Z_{p,T} = 1 + \frac{\beta^*}{V_{\text{Mol}}} + \frac{\gamma^*}{V_{\text{Mol}}^2} \quad (2.2.1-8)$$

Using the real gas factor it is now possible to calculate volumes, densities and pressures much more accurately than with the ideal gas laws. Using the equation (2.1.1-14) we convert to (2.2.1-3)

$$Z_{p,T} = \frac{V_{\text{Mol}} \cdot p}{R_{\text{Mol}} \cdot T} \quad (2.2.1-9)$$

For the density we obtain

$$\varphi_{p,T} = \frac{M_{\text{Mol}} \cdot p}{Z_{p,T} \cdot R_{\text{Mol}} \cdot T} \quad (2.2.1-10)$$

For the comparison of two states we form the quotients of the two Z .

$$\frac{Z_{p_1, T_1}}{Z_{p_2, T_2}} = \frac{v_2 \cdot V_1 \cdot p_1 \cdot T_2}{v_1 \cdot V_2 \cdot p_2 \cdot T_1} = \frac{v_2 \cdot \phi_2 \cdot M_1 \cdot p_1 \cdot T_2}{v_1 \cdot \phi_1 \cdot M_2 \cdot p_2 \cdot T_1} \quad (2.2.1-11)$$

Most calculations can be carried out using this equation.

Example E2.2.1-1: Calculating the gas volume of N_2 at $p = 200$ bar and 15°C in a 50 litre cylinder ($V_{\text{geom}} = 0.05 \text{ m}^3$).

The $Z_{p,T}$ can be taken from the table T10.6-1 including the necessary interpolation at 1.050. If one dispenses with a p, T point of reference then one assumes that there is $V_{\text{geom}} 0.05 \text{ m}^3$ of gas at 1 bar. Thus there are V_{ideal} at 200 bar

$$V_{\text{ideal}} = \frac{p}{1 \text{ bar}} V_{\text{geom}} = 200 \cdot 0.05 = 10 [\text{m}^3]$$

From equation 2.2.1-3 we obtain a V_{real}

$$V_{\text{real}} = \frac{V_{\text{ideal}}}{Z_{p,T}} = \frac{10}{1.050} = 9.522 [\text{m}^3]$$

As already mentioned in paragraph 1.2.3 many manufacturers of industrial gases prefer the operating conditions 15°C and 1 bar. In this case it is necessary to calculate a $Z_{\text{reference}}$. As in most cases the density for the point of reference is known accurately enough so that we can use equation (2.2.1-10) with the necessary conversion.

$$Z_{\text{reference}} = \frac{M_{\text{Mol}} \cdot p_{\text{reference}}}{\phi_{\text{reference}} \cdot R_{\text{Mol}} \cdot T_{\text{reference}}}$$

From the data sheet N_2 we obtain $M_{\text{Mol}} = 28.0134 \text{ kg}$, $\phi_{p=1\text{bar}, T=15} = 1.170 \text{ kg} \cdot \text{m}^{-3}$. In addition $T = 288.15 \text{ K}$ and $R_{\text{Mol}} = 0.0831441 \text{ bar} \cdot \text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$.

$$Z_{\text{reference}} = 0.99938$$

The very small deviation from 1.0000 shows that the operating conditions vary only a small amount from the standard state and this is marginal for many calculations. We now have to determine the volume of gas $V_{\text{reference}}$ at the point of reference which would result at the expansion from 200 bar. For this we use the equation (2.2.1-11). In addition we can simplify because of the number v of the moles and the T being the same in both states, $p_{\text{reference}} = 1 \text{ bar}$.

$$\frac{Z_{\text{reference}}}{Z_{p,T}} = \frac{V_{\text{reference}}}{p \cdot V_{\text{geom}}}$$

$$V_{\text{reference}} = \frac{Z_{\text{reference}}}{Z_{p,T}} p \cdot V_{\text{geom}} = \frac{0.99938}{1.0502} 200 \cdot 10 = 9.516 [\text{m}^3]$$

Then we should introduce a calculation which cannot be immediately solved with the equation (2.2.1-11) but requires the use of two virial coefficients.

Example E2.2.1-2: From a pressurised gas cylinder filled with CH_4 with $V_1 = 50$ litres volume and $p_1 = 200$ bar with stable temperature $T = T_1 = T_2 = 20^\circ C = 293.15$ K in a container with $V_2 = 200$ litres pressure equalization takes place. We are determined to find p_2 .

The new total volume is $V_{1+2} = V_1 + V_2$, $v_1 = v_2$. According to the equations (2.2.1-11) and (2.2.1-4) but only with the linear element $\beta \cdot p$ we obtain:

$$\frac{Z_{p1,T}}{Z_{p2,T}} = \frac{V_1 \cdot p_1}{V_{1+2} \cdot p_2} = \frac{1 + \beta \cdot p_1}{1 + \beta \cdot p_2} \quad (2.2.1-12)$$

It is possible to ascertain $Z_{p1,T}$ as 0.813 from table T10.6-1, p_2 and $Z_{p2,T=293}$ cannot be determined from the equation (2.2.1-11). Thus we use the two virial coefficients and solve the above-mentioned equation according to p_2 .

$$p_2 = \frac{V_1 \cdot p_1}{V_{1+2} + \beta \cdot p_1 (V_{1+2} - V_1)} \quad (2.2.1-12)$$

The second virial coefficient β at $20^\circ C$ is taken to be $-1.93 \cdot 10^{-3}$ bar $^{-1}$ including interpolation from the data sheet in chapter 9.

$$p_2 = \frac{200 \cdot 0.05}{0.25 - 1.93 \cdot 10^{-3} \cdot 200(0.25 - 0.05)} = 57.8 [\text{bar}]$$

The result deviates significantly from the ideal calculation (= 40 bar).

2.2.2 The Liquefied Gas

If a substance is in a gaseous state then its internal energy determined by the temperature is greater than the intermolecular (attracting) forces. If the temperature is lowered by removing heat from the outside then depending on the pressure at one particular temperature the intermolecular forces prevail and liquefaction takes place. At $p_{\text{stand}} = 1013.25$ mbar this point is referred to as boiling point T_{bp} . In order to change the state of aggregation it is necessary to supply energy in the form of heat (evaporation) or withdraw energy (liquefaction). This amount of energy corresponds with the enthalpy of evaporation or with heat of vaporization ΔH_{evap} in $\text{kJ} \cdot \text{kg}^{-1}$ mostly given at T_{bp} . The enthalpy of evaporation depends on the temperature and can be calculated as T between T_{Tri} and T_{Cri} according to Watson's formula for a particular temperature T using $\Delta H_{\text{bp,evap}}$ at T_{bp} .

$$\Delta H_{T,\text{evap}} = \Delta H_{\text{bp,evap}} \left(\frac{1 - T \cdot T_{\text{Cri}}^{-1}}{1 - T_{\text{bp}} \cdot T_{\text{Cri}}^{-1}} \right)^{0.38} \quad (2.2.2-1)$$

When the state of aggregation changes from solid to liquid there is a corresponding melting heat at T_{mp} .

Example E2.2.2-1: $3 \text{ m} \cdot \text{h}^{-1}$ are to be removed from a propane gas cylinder in a gaseous state at $T = 20^\circ\text{C} = 293.15 \text{ K}$. How much electrical energy has to be used for the water bath?

First of all, one will ask why it is necessary to have additional heating. The cylinder contains liquid propane, the gaseous propane in the upper part of the cylinder is used and must be replenished by evaporation. When removing small amounts of the substance, the amount of heat supplied by the surrounding air is sufficient to achieve more evaporation if the cylinder cools slightly. If larger amounts are removed the cylinder will cool significantly which could lead to the propane changing to the solid state of aggregation. In this case a water bath controlled by a thermostat is the appropriate means. One should use $T_{\text{Cri}} = 369.85 \text{ K}$, $T_{\text{bp}} = 231.08 \text{ K}$ and $\Delta H_{\text{bp, evap}} = 425.4 \text{ kJ} \cdot \text{kg}^{-1}$ from the propane data sheet.

$$\Delta H_{T=293, \text{evap}} = 425.4 \left(\frac{1 - \frac{293.15}{369.85}}{1 - \frac{231.08}{369.85}} \right)^{0.38} = 339.3 [\text{kJ} \cdot \text{kg}^{-1}]$$

As $1 \text{ kJ} = 1 \text{ kWh}$ (kilowatt second) the energy E for 3 kg per 1 hour ($= 3600 \text{ s}$) is shown in usual kWh as

$$E = \frac{3 \cdot 339.3}{3600} = 0.283 [\text{kWh}]$$

An important physical characteristic of the gas which has been liquefied under pressure is the vapour pressure p_D which is dependent on the temperature. The vapour pressures in the temperature range from -10 to $+20^\circ\text{C}$ are given in the data sheets as a means of orientation. The state equations for the transitional borderline between liquid and gaseous was historically derived from Clausius and Clapeyron's (19th century) mole-based differential equation.

$$\frac{dp_D}{dT} = \frac{\Delta H_{\text{Mol, evap}}}{(V_{\text{Mol, D}} - V_{\text{Mol, liq}})T} \quad (2.2.2-2)$$

As the molar volume $V_{\text{Mol, liq}}$ in a liquid is very small, it can be neglected in comparison to the molar volume $V_{\text{Mol, D}}$ of the vapor. One uses the ideal state equation again.

$$V_{\text{Mol, D}} = R_{\text{Mol}} \cdot T \cdot p_D^{-1}$$

$$\frac{dp_D}{p_D} = d \ln p_D = \frac{\Delta H_{\text{Mol, evap}}}{R_{\text{Mol}} \cdot T^2} dT \quad (2.2.2-3)$$

We will dispense with the mathematical method of integration and obtain as a solution for states 1 and 2.

$$\ln \left(\frac{p_2}{p_1} \right) = - \frac{\Delta H_{\text{Mol, evap}}}{R_{\text{Mol}}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2.2.2-4)$$

As the enthalpy of evaporation depends on the temperature there are various approximations for Eq. (2.2.2-4). Most frequently the following Eq. is applied using the decade logarithm (\lg). A to F are constants which depend on the type of gas. They have to be ascertained experimentally (see Table T10.5-1).

$$\lg p_D = A + \frac{B}{C+T} + D \cdot T + E \cdot T^2 + F \cdot \lg T \quad (2.2.2-5)$$

If not indicated otherwise, such Eqs. are always valid between the triple temperature and the critical temperature.

If a liquefied gas is in a pressurised container it is often necessary to know the volume proportion of the liquid phase and the gaseous phase at temperature T. With the geometric volumes V_{geom} and the contained mass M we obtain the Eqs.

$$V_{\text{geom}} = V_{\text{gas}} + V_{\text{liq}} \quad \text{and} \quad M = M_{\text{gas}} + M_{\text{liq}}$$

In order to calculate the densities depending on T are needed and in the gaseous state also on p_D . The densities are inserted into the Eq. for M.

$$M = \varphi_{\text{gas}} \cdot V_{\text{gas}} + \varphi_{\text{liq}} \cdot V_{\text{liq}}$$

$$V_{\text{gas}} = \frac{M - \varphi_{\text{liq}} \cdot V_{\text{liq}}}{\varphi_{\text{gas}}} \quad \text{and} \quad V_{\text{liq}} = V_{\text{geom}} - V_{\text{gas}}$$

After further steps, one obtains

$$V_{\text{liq}} = \frac{M - \varphi_{\text{gas}} \cdot V_{\text{geom}}}{\varphi_{\text{liq}} - \varphi_{\text{gas}}} \quad (2.2.2-6)$$

Example E2.2.2-2: According to (ADR 2005) a pressurised gas cylinder with a test pressure of 190 bar (g) can be filled with CO_2 with a filling factor f_{fill} of 0.66 kg/l. The filling is to be effected with cold CO_2 at 258 K (approx. -15°C). Later on the cylinder is due to be transported at 298 K (approx. $+25^\circ\text{C}$). How large is the V_{liq} at both temperatures?

CO_2 has been checked thoroughly and there are tables for the material data on the vapour pressure curve (T10.4-8). For 258 K we take the vapour pressure $p_D = 22.8$ bar (abs.), $\varphi_{\text{liq}} = 1.009$ kg \cdot l $^{-1}$, $\varphi_{\text{gas}} = 60.505$ kg \cdot m $^{-3}$, and for 298 K is $p_D = 64.09$ bar, $\varphi_{\text{liq}} = 0.7137$ kg \cdot l $^{-1}$, $\varphi_{\text{gas}} = 240.68$ kg \cdot m $^{-3}$. V_{geom} is 10 litres, as well as $M = f_{\text{fill}} \cdot V_{\text{geom}} = 6.6$ kg.

$$V_{\text{liq},258\text{K}} = \frac{6.6 - 0.0605 \cdot 10}{1.009 - 0.0605} = 6.32[1]$$

and

$$V_{\text{liq},298\text{K}} = \frac{6.6 - 0.24068 \cdot 10}{0.7137 - 0.24068} = 8.86[1]$$

As the temperature increases the density of the liquid falls and it takes up more and more volume. The filling factors are calculated so that at the maximum permitted temperature range for the pressurised gas cylinders of -20 to $+70^\circ\text{C}$ the pressure can't be higher than the tested one. If the container has been overfilled there is a great safety risk of the liquid filling the whole container and expanding through heat. In this case we do not consider the vapour pressure p_D any longer but we must use the pressure of the incompressible liquid which can rise over 1000 bar with a temperature increase of only a few K. This then leads to the destruction of the cylinder with usually significant damage to personnel and equipment.

For this reason the filling of liquefied gases is only allowed through gravimetric weighing. Accompanying measures require detailed written reports as well as an additional weighing by a second person. If an overfilling is discovered the excess amount has to be discharged immediately.

2.2.3 Diverse Properties

This section introduces the concept of adiabatic (isenthalpic) expansion. This means the expansion of a gas without the transfer of heat, thus not isothermally, e.g. in a system isolated from heat. The real gas combats the adiabatic expansion through cooling by using its internal energy to compensate for the intermolecular attraction forces. This effect was discovered by Joule and Thomson, later to be Lord Kelvin, in the 19th century. Thus there is the possibility of cooling and liquefying a gas with, if possible, isothermal compression and subsequent resultant adiabatic expansion. This was the basis of the first liquefaction of air by Carl von Linde in 1876.

One must be advised that the Joule-Thomson effect has an inversion temperature dependent on the type of gas. Above this temperature heating occurs during expansion, the so-called inverse Joule-Thomson effect. Thus H_2 has to be initially pre-cooled by liquid N_2 (-196°C) before the liquefaction is possible.

The resultant new pressure p_2 from the adiabatic expansion of volume V_1 at pressure p_1 into the total volume V_2 can be calculated, considering Eq. (2.1-25), using the formula

$$p_2 = \left(\frac{V_1}{V_2} \right)^\varepsilon \cdot p_1 \quad \text{with} \quad \varepsilon = \frac{c_{p,\text{Mol}}}{c_{v,\text{Mol}}} \quad (2.2.3-1)$$

For the temperature T_2 after expansion is defined as

$$T_2 = \left(\frac{V_1}{V_2} \right)^\phi \cdot T_1 \quad \text{with} \quad \phi = R_{\text{Mol}} \cdot c_{p,\text{Mol}}^{-1} \quad (2.2.3-2)$$

Example E2.2.3-1: Calculating the pressure p_2 and temperature T_2 after the adiabatic expansion of N_2 with V_1 , $p_1 = 30$ bar and $T_1 = 293.5$ in a $V_2 = 3 V_1$.

Ideally apply $c_{p,Mol} = (7/2) \cdot R_{Mol}$ and $\varepsilon = 7/5$. $R_{Mol} = 8.31441 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

$$c_{p,Mol} = \frac{7}{2} \cdot 8.31441 = 29.10 [\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] \quad \phi = \frac{8.31441}{29.10} = 0.2857$$

$$p_2 = \left(\frac{1}{3}\right)^{7/5} 30 = 6.44 [\text{bar}] \quad T_2 = \left(\frac{1}{3}\right)^{0.2857} \cdot 293.15 = 214.17 [\text{K}]$$

We compare the ideal molar heat capacity with the measured value of the specific heat capacity $c_{p,kg} = 1.040 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} = 1.040 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ as per data sheet N_2 .

$$c_{p,kg} = c_{p,Mol} \cdot M_{Mol}^{-1} = \frac{7 \cdot R_{Mol}}{2 \cdot M_{Mol}} \quad (2.2.3-3)$$

$$c_{p,kg} = \frac{7 \cdot 8.31441}{2 \cdot 28.0134} = 1.039 [\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}]$$

One can see that the deviation of the ideal calculation from the measured value of 0.1 % rel. is very small. However, one must be aware of the fact that for N_2 c_p and c_v depend significantly on pressure and temperature. These values have to be determined empirically and can be read out of standard tables (Messer 1989).

We are now considering the so-called transport phenomena of gases. This means the movement of particles (diffusion), energy (thermal conductivity) and impulse (viscosity). The differential equations which describe these properties are all constructed similarly.

Fick's first law adverts to diffusion

$$Q_V = \frac{dV}{dt} = -D \cdot A \frac{dC}{dx} \quad (2.2.3-4)$$

Q_V is the flow-rate of the volume or the mass ($= dM/dt$), t the time, and A the area contemplated, through which the diffusion is effected. X is the direction considered and D the diffusion constants in $\text{m}^2 \cdot \text{s}^{-1}$.

For the thermal conductivity the function of the energy flow dE/dt on the temperature gradients dT/dx is shown.

$$\frac{dE}{dt} = -\lambda \cdot A \frac{dT}{dx} \quad (2.2.3-5)$$

λ is the heat conductivity coefficient in $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, often simply referred to as thermal conductivity.

To understand viscosity we must consider the internal friction of a gas. If two adjacent layers of gas move with different speeds then particles move from one layer to the other. The layers become interlocked; this causes the faster layer to slow down and vice versa. To maintain the difference in speeds, the internal friction force F_{friction} has to be generated. As the force is equal to the derivation of impulse I_{mv} over the time we obtain

$$F_{\text{friction}} = \frac{dI_{\text{mv}}}{dt} = -\eta \cdot A \frac{dv}{dx} \quad (2.2.3-6)$$

with dv/dx as speed gradient and η the dynamic viscosity coefficient in $\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ or $\text{N} \cdot \text{s} \cdot \text{m}^{-2}$. To a certain extent we define a deviating kinematic viscosity when we consider the density.

$$\eta^* = \frac{\eta}{\varphi} [\text{m}^2 \cdot \text{s}^{-1}] \quad (2.2.3-7)$$

For the ideal gas the coefficients of transport phenomena are calculated *via* the kinetic gas theory. As the diffusion coefficient D plays a central role both for permeation (chap. 3.1.4) and for homogenisation (chap. 5.1.3) a short introduction is required. Without proof and with the help of Eqs. (2.1.2-1), (2.1.2-2) and (2.1.2-4) the diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$) is shown to be

$$D = \frac{1}{3} v_{\text{m,Maxwell}} \cdot S_{\text{particle}} = \frac{1}{3} \sqrt{\frac{8}{3 \cdot \pi}} \sqrt{\frac{3 \cdot R_{\text{Mol}} \cdot T}{M_{\text{Mol}}}} \frac{R_{\text{Mol}} \cdot T}{\sqrt{2} \cdot \pi \cdot p \cdot 4 \cdot r^2 \cdot k_{\text{Avogadro}}} \\ D = \frac{\sqrt{R_{\text{Mol}}^3}}{6 \cdot \sqrt{\pi^3} \cdot k_{\text{Avogadro}}} \sqrt{\frac{T^3}{M_{\text{Mol}}}} \frac{1}{p \cdot r^2} \quad (2.2.3-8)$$

Here $d = 2r$ was fixed with r as the particle radius. With respect to D the following dependencies are important:

- Inversely proportional to the pressure, i.e. as the pressure increases the diffusion decreases.
- Inversely proportional to the root of the molar mass as well as to the square of the particle radius. Small particles and particles with little mass diffuse more quickly.
- Proportional to $T^{3/2}$ and therefore an increase in temperature encourages diffusion.

The D from Eq (2.2.3-8) only applies for the so-called self diffusion in the cylinder containing only the observed gas. For the diffusion of two gases 1 and 2 in each other a binary diffusion coefficient applies. The extended formula, also provided without proof, is then:

$$D_{1,2} = \frac{\sqrt{R_{\text{Mol}}^3}}{6 \cdot \sqrt{\pi^3} \cdot k_{\text{Avogadro}}} \sqrt{\frac{T^3 \cdot (M_{\text{Mol},1} + M_{\text{Mol},2})}{M_{\text{Mol},1} \cdot M_{\text{Mol},2}}} \frac{1}{p \cdot (r_1 + r_2)^2} \quad (2.2.3-9)$$

For the real gases the dependency of the individual coefficients of p and T differ from the ideal calculation. The empirical data mostly serve a mathematical representation in the form of a series expansion based on p or T , similar to that for the real gas factor.

For flammable gases the so-called burning values (energy values) and heating values are interesting. The energy value H_{energy} is defined as the energy per kg, mole or m^3 which is produced by complete combustion in pure O_2 . After combustion the remains are exclusively gaseous CO_2 , N_2 , and SO_2 as well as liquid H_2O . For the heating value H_{heat} burning takes place in the air, it is $H_{\text{heat}} < H_{\text{energy}}$. After combustion the H_2O remnants are gaseous.

Let us now look at the solubility of gases in liquids. The simplest case is provided by atmospheric air over water. If we consider the main components N_2 , O_2 and Ar there is a thermodynamic system of 8 phases. Water forms the liquid phase with the vapour pressure $p_{\text{D,H}_2\text{O}}$ as a function of T . N_2 , O_2 and Ar each have a phase of which is soluble in water with the proportional amounts of substance $C_{\text{v,G,sol}}$

$$C_{\text{v,G,sol}} = \frac{v_{\text{G,sol}}}{v_{\text{liq}} + v_{\text{G,sol}}} \quad (2.2.3-8)$$

and the partial pressures exerted above the water p_{N_2} , p_{O_2} and p_{Ar} . $v_{\text{G,sol}}$ is the number of the moles of the gases dissolved in the liquid, v_{liq} is the number of the moles of the liquid. For small solubilities and pressures Henry's Law applies. $p_{\text{G,sat}}$ is the saturation vapour pressure of the gas G .

$$p_{\text{G,sat}} = \delta_{\text{Henry,G}} \cdot C_{\text{v,G,sol}} \quad (2.2.3-9)$$

Henry's coefficient δ_{Henry} has the dimension of a pressure. The Law describes the proportionality of the concentration in the liquid and the pressure above the liquid. To differentiate from the normal vapour pressure of a liquid this can also be referred to as saturation vapour pressure p_{sat} of the soluble phase and is dependent on T . In practice however the technical solubility coefficient δ_{techn} has prevailed.

$$\delta_{\text{techn}} = \frac{V_{\text{G,STP}}}{M_{\text{sol}}} [1 \cdot \text{kg}^{-1}] \quad (2.2.3-10)$$

δ_{techn} shows how many litres of gases at normal state are dissolved per kg liquid at p and T . For the amount of $p_{\text{G,sat}}$ we will use Dalton's Law in our example and thus apply ideal behaviour.

One uses more rarely

$$\delta_{\text{techn}}^* = \frac{V_{\text{G,STP}}}{M_{\text{G,sol}} \cdot p_{\text{G,sat}}} [1 \cdot \text{kg}^{-1} \cdot \text{bar}^{-1}] \quad (2.2.3-11)$$

2.3 Gas Mixtures

In this book we predominantly describe gas mixtures in pressurised cylinders. The manufacture is described in chapter 5. Gas mixtures close to atmospheric pressure, as required by the user, are mentioned briefly in chapter 8.2. In the case of the pure gases it became clear in the previous chapters that the real behaviour leads to a great deal of effort as far as the calculating is concerned. This is even more noticeable with the gas mixtures. The “triangular relationship” volume – pressure – temperature can be avoided if we can revert to the mass of the gases. One while dealing with densities in the area of only a few grams per litre very accurate scales are necessary. At the end of the seventies single-pan scales achieved accuracies better than 0.1% rel., thus the triumph of the gravimetric production of gas mixtures and especially calibration gases could not be sterner. This trend was connected with the use of the relationship of the amounts of substance C_v which we have already introduced as the number of moles. This leads to the fraction of molar concentration, the character of which is obviously a concentration.

$$C_{v,j} = \frac{v_j}{\sum_{i=1}^n v_i} \quad (2.3-1)$$

The designation as the fraction of the molar concentration was chosen because this information is most frequently used on the analytical certificate for a gas mixture. In addition, the definitions for the volume and mass fractions apply which are however often used without misunderstanding as the volume and mass concentration

$$C_{V,j} = \frac{V_j}{\sum_{i=1}^n V_i} \quad (2.3-2)$$

$$C_{M,j} = \frac{M_j}{\sum_{i=1}^n M_i} \quad (2.3-3)$$

The conversion of the different kinds of concentration with each other can be found in Table T2.3-1. It is complicated because the density φ depends on both p and T and has to be calculated from tables or by using virial coefficients.

Table T2.3-1: Conversion of the different kinds of concentration

	$C_{v,j}$	$C_{v,j}$	$C_{M,j}$
$C_{v,j} = \frac{V_j}{\sum_{i=1}^n V_i}$	_____	$\frac{\varphi_j \cdot C_{v,j}}{\sum_{i=1}^n \frac{\varphi_i \cdot C_{v,i}}{M_i}}$	$\frac{C_{M,j}}{\sum_{i=1}^n \frac{C_{M,i}}{M_i}}$
$C_{v,j} = \frac{V_j}{\sum_{i=1}^n V_i}$	$\frac{C_{v,j} \cdot M_j}{\sum_{i=1}^n \frac{C_{v,i} \cdot M_i}{\varphi_i}}$	_____	$\frac{C_{M,j}}{\sum_{i=1}^n \frac{C_{M,i}}{\varphi_i}}$
$C_{M,j} = \frac{M_j}{\sum_{i=1}^n M_i}$	$\frac{M_j \cdot C_{v,j}}{\sum_{i=1}^n M_i \cdot C_{v,i}}$	$\frac{\varphi_j \cdot C_{v,j}}{\sum_{i=1}^n \varphi_i \cdot C_{v,i}}$	_____

To calculate the composition of a calibration gas we introduce the ideal density of a gas.

$$\varphi_{G,\text{ideal}} = \frac{M_{G,\text{Mol}}}{V_{\text{STP}}} = \frac{M_i}{V_i} \quad (2.3-4)$$

Example E2.3-1: Calculating the composition of a test gas with 1% N₂, 2% Ar in H₂ for 2 m³ in a 10-litre cylinder.

The total volume is V = 2 m³, the supposed concentrations and the fraction of molar concentration C_{N₂} = 1 · 10⁻², C_{Ar} = 2 · 10⁻² and C_{H₂} = 0.97. The partial volumes are correspondingly shown to be

$$V_i = C_i \cdot V \quad \text{and} \quad V = \sum V_i = 2 [\text{m}^3]$$

From this: V_{N₂} = 0.02 m³, V_{Ar} = 0.04 m³ and V_{H₂} = 1.94 m³, which are idealised volumes can be calculated. From the data sheets we take the ideal densities as $\varphi_{N_2} = 1.250 \text{ kg} \cdot \text{m}^{-3}$, $\varphi_{Ar} = 1.782 \text{ kg} \cdot \text{m}^{-3}$ and $\varphi_{H_2} = 0.090 \text{ kg} \cdot \text{m}^{-3}$. The masses which have to be weighed are therefore provided by the formula $M_i = \varphi_i \cdot V_i$.

Table T2.3-2: Example of the composition of a calibration gas

gas	concentration [%]	mass [g]	partial volume [m ³]
N ₂	1	25.0	0.02
Ar	2	71.3	0.04
H ₂	to 100	174.6	1.94

It still needs to be proven that one is not dealing with the volume concentration but with the desired concentration of the fraction of the molar concentration.

$$C_j = \frac{V_j}{\sum_{i=1}^n V_i} = \frac{\frac{M_j}{\phi_j}}{\sum_{i=1}^n \frac{M_i}{\phi_i}} = \frac{\frac{M_j \cdot V_{STP}}{M_{j,Mol}}}{\sum_{i=1}^n \frac{M_i \cdot V_{STP}}{M_{i,Mol}}} = \frac{V_{STP}}{V_{STP}} \frac{v_j}{\sum_{i=1}^n v_i} = \frac{v_j}{\sum_{i=1}^n v_i}$$

Example E2.3-2: Pressure in the gas cylinder $T=15^\circ\text{C}$ for the mixture as per Example E 2.3-1

For these small fractions it should be calculated by using the ideal gas law. For N_2 it is

$$p_{N_2} = \frac{p_{1bar} \cdot V_{N_2}}{V_{geom}} = \frac{0.02}{0.01} = 2[\text{bar}]$$

and analogous with $p_{Ar} = 4$ bar. For H_2 the ideal calculation is added up to 194 bar. Nevertheless, it is necessary to carry out the calculation of pressure with the real gas factor. Analogous to Example E2.2.1-2 one proceeds:

$$\frac{V_1 \cdot p_1}{V_2 \cdot p_2} = \frac{1 + \beta \cdot p_1}{1 + \beta \cdot p_2}$$

$V_1 = 1.94 \text{ m}^3$, $p_1 = 1 \text{ bar}$, $V_2 = 0.01 \text{ m}^3$, $\beta = 0.595 \cdot 10^{-3} \text{ bar}^{-1}$ are inserted into the equation and from the data sheet we take

$$p_2 = \frac{V_1 \cdot p_1}{V_2 + \beta \cdot p_1 (V_2 - V_1)} = \frac{1.94 \cdot 1}{0.01 + 0.595 \cdot 10^{-3} \cdot 1(0.01 - 1.94)} = 219.2[\text{bar}]$$

Altogether for the gas mixture a pressure of 225.2 bar is obtained which is not acceptable for the normal cylinder with an operating pressure of 200 bar. Therefore one reduces the volume from 2 m^3 in the ratio 200/225.2 to approximately 1.77 m^3 and calculate the composition again.

For the real gases and their mixtures we have carried out only relatively simple calculations. The handbooks of (Messer 1989) and (Air Liquide 2005) are recommended for more detailed study.

2.4 Moisture Content

Of all the impurities in the purest gases moisture has a special position. For most users the omnipresent water is a very disturbing substance, the limit concentration which must be achieved moves continually into the lower ppb range. Water is often a basic prerequisite for chemical reactions. Thus dry oxygen does not cause the internal wall of the steel cylinder to rust but with a moisture content of as little as 50 ppm severe rusting can be expected. CO_2 and HCl (anhydrous inorganic

acids) in connection with liquid water in the steel cylinder cause corrosions negatively which effect safety. The strongly polarised H_2O molecule bonds with almost every means of adsorption and can be removed, e.g. by heating.

First of all one must differentiate between two marginal cases in the gas cylinder. If water is present in liquid form the vapour pressure p_{D,H_2O} which is dependent on the temperature is established. The concentration relation for removing the water is shown by the Eq.

$$C_{H_2O} = \frac{P_{D,H_2O}}{\sum_{i=1}^n P_i} \quad (2.4-1)$$

When p_i is the pressure of all n gases in the cylinder. The concentration increases sharply at the end of the removal. Liquid water in a gas cylinder is a terrible mistake by the filling company and is caused by inadequate preparation of the cylinder. For the purest gases this case is not relevant.

If only gaseous water i.e. water vapour with the partial pressure p_{H_2O} is in the cylinder then the types of concentration according to section 2.3 apply. The concentration, e.g. on the basis of the partial pressure (ideal calculation) remains constant during the removal.

$$C_{H_2O} = \frac{P_{H_2O}}{\sum_{i=1}^n P_i} = k \quad (2.4-2)$$

If water vapour has been adsorbed on the internal wall of the gas cylinder then there is a saturation pressure $p_{Ads,sat}$ for this adsorbed phase. If the partial pressure decreases to the level of the saturation one during the removal then there is an increase in concentration as the water vapour is supplied from the adsorbed phase.

(Schön 1999) reported about a special case of the concentration relation. If there are small amounts of oil (glyceride) in the cylinder, e.g. because the cylinder has been filled using compressors which have been lubricated, then a film of water can be formed, which is covered by a layer of oil, which is only a few molecules thick. In these cases for the concentration relation the following Eq. applies

$$C_{H_2O} = C_{H_2O}^{(A)} \left(\frac{p^{(A)}}{p} \right)^k \quad (2.4-3)$$

with (A) as the designation of the initial value and k is a constant which depends on the geometry of the pressurised container and the temperature. Strangely enough the maximum value is $37.2^\circ C$ which has given rise to the speculation that the human brain is thermostatically set at this value.

Measuring moisture content (humidity) takes place in meteorology in the temperature range surrounding us as well as in the extreme conditions of the upper atmosphere. To achieve this dew point is often determined (wet mirror method). Thus we are dealing with vapour pressures above water e.g. 6.11 mbar at $0^\circ C$

which correspond to a concentration of 0.603 volume-% at 1013.25 mbar in the air. The range which is of interest for the purest gases is the one with few ppm or ppb. As the wet mirror method has also been used successfully in this area the vapour pressures over ice are relevant.

The phase borderline solid-gaseous is described mathematically similarly to Clausius and Clapeyron's differential equations (Eqs 2.2.2-2 and -3) ΔH_{Subl} is the sublimation enthalpy.

$$\frac{d \ln p_{D,\text{Subl}}}{dT} = \frac{\Delta H_{\text{Mol,Subl}}}{R_{\text{Mol}} \cdot T^2} \quad (2.4-4)$$

The evaporation enthalpy is dependent on the temperature, as it is with sublimation. The concept of the sublimation point is connected with the pressure of 1013.25 mbar. When measuring moisture sublimation points at other pressures they are referred to as frost point.

For the following discussion, documents used were kindly provided by the PTB (Physikalisch-Technische Bundesanstalt, Germany) in Brunswick. (Sonntag 1998) gave an overview of the historical development of the formulas for the dependence of vapour pressure on the temperature. To calculate it over water or ice one often uses the Magnus formula with T in $^{\circ}\text{C}$, (Magnus 1844).

$$p_D(T) = p_{D,0C} \cdot \exp \frac{k_1 \cdot T}{k_2 + T} \quad (2.4-5)$$

One can obtain more recent values k_1 and k_2 of the Magnus' formula from (Weber 2002) work, $p_{D,0C}$ is the vapour pressure at 0°C .

(Sonntag 1990) gave a more exact Eq. with a series expansion, T in K and p_D in hPa.

$$\ln p_D = -\frac{6024.5282}{T} + 24.7219 + 1.0613868 \cdot 10^{-2} \cdot T - \frac{1.3198825}{10^5 \cdot T^2} - 0.49382577 \cdot \ln T \quad (2.4-6)$$

Table T2.4-1 uses Eq (2.4-6) and contrasts:

- The temperature at the phase borderline solid – gaseous, the frost point temperature T_{Frost} , sometimes also referred to the phase borderline liquid gaseous, called the dew point temperature.
- The pressure $p_{D,\text{Subl}}$, the saturation vapour pressure of the solid phase
- The fraction of the amount of substance in ppm (p assumed to be ideal, $p_{D,\text{Subl}}$ in mbar)

$$C_{v,\text{H}_2\text{O}} = \frac{p_{D,\text{Subl}}}{\left(\sum_{i=1}^n p_i \right)_{=1013\text{mbar}}} 10^6 \text{ [ppm]} \quad (2.4-7)$$

– The absolute moisture concentration

$$C_{\text{abs,H}_2\text{O}} = \frac{M_{\text{H}_2\text{O}}}{\sum_{i=1}^n V_i} [\text{g} \cdot \text{m}^{-3}] \quad (2.4-8)$$

The relationship between the types of concentrations applies with an ideal calculation and under normal conditions, $C_{\text{v,H}_2\text{O}}$ in ppm:

$$\begin{aligned} C_{\text{abs,H}_2\text{O}} &= \frac{M_{\text{Mol,H}_2\text{O}}}{V_{\text{Norm}}} C_{\text{v,H}_2\text{O}} \cdot 10^{-6} = \frac{18.0152}{22.41383} C_{\text{v,H}_2\text{O}} \cdot 10^{-3} \\ &= 0.80375 \cdot C_{\text{v,H}_2\text{O}} \cdot 10^{-3} [\text{g} \cdot \text{m}^{-3}] \end{aligned} \quad (2.4-9)$$

Table T2.4-1: Frost point temperature, moisture fractions and absolute moisture concentration for selected values in the temperature range from 0 to -120°C . Interim values can be taken from Table T10.7-1.

T_{Frost} in [°C] at 1013.25 mbar	p_{D,Subl} in [mbar]	C_{v,H₂O} in [ppm] at 1013.25 mbar	C_{abs,H₂O} [mg · m⁻³] STP
0	6.1115	6031.6210	4844.7
-10	2.5983	2564.3326	2059.7
-20	1.0324	1018.8904	818.4
-30	0.3800	375.0246	301.2
-40	0.1284	126.6910	101.8
-50	0.03936	38.8433	31.20
-60	0.01081	10.6656	8.567
-70	0.002615	2.5812	2.073
-80	$547.2 \cdot 10^{-6}$	0.54009	0.434
-90	$96.7 \cdot 10^{-6}$	0.09544	0.0767
-100	$14.0 \cdot 10^{-6}$	0.01384	0.0111
-110	$1.61 \cdot 10^{-6}$	0.001588	0.00128
-120	$0.140 \cdot 10^{-6}$	0.000138	0.000111

2.5 Leak Rate

With requirements for the purity of gases it was critically necessary to improve technical equipment with regards to leak tightness. In 1961¹ something was classified leak proof if it did not produce any bubbles when tested with a soap solution. Besides this test there was already the ultra-high vacuum technique used in which the concept of the leak rate was well established. This was determined for a

¹ In 1961 the author started his work at the Ostberliner Technische Gase Werken.

geometric volume V_{geom} by evacuating it separating it from the vacuum pump and measuring the increase in pressure Δp after a time t . We call this the vacuum leak rate L_{vac} .

$$L_{\text{vac}} = \frac{\Delta p \cdot V_{\text{geom}}}{t} [\text{mbar} \cdot \text{l} \cdot \text{s}^{-1}] \quad (2.5-1)$$

In the pressure technique the relationships are different. The cylinder is under a pressure p and the escaping amount of gas $Q_V = dV/dt$ at STP is measured. It is called the pressure leak rate L_p .

$$L_p = Q_V = \frac{V}{t} [\text{cm}^3 \cdot \text{s}^{-1}] \quad (2.5-2)$$

If neglecting the small corrections (e.g. cm^3 at STP) one obtains

$$1 \cdot \text{mbar} \cdot \text{liter} \cdot \text{s}^{-1} \cong 1 \cdot \text{cm}^3 \cdot \text{s}^{-1} \quad (2.5-3)$$

It is important to realize that the pressure leak rate L_p depends on the internal pressure of the container in question. This becomes clear when one looks at the Eq. for the relationships between the flows. One differentiates between two borderline cases.

The flow through a capillary with radius r and length l is referred to as laminar flow. The Hagen-Poiseuille's law of 1839/40 applies. p_1 is the pressure in the container, p_2 the atmospheric pressure under normal circumstances.

$$Q_{V,H-P} = \frac{\pi \cdot r^4}{8 \cdot \eta \cdot l} (p_1 - p_2) = \frac{\pi \cdot r^4}{8 \cdot \eta \cdot l} p_{1,(g)} \quad (2.5-4)$$

The other extreme case is easiest to show with an orifice plate with A as the area of the opening. According to Knudsen the molecular flow is given

$$Q_{V,Knudsen} = A \sqrt{\frac{R_{\text{Mol}} \cdot T}{2\pi \cdot M_{\text{Mol}}}} \frac{p_1 - p_2}{p_2} = A \sqrt{\frac{R_{\text{Mol}} \cdot T}{2\pi \cdot M_{\text{Mol}}}} p_{1,(g)} \quad (2.5-5)$$

with $p_2 = 1 \text{ bar}$.

Both kinds of flow express the relationship of the pressure difference between the container pressure and atmospheric one. Consequently, the pressure leak rate has to be supplemented by information about the pressure.

Vacuum and pressure leak rate can not be calculated from each other with any great accuracy. The rule of thumb is

$$L_p \approx p \cdot L_{\text{vac}} \quad (2.5-6)$$

Many manufacturers of leak-test mass spectrometers give $L_p = 100 L_{\text{vac}}$ without specifying p .

When considering the container pressure one peculiarity of the leak must be mentioned. At high pressures the form of the pressure containers is changed, sometimes leaks only occur at this stage. Thus it makes sense to check an industrial gas plant for leak tightness at the pressure production.

Eqs. 2.5-4 and -5 show the dependence on the type of gas. From the example of selected gases in Table T2.5-1 one can view the sometimes considerable differences, the Q_v for He were randomly fixed = 1. It is not possible to give a simple relationship of the leak rate to the density because the exact type of leak is normally unknown and is additionally a combination.

Table T2.5-1: The dependence of leak volume flow rate on the type of gas and flow.

gas	η in [Ns · m ⁻²] · 10 ⁻⁶	M _{Mol} in [kg]	Q _v Hagen-Poisselle	Q _v Knudsen
He	19.2	4.00	1	1
H ₂	8.92	2.02	2.20	1.40
N ₂	17.9	28.01	1.10	0.38
Ar	22.8	39.95	0.86	0.32
CF ₄	17.4	8.00	1.13	0.21
Xe	23.0	131.30	0.86	0.17

In general the leak rate serves as a measure of leak tightness and thus the quality e.g. of a component, it can however also be used to estimate volume flows.

Example E2.5-1: In a 50 litre gas cylinder with 200 bar (gauge pressure) He a leak rate of $5 \cdot 10^{-3} \text{ cm}^3 \cdot \text{s}^{-1}$ is measured at the point where the valve is screwed in. By how many bars has the pressure in the bottle fallen after 2 years (a)?

$$V = L_{p=200\text{bar}} \cdot t_{2a} = 5 \cdot 10^{-3} \cdot 60 \cdot 60 \cdot 24 \cdot 365 \cdot 2 = 315.360[\text{cm}^3] = 0.3154[\text{m}^3]$$

We continue to calculate perfectly using the relatively small amount of ideal gas. In 2 years the volume has decreased from 10 to 9.684 m³. Then the pressure is (A) = beginning

$$p^{(A)} \cdot V_{\text{geom}} = 0.05 \cdot 200 = 10[\text{m}^3]$$

$$\Delta p^{(2a)} \cdot V_{\text{geom}} = 0.05 \cdot p_{2a} = 9.684[\text{m}^3]$$

$$p^{(2a)} = \frac{9.684 \cdot 200}{10} = 193.7[\text{bar}]$$

If the filling company gives a 2-year guarantee, there must be complaint about this decrease in pressure. In most cases a tolerance of ± 5 bar is guaranteed.

Example E2.5-2: With a pipeline plant Ar 6.0 is supplied to different customers at a pressure of 6 bar (gauge pressure). The pipeline plant contains 40 sealing components in the pipes and fittings. The volumetric flow is $10 \text{ m}^3 \cdot \text{h}^{-1}$. The fraction of air in

the Ar should not be increased by more than 0.1 ppm by leakage. How large can the leak rate for the individual sealing element be?

Using $C_{\text{air}} = 0,1 \cdot 10^{-6}$ and $Q_V = 10 \text{ m}^3 \cdot \text{h}^{-1}$ we obtain

$$\begin{aligned} Q_{\text{air}} &= L_{\text{total}} = C_{\text{air}} \cdot Q_V = 0,1 \cdot 10^{-6} \cdot 10 \\ &= 10^{-6} \left[\text{m}^3 \cdot \text{h}^{-1} \right] = 10^{-6} \frac{10^{-6}}{60 \cdot 60} = 2,8 \cdot 10^{-4} \left[\text{cm}^3 \cdot \text{s}^{-1} \right] \\ L_{\text{single}} &= \frac{L_{\text{total}}}{40} = 7 \cdot 10^{-6} \left[\text{cm}^3 \cdot \text{s}^{-1} \right] \end{aligned}$$

Now there is a justified question: How can air get into a system which is operating at an gauge pressure of 6 bar. The answer: The flow through a leak is dependent on the partial pressure. The outside one is the atmospheric pressure of air, inside it is virtually = 0. This may seem paradoxical but even for an Ar supply pipe at a pressure of 250 or even 400 bar it is true that leaks cause the Ar to flow to the outside but air to the inside. If the volumetric flow of Ar is very large it is hardly noticeable. At times of less usage, e.g. during weekends the following phenomenon occurs: When the plant is put into operation at the beginning of the week a relatively high content of O_2 and N_2 , is found which slowly decreases again. It is hardly possible to deal with this mathematically.

Searching for leaks and establishing specification limits are described in chapter 4.