THERMODYNAMICS OF CHEMICAL PROCESSES

G. Maurer
Department of Mechanical and Process Engineering, University of Kaiserslautern, Germany

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Contents

Summary

The science of thermodynamics is one of the foundations on which the wide field of *Chemical Engineering* is based upon. This chapter attempts to give a brief introduction to thermodynamics. Thermodynamics is based on two fundamentals: One consists of the three basic laws of thermodynamics. The other one consists of the properties of the substances (in particular of mixtures) which are required to apply the fundamental laws to engineering problems. The fundamental laws of thermodynamics are empirical formulations which cannot

be reduced further. The first law describes the phenomenon that in any process energy has to be conserved. The second law summarizes the experience that although all real processes are irreversible, there is always an optimum, limiting process which is reversible, i.e., it allows us to find the best (most efficient) processes. For a universal mathematical formulation of the second law of thermodynamics, a new property (entropy) is introduced. The third law of thermodynamics allows for the calculation of absolute numbers for the entropy of a pure substance which is, e.g., required in the calculation of chemical reaction equilibria. The fundamental laws of thermodynamics are primarily applied here to phase equilibrium phenomena, i.e., the partitioning of components into coexisting phases (e.g., liquid and vapor phases) with and without chemical reactions. Most separation processes are based on such phase equilibrium phenomena. Some examples of such phase equilibria and the calculation methods are discussed.

1. Introduction

Thermodynamics is one of the sciences on which *Chemical Engineering* is based upon. There are many definitions of the science of thermodynamics. The word originates from the Greek language. The Greek words *thermo* and *dynamics* mean *heat* and *motion* respectively. Thus, thermodynamics can be explained as the science of processes and phenomena which are initiated by *heat*. Another interpretation starts from the fundamental units appearing in thermodynamics. Mechanics is the part of physics which deals with phenomena where all variables and parameters have units which can be reduced to the fundamental units of *length* (e.g., meter), *time* (e.g., second), and *amount of substance* (mass) (e.g., kilogram). In this context, thermodynamics can be considered as the extension of mechanics covering all phenomena which require *temperature* as an additional unit. The science of applied (or engineering) thermodynamics is based on two foundations: at first, the three basic laws of thermodynamics and, at second, the properties of matter. These properties have to be known when the basic laws are to be used in applications. Thermodynamics can be split into two subdivisions: *equilibrium thermodynamics* and *non-equilibrium thermodynamics*. A given (and fixed) amount of substance (i.e., a *thermodynamic system*) is in an equilibrium state when – without transferring heat and/or work from/to its surroundings – it does not change its macroscopic properties (i.e., its *thermodynamic state*). Transferring heat and/or work leads to a change of state of the system which finally results in a new equilibrium state. That activity leading to change is called a *process*. All real processes are irreversible and the transition from one equilibrium state to another is treated in the area of non-equilibrium thermodynamics. However, there is always an idealized case (a limiting case or reversible case) where the transition runs through equilibrium states. Heat transfer is a typical example. Any real heat transfer process requires a temperature difference as *driving force* and heat flows by itself from a high-temperature to a low-temperature. This is an irreversible process as heat never flows by itself from a low-temperature to a high-temperature. However, in the idealized situation (i.e., reversible) heat is transferred without a temperature difference. Certainly, heat can be transferred from a low temperature reservoir to a high temperature reservoir, but that transport does not occur *free of charge*. It requires work. The minimum work for a given amount of heat and given temperatures of both reservoirs is the work required in an idealized (reversible) process. Any real (irreversible) process requires more work than this minimum. Another example is the adiabatic compression of a gas from an initial state (e.g., pressure and temperature) to a final state where the pressure (and the density) is higher. The minimum amount of work required for such a compression is achieved in an idealized (i.e., reversible) process where the gas changes its state through equilibrium states. That amount of work is regained also when the gas expands in an idealized process (i.e., through equilibrium states) from the compressed into the expanded state. In a real compression process the required work is always higher than that in the idealized process and the amount of work recovered by a real expansion is lower than in the case of a reversible one. Although the reversible cases are never observed in reality they are very important for applications as they describe limits (*best cases*) for the real (i.e., irreversible) processes. Therefore, equilibrium thermodynamics is not a purely *theoretical* area, but it is required for solving real problems.

This chapter shortly recalls the basic laws of thermodynamics before it proceeds to the area of *phase equilibrium thermodynamics*. Phase equilibrium thermodynamics deals with the partitioning of substances into coexisting phases. For example, it can be used to describe the solubility of carbon dioxide in mineral water, the enrichment of low-boiling components in the vapor phase above a liquid mixture (both are examples for a vapor-liquid equilibrium VLE), the concentration differences when a solute partitions between two liquid phases (liquid-liquid equilibrium LLE), the precipitation of a solid substance from a liquid solution (solid-liquid equilibrium SLE) and similar phenomena. The thermodynamics of phase equilibrium is therefore a fundamental for the design and operation of separation processes in chemical engineering. The huge majority of separation processes is based on the enrichment of certain components in one of two phases which coexist in equilibrium. Only very few separation processes (e.g., membrane separation) are based on the kinetics of mass transfer (and perhaps also of chemical reaction) processes. But, again the thermodynamic equilibrium has to be known also for the design of such kinetically controlled processes as deviation from the equilibrium state provides the driving force for the kinetic process. The present chapter discusses thermodynamics mainly from a macroscopic point of view, i.e., it neither deals with the properties of a small number of atoms and molecules nor with the properties of atoms and molecules etc. themselves. This macroscopic point of view is often also called *phenomenological thermodynamics* in contrast to *statistical thermodynamics* which discusses the same object from a microscopic point of view by combining statistical methods and quantum mechanics.

2. Fundamental Laws of Thermodynamics

The fundamental laws of thermodynamics are briefly reviewed. For a more detailed introduction the reader is referred to a textbook on thermodynamics.

2.1. Temperature: Definition and Scale

Like the other fundamental units (i.e., for mass, time and length), temperature also is at first introduced through an equivalency criterion: Two systems have the same temperature when their macroscopic properties (state functions) do not change when they are brought merely into contact. However, a temperature scale has to be introduced for quantifying *temperature*. Introducing such a scale requires at first a phenomenon which depends reproducibly and uniquely on temperature and at second, one fixed point and a step width (or in principle two fixed points). A temperature scale can be derived from a variety of phenomena which depend on temperature, e.g. the volume expansion of mercury or the pressure exerted by a highly diluted gas (*ideal gas*) on the walls of its container at a fixed volume. The later scale is called the *temperature scale of the ideal gas thermometer*. The second law (2^{nd}) of thermodynamics (see below) provides another way to define a temperature scale. One of the many results following directly from the 2^{nd} law of thermodynamics is that the maximum efficiency (the ratio of *delivered work* to *supplied heat*) of a so-called *heat engine* (i.e., an engine which converts *heat* into *work* in a cyclic process) only depends on the temperatures of the heat source and the heat sink. All temperature scales which are in agreement with the 2^{nd} law are called *thermodynamic temperature scales*. The *temperature scale of the ideal gas thermometer* (also called Kelvin-scale) fulfills that requirement. It is defined by two fixed points: The first fixed point is the minimum temperature (its existence also follows from the basic laws of thermodynamics) set to zero Kelvin (K). The second fixed point is the triple point of pure water. Its temperature is set to 273.16 K. At that particular triple point three water phases (solid water (ice), liquid water and water vapor) coexist. Such a triple point is a characteristic property of any pure substance (see also below). The *ideal gas thermometer* is only used in a few reference laboratories, where so-called secondary fixed points (e.g., triple points of other substances, melting points, normal boiling points etc.) are determined with high accuracy. These secondary fixed points are required for defining *practical temperature scales* where common instruments (e.g., platinum resistance thermometers, thermocouples, radiation thermometers) are applied for realizing the temperature scale as it has been done for defining the *International Practical Temperature Scale* (IPTS).

2.2. The First Law of Thermodynamics

The first law of thermodynamics (*1^{st} law of thermodynamics*) is the universal form of the principle of the conservation of energy. It might also be called the introduction of the state function *energy*. A given (and constant) amount of substance (*thermodynamic system* or *system*) can experience two different types of interactions with its surroundings: it can receive/deliver *heat* (Q) and *work* (W). The transfer of heat and/or work changes the thermodynamic state of the *system*. The state function that is directly influenced by the transfer of heat and/or work is the *system's energy* E. *Heat*, *work* and *energy* have the same units. Usually, the signs of Q and W are defined as positive when the system receives heat and work and negative when Q and W are delivered by the system. The principle of the conservation of energy requires that when the surroundings delivers energy to the system (as Q and/or W), the energy of the system has to increase by the same amount as the energy of the surroundings decreases. *The first law of thermodynamics* for a *thermodynamic system* which undergoes a very small change from one equilibrium state into another therefore reads:

$$\delta Q + \delta W = dE \qquad (1)$$

The different symbols for a small (differential) change (δ and d) in Eq. (1) are to distinguish between path-dependent properties (*heat* and *work*) and state functions (*energy*). Equation (1) reveals that from the viewpoint of the first law of thermodynamics there is no need to distinguish between *heat* and *work* as the same energy difference can be achieved either by transferring Q or W. However, a distinction is necessary as there are differences between the conversion of *work* to *heat* on one side and of *heat* to *work* on the other side (cf. Section 2.3). The definition of heat is: The interaction observed when a *system I* of temperature T_{I} is (only) in thermal contact with a *system II* of temperature $T_{\mathrm{II}} < T_{\mathrm{I}}$ is called the transfer of heat from *system I* to *system II*. The definition of *work* is: A *system* has delivered *work* to its surroundings when the only change in the surroundings can be reduced to the lifting of a mass in a gravity field. When a *system* does not move, the first law of thermodynamics reduces to

$$\delta Q + \delta W_{\mathrm{i}} = dU \tag{1a}$$

Subscript i to W indicates that transferring work to/from the *thermodynamic system* changes the *thermodynamic state* (also called *internal state*) of the system. That change is expressed through the internal energy U which is a part of the (total) energy E. Like E, U is also a state function. A typical example for W_{i} is the work required to compress a gas in a cylinder.

For applications in engineering it is often more convenient to reformulate the first law of thermodynamics for the special case where the energy balance is applied to a closed boundary which is fixed in space and crossed by flows of mass. When, at all and any fixed positions in that space there is no change of any property with time, that arrangement is usually called a *steady-state open system*. When each flow that enters/leaves the *steady-state open system* is in thermodynamic equilibrium the first law of thermodynamics for a small change reads:

$$\delta Q + \delta W_{\mathrm{t}} = \sum d(E + pV) = \sum d(H + E - U). \tag{2}$$

The summation is over all mass flows. W_{t} is called *technical work*. It is the work transferred across those regions of the boundary of the *steady-state open system* which are not crossed by mass flows. H is the enthalpy, another state function:

$$H = U + pV \tag{3}$$

V is volume and p is pressure. Q and W_{t} are heat and work, respectively, transferred only at those parts of the boundary which are not crossed by flows of mass. When similar to Eq. (1a) a change of the total energy *E* is only due to a change in the internal energy *U*, Eq. (2) simplifies to:

$$\delta Q + \delta W_{\mathrm{t}} = dH \tag{2a}$$

A typical example for technical work is the work required to compress a flow of gas in a compressor (see Figure 1).

2.3. The Second Law of Thermodynamics

All experience tells us that by far not all processes which are in agreement with the 1st law of thermodynamics are really being observed. That experience tells us also that when a process is observed in reality, the reversion of that process is never observed. In other words, all real processes are irreversible. A reversible process is the ideal or limiting case of a real (i.e., irreversible) process. For example, the movement of a pendulum comes to an end after a certain period of time. The duration of that period of time depends on the friction. Reducing friction extends that period. In the idealized (i.e., reversible) case there is no friction and the pendulum moves for ever. This example also shows that – with sufficient efforts – one can approach the reversible process, but one never can reach it. That experience is summarized in the second law of thermodynamics (*2nd law of thermodynamics*). In wording that law can be formulated as: All observed (i.e., real) processes are irreversible. Other written formulations of the second law are e.g., "*Heat never flows by itself from a low-temperature reservoir to a high-temperature reservoir*" and "*There is no heat engine working in a cyclic process which converts all the supplied heat completely into work*". The last statement says that some part of the heat which is supplied to the engine (at a high temperature) in a cycle must be delivered by that engine to a reservoir of a lower temperature. Thus, the efficiency of a heat engine is always less than one. All written formulations of the second law of thermodynamics are equivalent. A contradiction to one formulation corresponds to a contradiction to any other formulation. Although, all real processes are irreversible, reversible processes are very important in engineering. For example, the efficiency of a reversible heat engine is the limitation which can not be overcome by any real heat engine. Conversely, the work required in a cyclic refrigeration engine which withdraws a certain amount of heat from a cold reservoir (e.g., a refrigerator) to a high-temperature reservoir (e.g., the kitchen) is at minimum when the refrigeration process is reversible. It can be shown that the second law of thermodynamics can be brought into a universal mathematical form using a state function. However, no state function introduced originally in connection with the first law is suited for that purpose. Therefore, a new state function had to be defined. Clausius proposed to call that state function *entropy* S (from the Greek language, meaning *in transition*). Thus, the second law of thermodynamics restricts all processes which do not contradict the first law of thermodynamics to those which are possible (irreversible/reversible processes) and those which are not possible (reversions of irreversible processes). Like energy also entropy is only defined through a differential equation:

$$TdS = \delta Q_{\mathrm{rev}} \qquad (4)$$

T is the temperature (in Kelvin) at which that heat is supplied/delivered and subscript 'rev' signifies that the heat is transferred in a reversible process. Expressing δQ_{rev} by the first law of thermodynamics results in

$$TdS = dU + pdV \qquad (4a)$$

or its equivalent

$$TdS = dH - Vdp\,. \qquad (4b)$$

Equations (4a) and (4b) allow for the calculation of entropy differences from expressions for the thermal behavior (i.e., equations for the internal energy U or the enthalpy H) and the volumetric behavior (e.g., from an equation of state , $f(T, p, V) = 0$, that describes the relation between pressure, temperature and volume of a given amount of substance).

Applying the concept of entropy, the universal expression for the second law of thermodynamics is:

$$TdS \geq \delta Q. \tag{5}$$

The equality sign “=” holds for a reversible process and the sign “>” for an irreversible process. In other words (and as $T > 0$ K) a step with $TdS < \delta Q$ is not possible at all, as that process would be the reversion of an irreversible process.

Two examples for an application of the state function entropy are given in Figures 1 and 2. Figure 1 shows a compressor which is treated as a *steady-state open system*. The compressor is used to compress a gas of flow rate $\dot{m}$ from an initial state at pressure p_1 to $p_2 > p_1$ in an adiabatic process (i.e., a compression without any transfer of heat). The second law of thermodynamics tells us that the entropy of the gas after the compression cannot be lower than before the compression. Vice versa, the minimum amount of technical work for such a compression is achieved when the compression occurs in a reversible process. And in a real (i.e., irreversible) adiabatic process more work is required to increase the pressure of that gas.

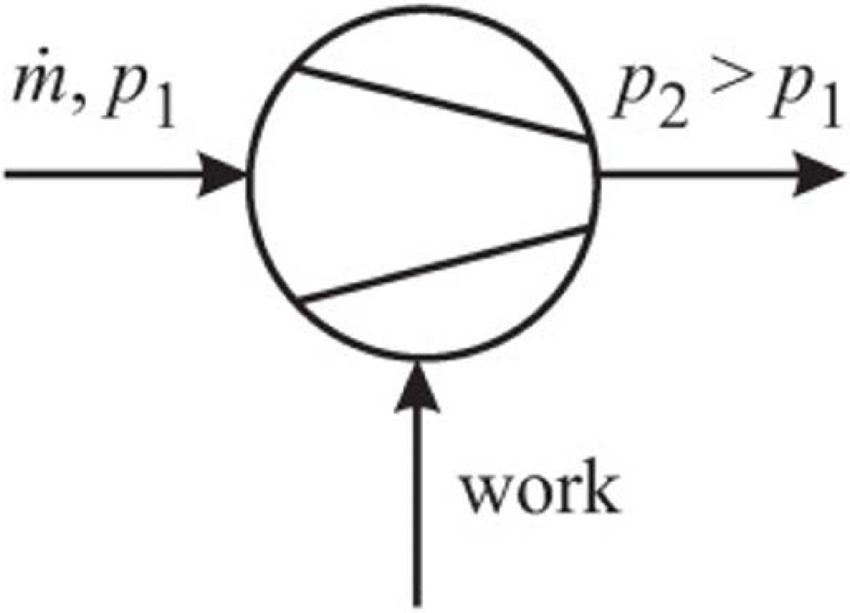

Figure 1: Scheme of a compressor

Figure 2 shows the principle of a heat engine. Heat is provided by a reservoir of a high temperature T_1 and transferred to a heat engine. In that engine a fluid medium experiences a series of changes resulting in a cyclic process. After that series the medium is in its initial state before it starts the next cycle. During a cycle some of the supplied heat is converted into work that is transferred to the surroundings, but also some heat is delivered to a reservoir at a lower temperature $T_2 < T_1$. Both reservoirs and the heat engine are considered to form an adiabatic system. $|Q_1|$ and $|Q_2|$ are the absolute amounts of heat provided by the high-temperature reservoir and delivered to the low-temperature reservoir, respectively. The resulting absolute amount of work is

$$|W| = |Q_1| - |Q_2| \tag{6}$$

and the efficiency η is

$$\eta = |W| / |Q_1| = 1 - |Q_2| / |Q_1|. \tag{7}$$

The entropy of the high-temperature reservoir decreases by

$$\Delta S_1 = -|Q_1| / T_1 \tag{8}$$

and the entropy of the low-temperature reservoir increases by

$$\Delta S_2 = |Q_2| / T_2 . \tag{9}$$

As the medium runs through a cyclic process and the entropy is a state function, there is no entropy change for that medium as long as one considers only full cycles. The total entropy change therefore is:

$$\Delta S = \Delta S_1 + \Delta S_2. \tag{10}$$

According to the second law of thermodynamics for an adiabatic process:

$$\Delta S \geq 0. \tag{11}$$

Thus, for a reversible adiabatic process

$$\Delta S = 0 \tag{11a}$$

resulting in

$$\Delta S_1 = -\Delta S_2 \tag{12}$$

and

$$|Q_2| / |Q_1| = T_2 / T_1 \tag{13}$$

Consequently,

$$\eta_{\text{rev}} = 1 - T_2 / T_1 \tag{14}$$

Conversely, for an irreversible process

$$\Delta S > 0. \tag{15}$$

For the same amount of supplied heat $|Q_1|$, the amount of heat delivered to the low-temperature reservoir becomes

$$|Q_2|_{\mathrm{irrev}} > |Q_{2,\mathrm{rev}}| \tag{16}$$

resulting in

$$\eta_{\mathrm{irrev}} < 1 - T_2 / T_1 \tag{17}$$

and

$$\eta_{\mathrm{irrev}} < \eta_{\mathrm{rev}}. \tag{18}$$

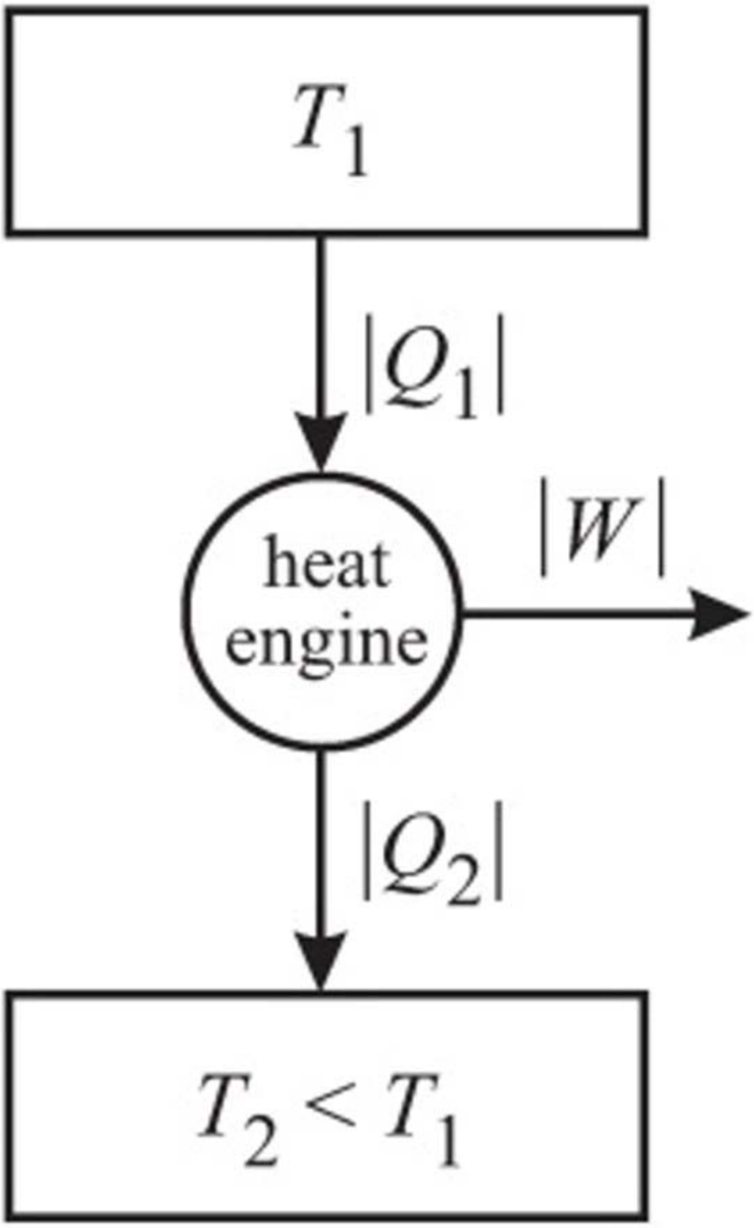

Figure 2: Principle of a heat engine

2.4. Absolute Numbers for the Internal Energy and the Enthalpy

The definitions of internal energy U, enthalpy H and entropy S given above allow only for the calculation of differences of these state functions as long as the chemical nature of the substance under consideration does not change (i.e. there are no chemical reactions or chemical reactions can be neglected). However, thermodynamics is a universal science that can be applied to all processes including chemical reactions. When, for example, the first law of thermodynamics is applied to a chemical reaction where – at constant temperature and constant pressure – in a *steady-state open system* one mole of pure substance A undergoes a chemical reaction resulting in 2 moles of pure substance B:

$$\mathrm{A} \rightleftharpoons 2\mathrm{B}. \qquad \text{(I)}$$

The transferred heat Q for a complete reaction is the difference between the enthalpy of the product and the educt (cf. Figure 3):

$$Q = 2h_{\mathrm{B}}(T,p)_{\mathrm{pure}} - h_{\mathrm{A}}(T,p)_{\mathrm{pure}} \qquad (19)$$

where $h_i(T,p)_{\mathrm{pure}}$ is the molar enthalpy of pure component i at temperature T and pressure p.

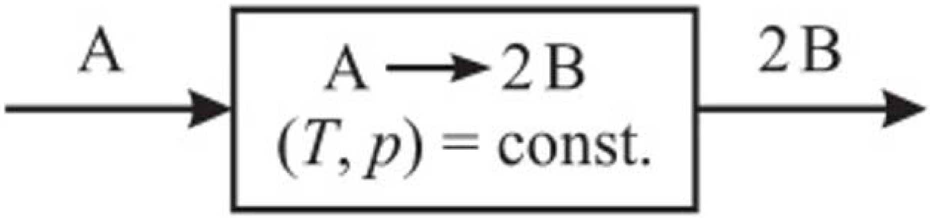

Figure 3: Scheme of a “steady-state open system” reactor

Measuring the heat of reaction Q thus provides one equation for two unknowns $(h_{\mathrm{B}}(T,p)_{\mathrm{pure}}$ and $h_{\mathrm{A}}(T,p)_{\mathrm{pure}})$. Consequently, one of those molar enthalpies can be selected arbitrarily and the other one follows from the heat of reaction. This principle can be generalized to allow for the determination of absolute numbers for the enthalpy (and also for the internal energy) of a pure substance. Depending on the particular application, several such *energy standards* are common – for details see textbooks on thermodynamics. Only one of these methods is discussed here as an example: The enthalpy of a pure chemical element at 298.15 K and 0.1 MPa in thermodynamic equilibrium in its stable state (which might be a vapor, a liquid, or a certain form of a solid in atomic or molecular form) is arbitrarily set to zero and the molar enthalpy of a pure molecular chemical component (also equilibrated in its stable thermodynamic state) at 298.15 K and 0.1 MPa is then determined from experimental heat of reaction data. The enthalpy of a given amount of substance under other conditions (including other reference states) can be calculated from these so-called *standard state enthalpies* (cf. below).

2.5. The Third Law of Thermodynamics - Absolute Entropy

For finding absolute numbers for the entropy of a substance another method had to be found. In the beginning of the 20th century, Walter Nernst found by investigating chemical reactions at low temperatures, that for a reaction

$$\alpha\mathrm{A} + \beta\mathrm{B} \rightleftharpoons \gamma\mathrm{C} + \delta\mathrm{D} \qquad \text{(II)}$$

the entropy difference

$$\Delta S = \gamma s_{\mathrm{C}}(T,p)_{\mathrm{pure}} + \delta s_{\mathrm{D}}(T,p)_{\mathrm{pure}} - \alpha s_{\mathrm{A}}(T,p)_{\mathrm{pure}} - \beta\, s_{\mathrm{B}}(T,p)_{pure} \qquad (20)$$

where $s_i(T,p)_{\mathrm{pure}}$ is the molar entropy of pure component i at all pressures p converges to zero when the minimum temperature ($T = 0$ K) is approached. From this finding Max Planck concluded that the entropy of any pure component i at equilibrium at any pressure but at $T = 0$ K has to be zero:

$$s_i(T = 0\mathrm{K}, p)_{\mathrm{pure}} = 0\,. \qquad (21)$$

That finding has many important consequences. For example, it allows for the calculation of absolute numbers of the entropy of a pure substance at any temperature and pressure from information on its thermal and volumetric properties (cf. also Eqs. (4a) and (4b)) and it might be used to prove that one can approach, but never reach the lowest temperature ($T = 0$ K). Eq. (21) is so important that it is called the *third law of thermodynamics*.

3. Properties of Pure Fluids

An application of the basic laws of thermodynamics in areas such as chemical engineering always requires the knowledge of the thermodynamic properties of the substances under consideration. In other words, applied thermodynamics is based on two foundations: The basic laws of thermodynamics and the thermodynamic properties of matter, the so-called state functions. This section deals with the state functions of pure substances. A pure substance follows the so-called *two-properties rule*. That empirical rule states that any thermodynamic state function of a given amount of a pure substance depends only on two other, independent state-functions.

3.1. Volumetric Properties

The *equation of state* (EoS) , $f(V,\ T,\ p)$, describes the relation between the state functions *volume* V , *temperature* T and *pressure* p of a substance in a single phase (e.g. in a gaseous or liquid state, but not in two, coexisting phases $-$ where p and T depend on each other):

$$f(V,T,p) = 0 \qquad (22)$$

For example, the EoS of any gas at sufficiently low pressure and sufficiently high temperature (i.e., the so-called *ideal gas*) is

$$pV - nRT = 0 \qquad (23)$$

where n is the number of moles (i.e., the amount of substance) and R is the universal gas constant (i.e. the gas constant per mole):

$$R = N_A \cdot k = 8{,}31441 \text{ J mol}^{-1} \text{ K}^{-1}. \qquad (24)$$

N_A is Avogadro's number, i.e., the number of molecules that define one mole of a substance:

$$N_\mathrm{A} = 6{,}02205 \cdot 10^{23} \text{ mol}^{-1} \qquad (25)$$

and k is Boltzmann's constant, i.e., the gas constant per molecule:

$$k = 1{,}38066 \cdot 10^{-23} \text{ J}\times\text{K}^{-1}. \qquad (26)$$

A pure substance can exist either in a single phase (gaseous or liquid or solid), in a two-phase system where two phases coexist (e.g., in vapor-liquid equilibrium (VLE), in solid-liquid equilibrium (SLE) or in solid-vapor equilibrium (SVE)), or in a three phase equilibrium (e.g., in vapor-liquid-solid equilibrium (VLSE)). The temperature/pressure pair in a three-phase equilibrium (e.g., in VLSE) is a characteristic property of each pure substance. Temperature and pressure depend on each other in a two-phase equilibrium of a pure substance, resulting in the vapor-pressure curve (for VLE), the sublimation pressure curve (for SVE) and the melting pressure curve (for SLE). These three curves meet at the (T, p)-pair of the three-phase VLSE. That point is called the triple-point. As shown in Figure 4, the sublimation pressure curve runs from the triple point to lower temperatures (and pressures), the vapor-pressure curve to higher temperatures (and pressures) and the melting curve to higher pressures (at nearly constant temperature). The vapor-pressure curve has another endpoint which is usually called the *critical point*. At that particular point all differences between the coexisting vapor and liquid phases disappear. No such critical endpoint has been observed for the melting curve. A point on a two-phase line characterizes the (T, p)-pair where two phases coexist, but it does not say anything about the amount of substance which is in one of the coexisting phases. For example, the substance under a condition of the vapor-pressure curve can be either completely liquid (boiling liquid) or it can be a mixture of liquid and vapor (wet-vapor) or it can be completely gaseous (saturated vapor).

The three two-phase equilibrium curves in a (T, p)-diagram for a pure substance separate the solid, liquid and gaseous regions. A phase transition occurs when such a line is crossed. For example, melting occurs when at constant pressure a solid is heated to such a temperature that the melting curve is crossed. However, as the vapor-pressure line has an upper endpoint, the state of a pure substance might be changed from liquid to vapor (and vice versa) without crossing the vapor-pressure line, i.e., without observing a phase transition (vaporization or condensation, respectively). Therefore, the *liquid* and the *vapor* states are commonly combined to form the *fluid* state. Figure 5 shows a scheme of the volumetric behavior of a pure substance in a three-dimensional p,V,T - diagram (V is the volume). It is worth to mention that the corresponding diagram for water reveals some differences as for example, the volume decreases on melting. As the densities of the coexisting phases differ (except at the critical point) the two-phase lines shown in Figure 4 spread to two-phase regions in Figure 5.

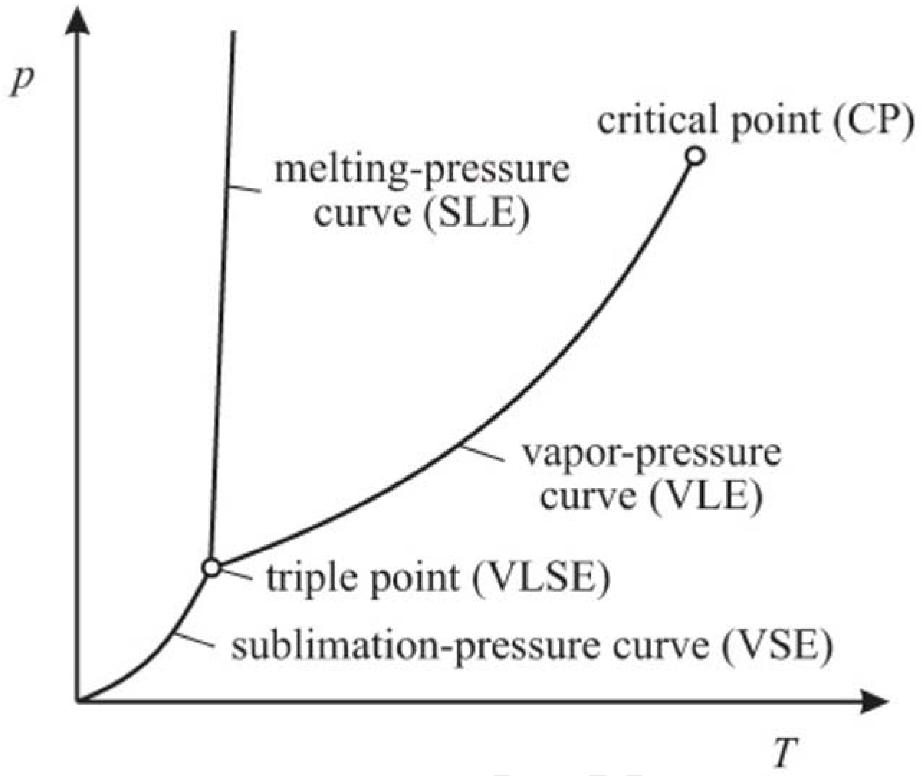

Figure 4: $(p,\ T)$ -diagram of a pure substance

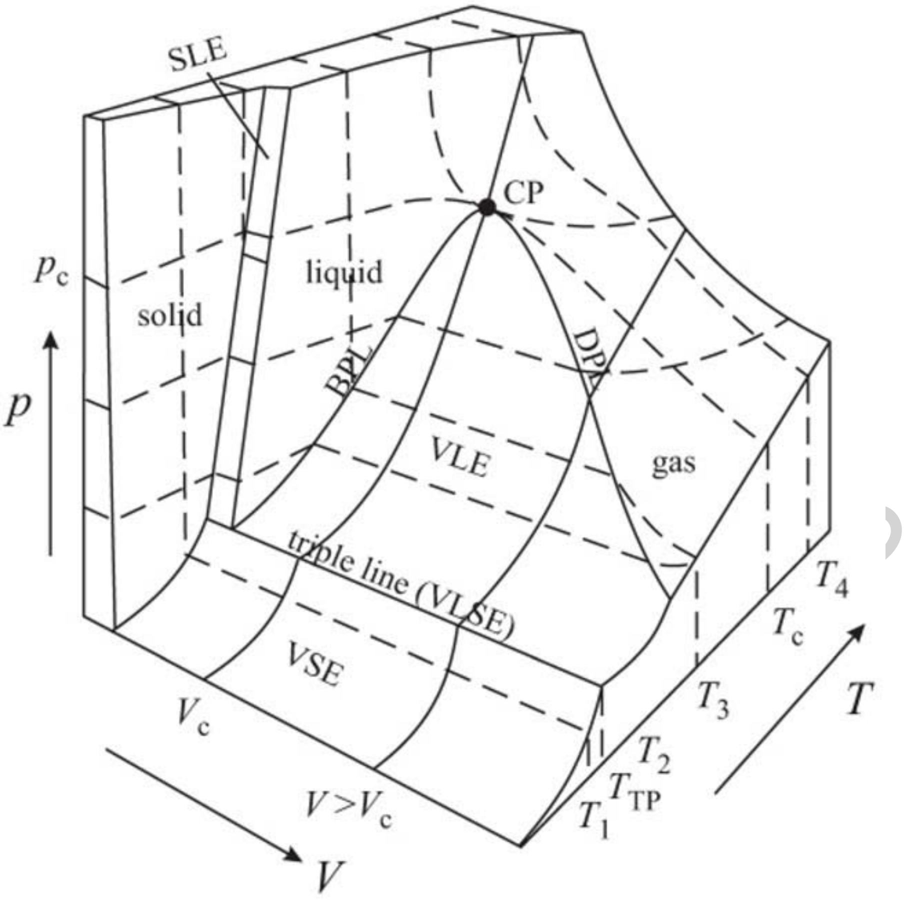

Figure 5: Three-dimensional p,V,T -diagram of a pure substance

It is common practice to use either a volume-explicit or a pressure-explicit form of Eq. (22) for one mole of substance in a single phase region:

$$v = V/n = v(T, p) \tag{22a}$$

$$p = p(T, v). \tag{22b}$$

The differential change of the molar volume caused by small changes in temperature and pressure is:

$$dv = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp = v\,\alpha\, dT - v\,\chi\, dp \tag{27}$$

where α is the isobaric expansion coefficient:

$$\alpha(T, p) = \left(\frac{1}{v}\right) \cdot \left(\frac{\partial v}{\partial T}\right)_p \tag{28}$$

and χ is the isothermal compressibility:

$$\chi(T,p) = -\left(\frac{1}{v}\right)\cdot\left(\frac{\partial v}{\partial p}\right)_T . \tag{29}$$

For an ideal gas one finds that the expansion coefficient does not depend on pressure and the compressibility does not depend on temperature:

$$\alpha = \frac{1}{T} \tag{28a}$$

and

$$\chi = \frac{1}{p} \tag{29a}$$

There are many equations of state being used to express the volumetric behavior of pure substances. Statistical thermodynamics provides means to derive such equations. However, currently, such derivations are only possible for model fluids (e.g., an ideal gas, or gases consisting of hard-spheres). Therefore, equations of state used in chemical engineering are usually semi-empirical extensions of theoretically derived equations. They contain adjustable parameters which have to be fitted to experimental data.

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Biographical Sketch

Gerd Maurer received his academic education at the University of Karlsruhe in Karlsruhe, Germany (diploma degree in Chemical Engineering (in 1967), doctoral degree (Dr.-Ing. in 1971) and Habilitation (in Applied Thermodynamics in 1977). He was a member of the faculty of the Chemical Engineering Department at that university until 1980, interrupted by a research stay at the University of California at Berkeley, Ca., USA, in 1977/1978 where he worked with Prof. J. M. Prausnitz at the Department of Chemical Engineering. In 1980 he joined BASF AG, Ludwigshafen, Germany where he worked in engineering development and research, but also as a product manager. In 1985 he was appointed full professor of Chemical Engineering at the University of Kaiserslautern, Germany, where he is still working. He taught as visiting professor at several universities in Europe as well as overseas. He was/is a member of various national as well as international boards, committees and of the editorial teams of several reviewed international journals. In 2002 he was appointed honorary professor at the State University of St. Petersburg/Russia. His main scientific interest is on the thermodynamic properties of complex fluid mixtures which are of interest in a large variety of areas, e.g. in the chemical and petrochemical industries, in environmental protection and sustainable development as well as in downstream processing in biotechnology. He has published about 250 research articles and books predominantly in the area of thermodynamics of fluid phase equilibrium.