BASIC CONCEPTS OF THE GAS PHASE

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Summary

This chapter presents a number of important properties of gases and situates these as a form of matter. Most of these properties can be explained rather well on the basis of the kinetic theory of gases. More on transport properties is given in Control of Gaseous Emissions and thermal properties are further treated in Pollution Control through Efficient Combustion Technology.

1. Survey

Gases appear to have no structure, size or shape. Different gases are always completely miscible and fill all space at their disposal, in contrast to liquids or solids, in which cohesive forces and surface tension restrain the thermal movement of molecules.

Under the same conditions of temperature and pressure, equal volumes of different gases contain an equal number of molecules. The volume occupied by one mol of gas at standard temperature and pressure (0°C, 1 atmosphere) is 0.0224 m³ and the same for all gases, according to Avogadro's law. The most important physical properties of gases and their mixtures are pressure, temperature, density, viscosity, internal energy, heat conductivity, and diffusivity. These are interdependent properties: if two are known, all others can be derived. The two properties most usually chosen are temperature and either pressure or density. Gibbs' phase rule states the number of such State Variables required for fixing all properties of gaseous mixtures.

Gases consist of vast numbers of molecules traveling in all directions at speeds that are distributed randomly around an average determined by their temperature. Molecules are distributed randomly in space, colliding with one another and with the walls of their container, exerting pressure.
The **Critical Point**, where gas, liquid and dense gas are in equilibrium, is an important reference for all physical properties, according to the **Law of Corresponding States**.

The **ideal gas law** is a simple representative of **equations of state**, correlating temperature, pressure and volume of a given amount of gas. **Temperature** also governs the transfer of heat between one system and another. Gases condense to liquids or solids, when the temperature is sufficiently decreased. **Phase changes** are accompanied by a ‘latent’ heat effect, which plays an important role, e.g. in cloud forming processes.

More complicated equations of state are required to describe the conditions of vapors and dense gases. Several fundamental and empirical examples are cited: van der Waals, virial expansions, Redlich-Kwong.

The **kinetic theory** explains the concepts of pressure, temperature, viscosity, internal energy, heat conductivity, and diffusivity on the basis of the velocity of molecules, molecular collisions and mean free path. It accounts with fair precision for all relevant properties of gases in terms of forces between molecules, assuming that their motions are described by the laws of either classical Newtonian mechanics or quantum mechanics.

### 2. Elementary Particles in Chemistry and Physics

#### 2.1. Molecules

Matter is composed of molecules and atoms, and under circumstances - of ions and free radicals.

In chemistry, the **molecule** is the smallest indivisible portion of a pure compound that retains all its chemical and physical properties. Gases are composed of:

- Individual atoms (the **noble gases**, also present in the atmosphere: helium He, argon Ar, krypton Kr, xenon Xe, Radon Rn),
- Diatomic molecules (e.g., nitrogen and oxygen),
- Triatomic molecules (e.g., water vapor H₂O and carbon dioxide CO₂) or even
- Polyatomic molecules, as for organic vapors, the molecules present in gasoline vapor typically contain 5 to 10 carbon atoms, together with 10 to 22 hydrogen atoms!

**Semi-volatiles** are important substances, such as Polycyclic Arene Hydrocarbons (PAHs), PCBs, and dioxins. They have a number of specific characteristics, such as their partition in the various compartments of the environment, as well as their movement in the atmosphere (global distillation, mass exchange with oceans).

#### 2.2. Atoms – Chemical Elements

An **atom** is the smallest, irreducible constituent of a chemical system; it is not divisible either mechanically or by chemical reactions. The atoms range in size from 10 pm to 100 pm. Atoms are composed of a nucleus composed of positively charged
protons and non-charged neutrons, and of fairly flexible electron shells, responsible for chemical interactions. Atoms are electrically neutral with as many electrons as protons. When losing one or more electrons they are termed ions.

Atoms are classified by their atomic number, which is distinct for a certain chemical element and corresponds to the number of protons in the atom. The various kinds of atoms are listed in the Periodic table of Elements.

Atoms with the same atomic number share a wide variety of physical properties and exhibit the same chemical behavior. Atoms having the same atomic number, but different atomic masses (due to different numbers of neutrons), are called isotopes.

2.3. Ionic and Covalent Bonding

Ions are atoms or groups of atoms that possess a net charge. When one or more electrons are thermally or chemically removed from an atom, ions are formed: Anions, e.g. Cl⁻, are negatively charged. Cations, e.g. Na⁺, are positively charged. Coulomb forces between positive and negative charges attract both to each other. In chemistry this leads to ionic bonding, as in kitchen salt crystals; it is weaker than covalent bonding.

2.4. Chemical Reactivity of Atoms

The chemical reactivity of atoms is largely due to interactions between the electrons. In particular the electrons in the outermost shell, the valence electrons, determine chemical behavior.

There is a strong tendency for atoms to try and completely fill or empty the outer electron shell, which in hydrogen and helium has space for two electrons, and in all other atoms has space for eight. This is achieved either by sharing electrons with neighboring atoms or by completely removing electrons from other atoms. When electrons are shared a covalent bond is formed between the two atoms. Covalent bonds are the strongest type of atomic bond.

2.5. Free Radicals

At high temperature and in flame reactions free radicals are highly reactive intermediates that carry the reactions. (See Pollution Control through Efficient Combustion Technology).

3. The states of Aggregation

3.1. The Solid – Liquid – Gaseous State of Aggregation

Matter may appear under three distinct states of aggregation: solids, liquids, and gases. These states are conveniently represented in a phase diagram (Figure 1) showing the different domains of stability for each phase, separated by lines of transition, the phase boundaries.
In the **Solid State** each atom in matter has limited freedom for motions around its equilibrium position. It is the stable state at low temperatures. As temperature rises the system acquires more Internal Energy and gradually evolves towards the Liquid Phase (**melting**), or – at low pressure - the gas or vapor phase (**sublimation**).

In the **Liquid Phase** individual molecules (or aggregates thereof) enjoy considerable freedom of movement within the boundaries of liquid mass that still is kept together by cohesive forces and surface tension. As temperature rises, so does the **vapor pressure** above the liquid in equilibrium with vapor. Varying the pressure thus allows us to modify the **boiling point**, the temperature at which there is an active exchange between the liquid and vapor phase, yet also (dynamic) equilibrium conditions, i.e. as much mass being transferred from liquid to vapor by boiling as there is vapor condensing to the liquid state. It follows that thermodynamic equilibrium is not at all synonymous with standstill, but rather with an equivalence of movement to and for over a hypothetical boundary line, describing a dynamic equilibrium of phases.

In contrast to the solid or the liquid state, a **gas phase** tends to fill the entire space at its disposal. This phenomenon is generally explained by means of the **kinetic theory of gases**. In this theory a gas is considered being composed of an enormous number of molecules moving around at high speed: One mol contains 6.02 $10^{23}$ molecules, i.e. the **Avogadro number** $N_A$. The probability that all these molecules simultaneously would leave a given volume is substantially zero.

Two states of a system are in the same solid or liquid phase if they can be transformed into each other without any abrupt change in their **thermodynamic and physical properties**. Two solid phases or two liquid phases may coexist together. The gas phase is always unique: no two distinct gas phases ever coexist in equilibrium!

### 3.2. Allotropy – Associated Molecules

**Allotropy** is the property of certain substances, usually pure elemental solids, to exist in different chemical modifications, e.g. phosphorus (white and red) and carbon (graphite, diamond, or fullerenes). The term also refers to molecular forms of an element, such as diatomic oxygen $O_2$ and triatomic ozone $O_3$.

In the liquid and the gas phase there is a tendency for molecules to associate at lower temperatures: water molecules associate to clusters, close to the freezing point, and nitrogen oxide $NO_2$ to $N_2O_4$. Below 500° C CuCl vapors are more stable as CuCl$_3$.

### 3.3. Phase - Phase Diagrams - Phase Transitions

Familiar examples of **phase transitions** are melting (solid to liquid), freezing (liquid to solid), boiling (liquid to gas), and condensation (gas to liquid). At low pressures, below the pressure of the Triple point, sublimation - a solid/gas transition, occurs. The different phases of a system may be represented in a **phase diagram** (Figure 1).
Figure 1: The three States of Aggregation, represented in a Phase Diagram, the Phase Boundaries, the Triple Point and the Critical Point.

This diagram has two very special points:

- The Triple Point, in which the three States of Aggregation are in equilibrium together, and
- The Critical Point, an important point of reference for all physical properties, since they may serve as a basis for the prediction of other properties.

3.4. Components

In thermodynamics, a **component** is any distinct chemical constituent of a system. The number of components is equal to the number of independent chemical compounds, minus the number of chemical reactions between them, minus the number of any constraints (like charge neutrality or balance of molar quantities). For example, a system that contains water in the liquid state also contains hydrogen ions and hydroxyl radicals according to the dissociation reaction:

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \]  \hspace{1cm} (1)

The number of components in such a system is one, obtained as:

3 (independent chemical constituents) - 1 (chemical reaction) - 1 (constraint of charge neutrality).

The concentration of each component may be varied independently in the various phases. Defining the number of components in a system is necessary, when applying Gibbs phase rule in determination of the number of degrees of freedom of a system.
Air, for all practical purposes, is regarded as a single component in processes in which the various constituents (nitrogen, oxygen, noble gases; NOT water vapor!) share the same fate!

### 3.5. Gibbs' Phase Rule - Degrees of Freedom

In thermodynamics the number of **degrees of freedom** is the smallest number of intensive variables (i.e., pressure, temperature, and concentrations of components in each phase) that must be specified to describe the state of the system completely.

Gibbs' phase rule specifies the number of degrees of freedom for a given system at equilibrium as: $V = C + 2 - \phi$, where $C$ is the number of compounds, and $\phi$ - the number of phases in the system. The number of degrees of freedom increases when there are more components in the system and decreases when there are more phases in equilibrium.

For example a system with only one phase and a single component, such as water vapor, has 2 degrees of freedom: temperature and pressure (or any other feasible selection of two intrinsic properties). Hence the system can exist in equilibrium for any arbitrary combination of temperature and pressure. (It is also possible to select other state variables to define the state of the system, e.g. its values for density $\rho$ and viscosity $\mu$, which – in that case – would fix $p$ and $T$).

Two phases can only co-exist at equilibrium for specific combinations of temperature and pressure: those indicated by the vapor pressure line. For a vapor-liquid system liquid will tend to evaporate either until the vapor pressure reaches the appropriate level (the equilibrium vapor pressure), or all of the liquid is consumed. Conversely, if the vapor pressure is too great for the given temperature condensation will occur. Establishing equilibrium between two phases creates a link between them, consuming one degree of liberty!

For a single component with three phases (gas, liquid, and solid) there are no residual degrees of freedom left: such a system is only possible at the temperature and pressure corresponding to the Triple point. At the Critical point these phases are: the gas, liquid, and dense gas.

### 3.6. Latent Heat associated with Phase Changes

Phase changes are normally accompanied by a heat effect, even though they are not chemical reactions.

<table>
<thead>
<tr>
<th>Heat Effect</th>
<th>Enthalpy of Fusion</th>
<th>Enthalpy of Vaporization</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase Change</td>
<td>$\Delta H_{\text{fusion}} = 6.007$</td>
<td>$\Delta H_{\text{vapor}} = 40.7$</td>
<td>$\text{kJ/mol}$</td>
</tr>
</tbody>
</table>


Table 1: Heat Effect by Phase Changes.
At a given temperature, raindrops in the atmosphere (gas phase) will evaporate or condense until the corresponding equilibrium water vapor pressure is reached. The associated consumption or liberation of latent heat plays an important role in steering atmospheric processes and their thermal balance.

Bibliography

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Biographical Sketch

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).