

# Physical Chemistry I

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# Chapter 1

# Thermodynamics and the Properties of Gases

## 1.1 Introduction

Physical chemistry is the discipline that applies physical and mathematical methods to the study of chemical phenomena. There are four main branches of physical chemistry:

- **Thermodynamics** deals with the measurable macroscopic properties (energy, pressure, temperature,...) of systems and the relations between them. The application of thermodynamic principles to the study of chemical reactions constitutes the field of **chemical thermodynamics**.
- The interactions between atoms and between their constituent particles (nuclei, electrons) are described by the laws of quantum mechanics. **Quantum chemistry** uses the laws of quantum mechanics to study the microscopic properties of molecules and solids. A particularly important and useful branch of quantum chemistry is **spectroscopy**, which deals with the interaction between light and matter.
- The field of **statistical thermodynamics** allows the prediction of macroscopic thermodynamic properties of systems from the microscopic behavior of its constituent particles using statistical methods.
- **Chemical kinetics** studies the rates of chemical reactions, i.e., the velocity at which they occur. Chemical kinetics can describe chemical reactions either macroscopically or microscopically. The microscopic study of the molecular events involved in a chemical reaction is the purview of the field known as **reaction dynamics**.

In this course, we will study **classical thermodynamics**, which deals with the description of macroscopic systems at equilibrium and the relations between their properties. There are two particularly important types of systems we will examine in detail: gases and solutions.

Classical thermodynamics is purely phenomenological, because its laws are postulated based on experimental evidence, and macroscopic, because at no point is it necessary to invoke the existence of atoms and molecules to develop the theory. In fact, classical thermodynamics originated from the study of steam engines in the context of industrial revolution at the beginning of the XIX century. As such, it predates the origin of physical chemistry and the modern atomic theory by almost a century. Nevertheless, we will often employ microscopic arguments to explain thermodynamic results in the light of our current understanding.

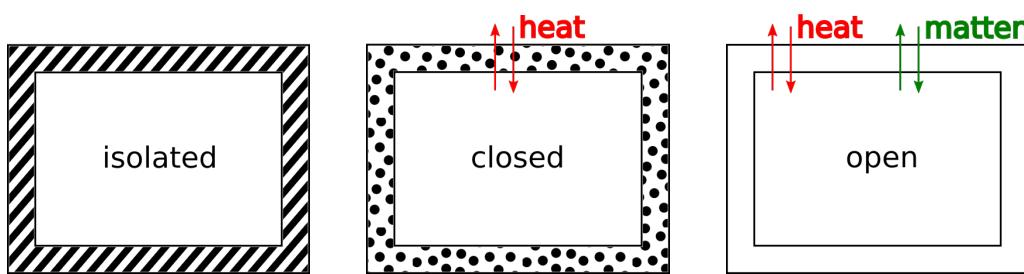


Figure 1.1: The three types of thermodynamic systems: isolated (left), closed (middle), and open (right).

## 1.2 Definitions

### 1.2.1 Systems and Walls

The following definitions will be used throughout the course. A **thermodynamic system** is the part of the universe under study. The system can be small, like a flask where a chemical reaction is taking place, or large, like an ocean or a planet. The only requirement imposed on the system is that it needs to be macroscopic, that is, the number of atoms in the system must be at least in the order of Avogadro's number. The system contains one or more different chemical species, known as its **components**.

The outside of the system is known as the **surroundings**. The system plus its surroundings is the **universe**. System and surroundings interact via **walls**, which are the boundaries that separate them. These walls can be real, like the glass sides of a beaker, or imaginary, like the separation between a planet and the vacuum of space. Depending on the characteristics of the walls, we distinguish the following types:

- A wall that allows matter to pass through is **permeable**. Otherwise, it is **impermeable**. In systems containing several components, the walls may be permeable to some species but not to others. For example, an osmosis membrane that lets the solvent of a solution through but not the solute, or an ion-selective electrode, which only allows a specific chemical species to pass through it. In these cases, the wall is **semi-permeable**.
- A **rigid** wall does not move when force is exerted on it by the system or its surroundings. The opposite is a **nonrigid** or **movable** wall. A glass beaker has rigid walls, while a piston in an internal combustion engine or the surface of a balloon are movable walls.
- A wall is **adiabatic** or **thermally insulating** if it does not allow the exchange of energy in the form of heat between the system and its surroundings. Heat and temperature will be defined later. For now, it is sufficient to say that heat is energy transferred due to a difference in temperature between system and surroundings, and that temperature is a measure of the average kinetic energy of the constituent particles in a system. If a wall allows the transfer of heat, it is **nonadiabatic** (also, **thermally conducting**, **diathermal**, or **diathermic**). Thermos and Dewar flasks have approximately adiabatic walls.

The properties of the walls determine the type of system and its interaction with the surroundings. We distinguish three types of systems:

- In an **open system**, matter and energy can be exchanged between the system and its surroundings. A lake is an open system because it can exchange matter (e.g. rain) and heat (e.g. absorb radiation from the sun) with its surroundings.

- A **closed system** may exchange energy in the form of heat with its surroundings, but not matter. A stoppered glass flask immersed in a water bath is a closed system.
- An **isolated system** is a particular case of closed system that exchanges neither energy nor heat with its surroundings. A closed thermos is an approximately isolated system.

Diagrams for the three types of systems are shown in Figure 1.1.

### 1.2.2 Thermodynamic Properties

Each system has a number of observable **thermodynamic properties**, such as volume, temperature, or pressure that are the object of study in classical thermodynamics. The set of values for all thermodynamic properties of a system constitute its **thermodynamic state**. Two systems with the same thermodynamic properties are said to be in the same state. It has been determined experimentally that relations exist between the different thermodynamic properties of a system such that only a subset of all thermodynamic properties are required to completely determine its state. For instance, the state of a pure gas is determined by the number of molecules, its temperature, and its pressure. The other thermodynamic properties (volume, internal energy, etc.) can be written as functions of the thermodynamic state. Consequently, these properties are said to be **state functions**. The thermodynamic variables used to determine the thermodynamic state, temperature, pressure, and number of molecules in this example, are known as **state variables**.

A list of basic thermodynamic properties follows; more will be defined in later chapters. In general, the International System of Units (SI) will be used throughout the course, except for those properties where the use of SI units is not common practice.

**Volume.** The volume ( $V$ ) of the system is the amount of space it occupies. The SI units for volume are  $\text{m}^3$  but a common unit is the liter,  $1 \text{ L} = 1 \text{ dm}^3 = 1 \times 10^{-3} \text{ m}^3$ .

**Composition.** The composition of a system is the amount of each component ( $i$ ) inside it. The composition can be given in terms of the mass of each component ( $m_i$ ) or in terms of the amount of component ( $n_i$ ). The SI unit for mass is the kilogram (kg). The amount of substance refers to the number of constituent entities (atoms, molecules, or unit formulas) and its SI unit is the mole (mol).

One **mole** is the amount of matter that has a number of microscopic entities (atoms, molecules, unit formulas) equal to the number of atoms in a sample of exactly 12 g of  $^{12}\text{C}$ . This number has been determined experimentally with great precision, and is known as Avogadro's constant ( $N_A$ ):

$$N_A = 6.022\ 140\ 76 \times 10^{23} \text{ mol}^{-1} \quad (1.1)$$

Note that Avogadro's constant has units of  $\text{mol}^{-1}$ , because the number count is adimensional.

Closely related to the definition of mole is the concept of **relative atomic (molecular) mass**, also known as the **atomic (molecular) weight**, which is an adimensional quantity equal the ratio between the mass of an atom or molecule and  $1/12$  of the mass of a  $^{12}\text{C}$  atom. Typical macroscopic samples contain different isotopes of the same atom, and therefore the relative atomic/molecular masses are usually given as an average over this isotopic distribution. For instance, the standard atomic weight of Cl is 35.45 because there are two main isotopes of chlorine,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  with approximately 3:1 abundance.

Two related concepts are those of atomic (molecular) mass and molar mass. The **atomic (molecular) mass** is the mass of a single atom or molecule. A common unit for this quantity is the **dalton (Da)** (also known as an **atomic mass unit**, amu) which is defined as  $1/12$  of the

mass of a  $^{12}\text{C}$  atom,  $1\text{ Da} = 1.660\,539\,066\,60 \times 10^{-27}\text{ kg}$ . The **molar mass** ( $M$ ) is the mass of a mole of substance. The SI units for molar mass are  $\text{kg/mol}$  but  $\text{g/mol}$  is much more commonly used. As a consequence of these three definitions, the numerical value of the atomic (molecular) mass in Da is equal to the value of the molar mass in  $\text{g/mol}$  and is also equal to the relative atomic (molecular) weight.

**Example.** The relative molecular weight of benzene is:

$$M_r = 6 \times 12.0107 + 6 \times 1.00794 = 78.11184$$

Note how the relative atomic weight of carbon is not exactly 12 because it is an average over its isotopes, of which  $^{12}\text{C}$  and  $^{13}\text{C}$  are the most abundant. The molecular mass of benzene is the mass of a single benzene molecule. Since the mass of a benzene molecule is  $M_r$  times  $1/12$  the mass of a  $^{12}\text{C}$  atom and the latter is exactly 1 Da, we have:

$$m_{\text{C}_6\text{H}_6} = 78.111\,84 \text{ Da} \times \frac{1.660\,539\,1 \times 10^{-27} \text{ kg}}{1 \text{ Da}} = 1.297\,078 \times 10^{-25} \text{ kg}$$

The molar mass is the mass of one mole of benzene molecules. One mole of  $^{12}\text{C}$  weighs exactly 12 g and a benzene molecule is  $M_r/12$  times heavier than a  $^{12}\text{C}$  atom. Therefore, the molar mass of benzene is:

$$M_{\text{C}_6\text{H}_6} = 78.111\,84 \text{ g/mol}$$

The **amount** a given substance can be calculated as the ratio between its mass and its molar mass:

$$n = \frac{m}{M} \quad (1.2)$$

The amount is almost always measured in moles, hence  $n$  is commonly referred to as the “number of moles” of that substance. If the amount is  $n$ , then the number of molecules (or atoms or formula units),  $N$ , can be calculated by multiplying by Avogadro’s constant:

$$N = nN_A \quad (1.3)$$

**Concentration and Density.** The **molar concentration** or **molarity** ( $c$ ) is the amount of substance divided by the volume of the system:

$$c = \frac{n}{V} \quad (1.4)$$

The SI unit for molar concentration is  $1\text{ mol/m}^3$  but the far more commonly used unit is the molar,  $1\text{ M} = 1\text{ mol/L}$ . Alternatively, the **number concentration** ( $C$ ) is the number of atoms or molecules divided by the volume:

$$C = \frac{N}{V} = \frac{nN_A}{V} = cN_A \quad (1.5)$$

It has units of inverse volume ( $\text{m}^{-3}$  in the SI). The **density** ( $\rho$ ) of a pure substance is its mass divided by its volume:

$$\rho = \frac{m}{V} = \frac{nM}{V} = cM \quad (1.6)$$

The SI units of density are  $\text{kg/m}^3$  although  $\text{g/cm}^3$  are commonly used.

**Pressure.** Pressure is defined as the force ( $F$ ) exerted on the walls of the system per unit area ( $A$ ):

$$p = \frac{F}{A} \quad (1.7)$$

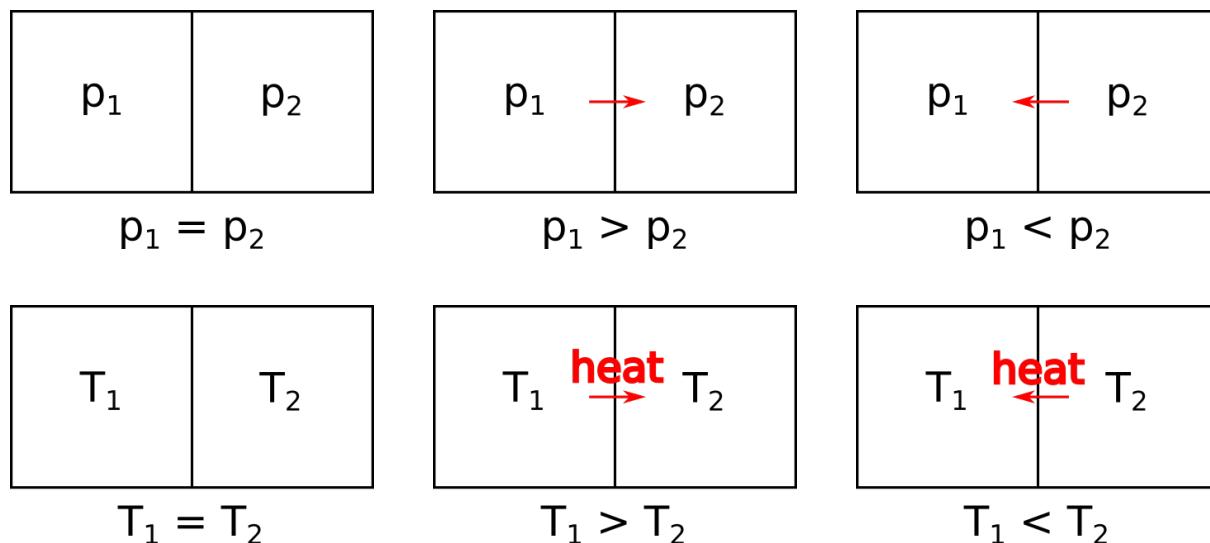


Figure 1.2: Top: mechanical equilibrium conditions. Bottom: thermal equilibrium conditions.

Microscopically, pressure arises from the random collisions of the particles within the system with its walls. These collisions are so frequent that a steady force is perceived. The higher the energy of the molecular collisions and the more numerous they are, the higher the pressure.

The SI unit of pressure is the pascal ( $1 \text{ Pa} = 1 \text{ N/m}^2$ ). One pascal is a relatively small pressure, so other units are in common use. These include the bar ( $1 \text{ bar} = 1 \times 10^5 \text{ Pa}$ ), the atmosphere (approximately equal to the average atmospheric pressure at sea level,  $1 \text{ atm} = 101\,325 \text{ Pa}$ ), the millimeter of mercury or torricelli (the pressure exerted by a column of mercury 1 mm high,  $1 \text{ mmHg} = 1 \text{ torr} = 133.322 \text{ Pa}$ ), and the psi (pounds per square inch,  $1 \text{ atm} = 14.7 \text{ psi}$ ). Atmospheric pressure is experimentally determined using a **barometer**.

Because the walls separate the system from the surroundings, we can distinguish between the system's pressure ( $p$ ), exerted by the system, and the **external pressure** ( $p_{\text{ext}}$ ), exerted by the surroundings. If we put two systems with pressures  $p_1$  and  $p_2$  in contact via a nonrigid wall, the wall moves depending on the values of the two pressures. The system with lower pressure is compressed and the system with higher pressure expands, as indicated in Figure 1.2 (top). When the two pressures equalize ( $p_1 = p_2$ ), the systems achieve mechanical equilibrium and the wall stops moving. In general, a system is said to be in **mechanical equilibrium** if there are no unbalanced internal or external forces acting on the system. The pressure inside a system can be measured experimentally with a **manometer**, which is a device that responds to changes in pressure. A manometer is used by putting it in contact with the system under study through a movable wall and then waiting until the two achieve mechanical equilibrium. The numerical value for the pressure is read from the manometer's gauge, which responds to the pressure inside the device.

**Temperature.** By our previous discussion, pressure can be understood as an indicator of the way in which two systems in contact via a movable wall evolve, and a quantitative measure of how far they are from mechanical equilibrium. Similarly, temperature is the thermodynamic property that determines the direction of the flow of energy between two systems in contact via a rigid, impermeable, thermally conducting wall. The energy transferred as a consequence of a temperature difference is known as **heat**. Energy flows from the hotter system to the colder system until the temperature in both equalizes, at which point **thermal equilibrium** is achieved (see diagram in Figure 1.2).

Microscopically, temperature is a measure of the average kinetic energy of the molecules in the

system. The higher the temperature, the faster the molecules are moving on average. Because temperature is a statistical property arising from the average over many molecules, it can only be defined for macroscopic systems.

The device used to quantify temperature is called a **thermometer**. A thermometer consists of a system in which one of its measurable thermodynamic properties has a one-to-one correspondence with its temperature. For instance, a common household thermometer is a bulb containing mercury, a substance whose volume ( $V_t$ ) depends approximately linearly on its temperature. (Not all substances do this. Water, for instance, has a minimum in the volume-temperature curve at around 4 °C.) When a mercury thermometer is brought into contact with a system and both are allowed to reach thermal equilibrium, the temperature ( $\theta$ ) in the system can be read from the volume occupied by the mercury in the bulb ( $V_t$ ):

$$\theta = aV_t + b \quad (1.8)$$

where the  $a$  and  $b$  constants are determined by assigning an arbitrary value of 0 to the temperature of pure ice in contact with liquid water (the ice point) and a value of 100 to steam in contact with liquid water (the steam point), both at 1 atm. This is the **Celsius temperature scale**, and its unit is the degree Celsius (°C).

The Celsius temperature scale has two drawbacks. First, it is tied to the properties of a particular substance (mercury, in this case). Second, it is known experimentally that there is a lower limit to the temperature scale (called absolute zero), and the Celsius scale assigns an arbitrary non-zero value to that temperature, which makes the thermodynamic equations we will see awkward to write. The **thermodynamic temperature** ( $T$ ) is an absolute temperature scale with a value of  $T = 0$  at absolute zero. The SI units for the thermodynamic temperature (the **Kelvin scale**) are the kelvin (K), and they are defined such that one K is exactly the same size as one degree Celsius. Specifically, a value of 273.16 K is assigned to the triple point of water (the unique temperature at which ice, steam, and liquid water coexist), which makes the conversion between kelvin and degrees Celsius particularly simple:

$$\theta/^\circ\text{C} = T/\text{K} - 273.15 \quad (1.9)$$

The definition of the thermodynamic temperature can be done via the properties of ideal gases (ideal gases tend to  $T = 0$  when  $V \rightarrow 0$  regardless of pressure and the nature of the gas, see Figure 1.3) or, more generally, using the properties of reversible heat engines, which we will study later. Unlike the Celsius scale, the thermodynamic temperature scale has fundamental significance, since  $T$  is directly proportional to the average kinetic energy of the constituent particles in a system.

### 1.2.3 Equilibrium

An isolated system is in **thermodynamic equilibrium** if its macroscopic properties do not change with time. A non-isolated system (open or closed) is in equilibrium if a) its properties do not change with time and b) insulating the system, i.e. removing it from contact with its surroundings, results in a system that is also at equilibrium. A non-isolated system for which condition (a) holds (its properties are constant in time) but condition (b) does not hold is in a **steady state**. An example of a system in steady state is a metal bar in contact with a hot object on one end and a cold object on the other. This system is not at equilibrium because, even though the temperature at each point along the bar does not change with time, if we remove the bar from its surroundings, then the temperature will change.

There are three different types of equilibrium, two of which have already been mentioned:

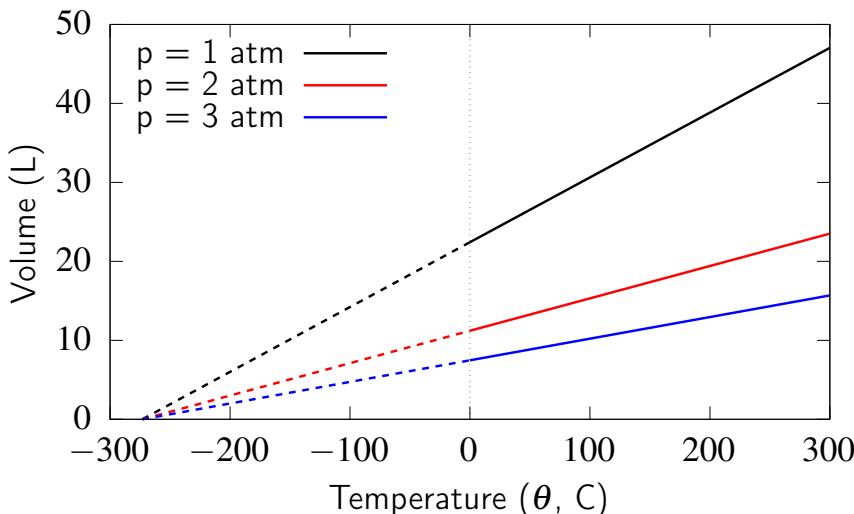


Figure 1.3: Volume-temperature curves for an ideal gas at three different (constant) pressures. The three curves are extrapolated to the same temperature at zero volume, the absolute zero ( $-273.15^\circ\text{C}$ ).

- **Mechanical equilibrium.** There are no unbalanced internal or external forces acting on the system. If connected via a movable wall with its surroundings, the pressure in the system equals the external pressure ( $p = p_{\text{ext}}$ ). A system in mechanical equilibrium is guaranteed to have a well-defined constant pressure throughout.
- **Thermal equilibrium.** There is no flow of heat within parts the system or between the system and its surroundings. If connected via a diathermal wall with its surroundings, the temperature of the system must equal the temperature of the surroundings ( $T = T_{\text{ext}}$ ). A system in thermal equilibrium is guaranteed to have a well-defined constant temperature throughout.
- **Material equilibrium.** There are no chemical reactions or transfer of mass between parts of the system or between the system and its surroundings. A system in material equilibrium is guaranteed to have a well-defined constant composition in each of its phases.

For thermodynamic equilibrium to occur, these three types of equilibrium must happen at the same time.

#### 1.2.4 Intensive and Extensive Properties

Thermodynamic properties can be classified as extensive and intensive. **Extensive properties** are those whose value is proportional to the size of the system. For an extensive property, if we take a system at equilibrium and separate it into parts, the value of the property in the system equals the sum of the same property in all its parts. Volume and mass are extensive properties.

An **intensive property** is one whose value does not depend on the size of the system. If an intensive property has a value that is uniform throughout the system and we separate the system in parts, each part has the same value for this property as the whole system. Examples of intensive properties are density, pressure, and temperature.

A system at equilibrium that has constant intensive properties throughout is **homogeneous**. A system that is not homogeneous is **heterogeneous**, and may consist of several homogeneous parts, each with different intensive properties. These homogeneous parts are known as **phases**, and they need not be physically connected; a single phase can be dispersed throughout the system. The aggregation state of a phase is described using standard abbreviations ( $s$  = solid,  $l$

Table 1.1: Names used for colloidal systems and a few examples.

Dispersed	Continuous	Name	Example
Solid	Liquid, solid	Sol	Ink, blood
Solid, liquid	Gas	Aerosol	Smoke, fog
Gas	Liquid, solid	Foam	Whipped cream, pumice
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Gel	Agar, gelatin, silica gel

= liquid,  $g$  = gas). For instance, in the reaction:



the subscripts indicate that  $\text{H}_2$  and  $\text{O}_2$  are gases and  $\text{H}_2\text{O}$  is a liquid. Species in aqueous solution are denoted with the subscript *aq*.

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**Examples:** A pure crystalline solid, a mixture of gases, and two perfectly mixed liquids are single-phase systems because they have uniform intensive properties throughout their extent. A mixture of immiscible liquids like oil and water has two phases because the oil and water phases are homogeneous but have different densities and compositions. Ice in contact with liquid water at  $0^\circ\text{C}$  has two phases because ice and liquid have different intensive properties (for instance, different densities). A solution of salt in water is a single phase but a dispersion has two phases even if the dispersed phase is microscopic and is not observable to the naked eye (for instance, milk).

Alloys such as bronze (copper and tin) and brass (copper and zinc) are substitutional alloys, meaning that the atoms of one component can replace the atoms of the other component in the crystal structure. Since the intensive properties of a substitutional alloy are the same throughout its extent, bronze and brass are single-phase systems. The components of steel (iron and carbon) form a homogeneous solid solution at high temperature known as austenite. When cooled slowly, steel differentiates into a microscopic mixture of pure iron (ferrite) and  $\text{Fe}_3\text{C}$  (cementite). Therefore, steel is a single-phase system at high temperature and a two-phase system at low temperature.

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A particularly important instance of heterogeneous systems are **colloidal systems**, which are composed of microscopic particles at most 1000 nm in diameter (the **dispersed phase**) dispersed in a medium (the **dispersion medium** or **continuous phase**). Colloidal systems receive different names based on the states of aggregation of the continuous and the dispersed phases. Some common terms and examples are given in Table 1.1. Since there is a very large interface between the two phases in colloidal systems, the contribution of the interface to the thermodynamic properties of a colloidal system (the surface effects) is not negligible.

Colloidal systems are technologically very important. A simple example of a colloidal phenomenon is the detergent effect of soap. Soap is composed of salts of long-chain carboxylic acids. When soap is dissolved in water, the concentration of these charged long-chain molecules in solution increases. Once their concentration is higher than the **critical micelle concentration** they self-assemble into globular shapes known as **micelles**. The hydrophobic chains face the inside of the micelles and keep away from the water. The formation of micelles is responsible for the detergent properties of soap, since these structures can trap other hydrophobic substances (like oil) inside. Oil in soapy water is an example of an **emulsion** (Table 1.1). In this case, we say the soap acts as **emulsifying agent** by decreasing the surface tension of the oil/water interface.

### 1.3 Ideal gases

The ideal gas is an important theoretical model whose simple properties stem from the assumption that the gas molecules are not interacting with each other. Even though it is an

idealization, the ideal gas is a reasonably good approximation to the behavior of real gases at low pressure.

Consider a closed system containing a pure gas, with thermodynamic properties  $n$ ,  $V$ ,  $p$ , and  $T$ . Experimentally, it has been determined that these variables are related to each other such that fixing three of them determines the fourth. Therefore, there is a function that links the values of these four variables:

$$f(V, p, T, n) = 0 \quad (1.11)$$

This relation is known as the **equation of state** of the system and it can be variously written by solving for either of the variables:  $V(n, p, T)$ ,  $p(n, V, T)$ , etc.

Let us assume that we solve the volume as a function of the other properties. Since the volume is an extensive property, it is directly proportional to the total amount of gas:

$$V = n \times g(p, T) \quad (1.12)$$

and we define the **molar volume** of a pure substance as:

$$V_m = \frac{V}{n} \quad (1.13)$$

with SI units  $\text{m}^3/\text{mol}$ . With this change, the equation of state simplifies to:

$$V_m = g(p, T) \quad (1.14)$$

The molar volume is an intensive quantity because it is a function of the intensive quantities  $p$  and  $T$ .

The properties of gases were thoroughly studied experimentally in the XVII and XVIII centuries. Three approximate laws governing the behavior of gases are important for us:

$$pV = \text{constant}, \quad \text{at fixed } T, n \quad (\text{Boyle's law}) \quad (1.15)$$

$$V = \text{constant} \times T, \quad \text{at fixed } p, n \quad (\text{Charles' law}) \quad (1.16)$$

$$V = \text{constant} \times n, \quad \text{at fixed } p, T \quad (\text{Avogadro's principle}) \quad (1.17)$$

Note that Avogadro's principle implies that the volume of a gas is proportional to the amount of matter, regardless of the nature of the constituent molecules. In other words, the  $g(p, T)$  function in Eq. 1.12 is the same for all substances. These observations are exactly correct only in the zero-pressure limit ( $p \rightarrow 0$ ) and so they constitute examples of **limiting laws**. The three results can be combined into a single equation:

$$pV = nRT \quad (1.18)$$

where  $R$  is the **(molar) gas constant** ( $R = 8.314\,462\,618\,\text{J K}^{-1}\,\text{mol}^{-1}$ ). An **ideal gas** is a system that follows Eq. 1.18 under all conditions of volume, pressure, and temperature.

Eq. 1.18 itself is known as the **ideal gas equation of state** or the **ideal gas law**.

A gas that is not ideal is a **real gas** and only obeys the ideal equation of state exactly in the zero-pressure limit. Nonetheless, the ideal gas law is a good approximation for the behavior of real gases at low pressure. From the microscopic point of view, an ideal gas is characterized by the fact that its molecules do not interact with each other, and each molecule behaves as if it were alone in the system. Note that ideal gases obey the same law regardless of the chemical nature of its component molecules. In particular, a mole of ideal gas always occupies 24.8 L at the **standard ambient temperature and pressure** (SATP, 298.15 K and 1 bar) and 22.4 L at the **standard temperature and pressure** (STP, an earlier version of the standard conditions, 0 °C and 1 bar), independently of the the chemical identity of the gas molecules.

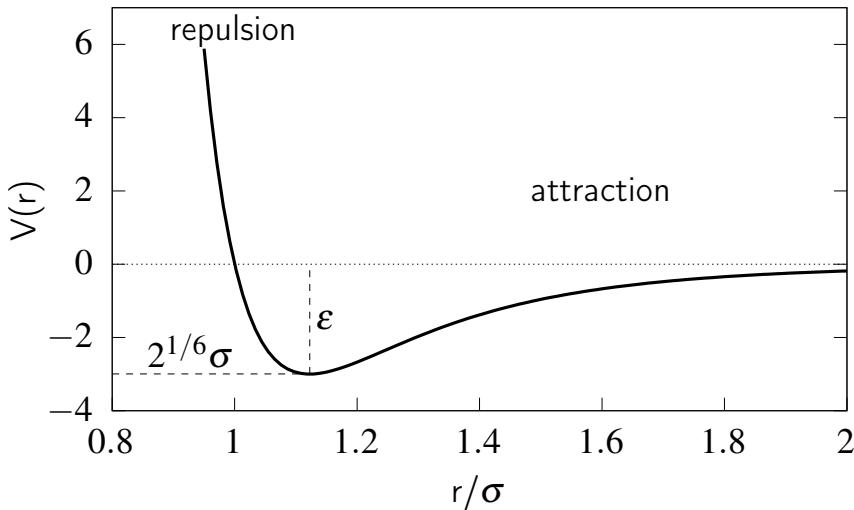


Figure 1.4: The Lennard-Jones potential with parameters  $\epsilon$  and  $\sigma$ . The minimum is at  $(2^{1/6}\sigma, \epsilon)$ .

## 1.4 Mixtures of gases

The system is a **mixture** if it has more than one component. The composition of a mixture is determined by the amount of each component  $n_i$ , and the total amount is:

$$n = n_1 + n_2 + \dots \quad (1.19)$$

In a mixture, it is useful to define the **mole fraction** of component  $i$  as the amount of  $i$  divided by the total amount:

$$x_i = \frac{n_i}{n} \quad (1.20)$$

Alternatively, the **mass fraction** (or **weight fraction**) is occasionally used:

$$w_i = \frac{m_i}{m} = \frac{m_i}{m_1 + m_2 + \dots} \quad (1.21)$$

Both the mole fraction and the mass fraction are adimensional and, by definition, the sum of all mole fractions is equal to one:

$$x_1 + x_2 + \dots = 1 \quad (1.22)$$

If the mixture is composed of gases, the **partial pressure** of component  $i$  ( $p_i$ ) is defined as:

$$p_i = p x_i \quad (1.23)$$

where  $p$  is the total pressure of the mixture. If the mixture behaves ideally, then:

$$p_i = p x_i = \frac{n_i R T}{V} = \frac{n_i R T}{n V} \quad (1.24)$$

Therefore, in an ideal gas mixture, the partial pressure of a component is equal to the pressure that component would have if it were alone in the container. This is **Dalton's law**. Dalton's law is only exact if the gas mixture behaves ideally, but partial pressures can still be defined for real gas mixtures.

## 1.5 Real gases

### 1.5.1 Experimental Behavior

In real gases, the interactions between molecules cause deviations from the ideal gas law (Eq. 1.18). A good approximation to the potential energy of intermolecular interactions in a

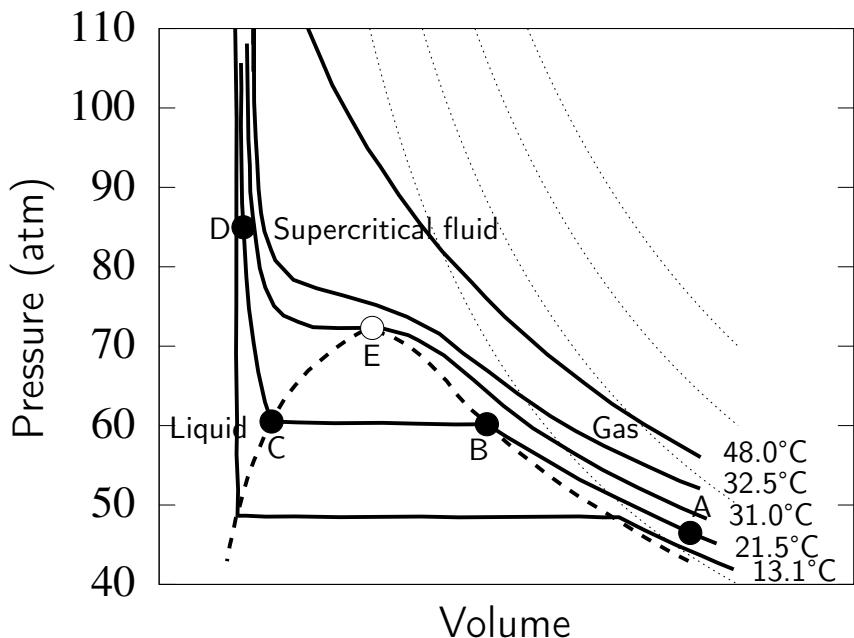


Figure 1.5: Experimental  $\text{CO}_2$  isotherms obtained by Andrews (1861–1870). The dotted lines represent the ideal gas isotherms.

gas is the Lennard-Jones potential:

$$V_{\text{LJ}}(r) = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (1.25)$$

which is represented in Figure 1.4. As shown in the figure, the Lennard-Jones potential has two regimes of interaction, depending on distance. At long intermolecular distances, the molecules attract each other, and this attraction is relatively weak. At short range, the molecules repel each other very strongly because of the overlap between their electron clouds. In the limit of infinite separation, the energy of the interaction tends to zero. The ideal gas law is exact when there are no interactions between molecules. Therefore, the ideal gas law is exact in the limit of zero pressure, when the average intermolecular distances in the gas are much greater than the molecular diameters.

Figure 1.5 represents the experimental constant-temperature  $p(V)$  curves, known as **isotherms**, for a real gas (carbon dioxide). In an ideal gas, the isotherms are hyperbolas under any conditions:

$$p = nRT \times \frac{1}{V} \quad (1.26)$$

and are shown in the diagram as dotted lines. At high volume, the experimental  $\text{CO}_2$  isotherms resemble hyperbolas like in the ideal gas, because the molecules are relatively far apart and the intermolecular interactions are negligible. At lower volumes, the molecules of the gas are forced closer to each other and the behavior of the gas deviates from ideality until ultimately the gas condenses into a liquid. The liquid phase of  $\text{CO}_2$  is represented by the left-hand side of the diagram in Figure 1.5, and the area under the dashed line represents the zone where  $\text{CO}_2$  transitions from gas to liquid.

Consider the experimental  $21.5^\circ\text{C}$  isotherm of  $\text{CO}_2$  in Figure 1.5. Point A has relatively low pressure (high volume) and the behavior of  $\text{CO}_2$  at this point is similar to an ideal gas. As the gas is isothermally compressed, the point moves to the left until point B is reached. At B, liquid  $\text{CO}_2$  starts condensing and any further decrease in volume results in an increase in the amount of condensed liquid but does not change the pressure. At point C, all  $\text{CO}_2$  has been

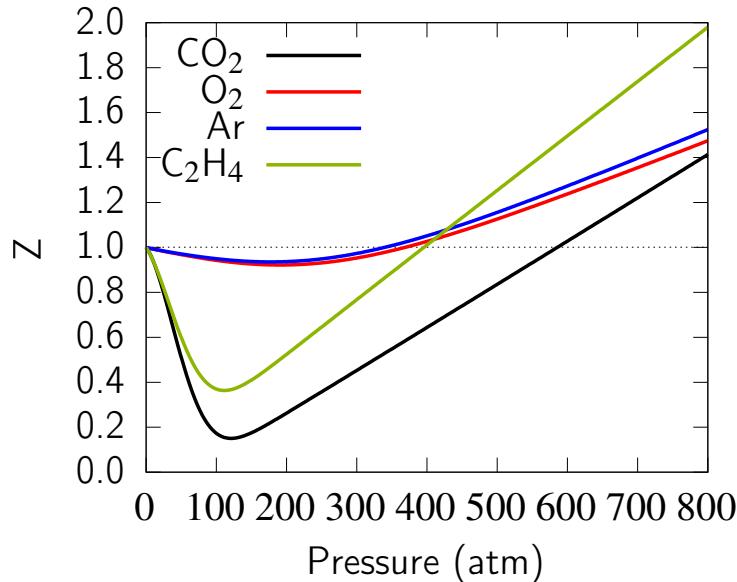


Figure 1.6: Compression factor of four real gases as a function of pressure.

condensed into a liquid. The rest of the curve is the compression isotherm of liquid CO<sub>2</sub>. Since liquids are relatively incompressible compared to gases, a further decrease in volume results in a very large increase in pressure (point D).

All isotherms with temperatures below that of point E, which is an inflection point of the corresponding isotherm, show the behavior just described. For temperatures above point E, compression of the gas does not result in the condensation of a liquid. The temperature of point E is known as the **critical temperature** ( $T_c$ ), and the pressure and molar volume associated with this point (known as the **critical point**) are the **critical pressure** ( $p_c$ ) and the **critical (molar) volume** ( $V_c$ ). These values are unique for each gas. For instance, in CO<sub>2</sub>,  $p_c = 72.9$  atm,  $V_c = 94.0$  cm<sup>3</sup>/mol, and  $T_c = 304.2$  K. In general, the critical temperature is defined as the temperature above which it is not possible to condense a gas by compression. Above the critical temperature, the distinction between gas and liquid disappears, and the phase is referred to as a **supercritical fluid**.

### 1.5.2 The Virial Equation of State

The deviation of a real gas from ideality can be measured using the **compression factor** (or compressibility factor,  $Z$ ):

$$Z = \frac{V_m}{V_m^{\text{id}}} = \frac{p}{p^{\text{id}}} = \frac{pV_m}{RT} \quad (1.27)$$

where  $V_m$  is the molar volume of the real gas,  $V_m^{\text{id}}$  is the molar volume of the equivalent ideal gas under the same conditions,  $p$  is the pressure, and  $p^{\text{id}}$  is the pressure of the equivalent ideal gas under the same conditions. For an ideal gas,  $Z = 1$  always. In a real gas,  $Z$  is a state function and depends on the state variables (for instance, on temperature and pressure,  $Z(T, p)$ ).

The compression factor of a few real gases is shown in Figure 1.6. As expected, all gases tend to the ideal compression factor ( $Z = 1$ ) at low pressure. For most gases, including those shown in the figure,  $Z < 1$  at low pressure and then the compression factor increases above one at higher pressure. This can be explained by the interactions that dominate in each of those ranges. At moderately low pressure, the molecules interact with each other but are not forced into close proximity, so attraction dominates and the volume of the real gas is lower than the

ideal gas, and therefore  $Z < 1$ . At higher pressures, molecules are brought closer together and intermolecular repulsion dominates, the volume of the real gas is higher than the ideal gas and  $Z > 1$ .

Since even for real gases  $Z$  is close to one at moderate pressures, one way of modeling the equation of state of a real gas is to perform a Taylor expansion of  $Z$  around  $p = 0$ . Using the inverse molar volume as the expansion variable results in:

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \quad (1.28)$$

or:

$$pV_m = RT \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right) \quad (1.29)$$

which is the **virial equation of state**. The coefficients  $B(T)$ ,  $C(T)$ , etc. are the second, third, etc. **virial coefficients**. They depend only on temperature and they can be determined from experimental measurements of the compressibility factor at various pressures. For instance, the second virial coefficient  $B$  of various real gases is:  $-149.7 \text{ cm}^3/\text{mol}$  ( $\text{CO}_2$ ),  $-10.5 \text{ cm}^3/\text{mol}$  ( $\text{N}_2$ ), and  $-21.7 \text{ cm}^3/\text{mol}$  ( $\text{Ar}$ ). Alternative forms of the virial equation of state can be written depending which variable we use for the Taylor expansion. For instance, using pressure as the expansion variable results in:

$$pV_m = RT \left( 1 + B^\dagger(T)p + C^\dagger(T)p^2 + \dots \right) \quad (1.30)$$

The  $B^\dagger$ ,  $C^\dagger$ , etc. coefficients are related to  $B$ ,  $C$ , etc. and one set of coefficients can be calculated from the other.

### 1.5.3 The Van der Waals Equation of State

An extension of the ideal gas law for real gases can be derived using simple arguments. The molecules in an ideal gas are non-interacting. If the molecules in a gas interact, we expect two effects on the volume and pressure of the gas. First, molecules have a finite size, so they occupy a certain volume from which the other molecules are excluded. Therefore, instead of using  $V$  as the gas volume, we use:

$$V - nb \quad (1.31)$$

where  $b$  is a parameter related to the molecular size and to the strength of the intermolecular repulsion.

Molecules also attract each other at moderately long distances. This attraction reduces both the frequency and the kinetic energy of the molecular collisions with the system walls, each by an amount proportional to the molar concentration ( $n/V$ ). Therefore, the pressure is reduced by:

$$a \left( \frac{n}{V} \right)^2 \quad (1.32)$$

where  $a$  is another empirical parameter related to the strength of the intermolecular attraction. Putting both results together leads to the **van der Waals equation of state**:

$$p = \frac{nRT}{V - nb} - a \frac{n^2}{V^2} = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (1.33)$$

The values of  $a$  and  $b$  are particular for each gas, and can be determined from experiment. For instance, for  $\text{CO}_2$ , they are  $a = 3.610 \text{ atm L}^2 \text{ mol}^{-2}$  and  $b = 4.29 \times 10^{-2} \text{ L mol}^{-1}$ .

Figure 1.7 shows the isotherms at several temperatures for the van der Waals gas. Compare these curves to the experimental and ideal-gas isotherms in Figure 1.5. Clearly, the van der

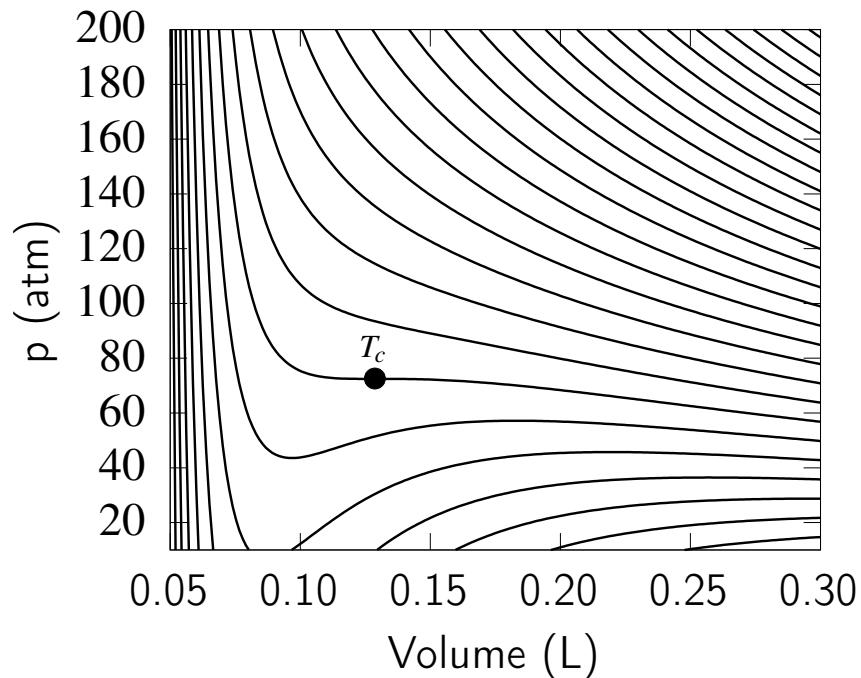


Figure 1.7: Isotherms for the  $\text{CO}_2$  van der Waals equation of state. The critical point is indicated as a dot. The critical temperature is  $T_c = 303.85 \text{ K}$ .

Waals equation of state is in much better agreement with experiment than the ideal gas law. However, the behavior of the van der Waals gas in the region of the diagram corresponding to the phase transition between gas and liquid is unphysical. The inversion in the slope of the van der Waals curves below the critical temperature ( $T_c$ , indicated as a point in the diagram) means that the van der Waals equation predicts states where a decrease in volume at constant temperature leads to a decrease in pressure, something that is not possible.

These spurious features of the van der Waals equation originate from the fact that, if expanded, this equation of state predicts that the pressure is a cubic polynomial in the molar volume. Therefore, for a given pressure and temperature below the critical temperature, this polynomial has three real roots and, therefore, the van der Waals equation of state predicts three possible different volumes for a given pressure and temperature. This unphysical behavior causes the oscillating features shown in Figure 1.7, known as the **van der Waals loops**. A reasonable

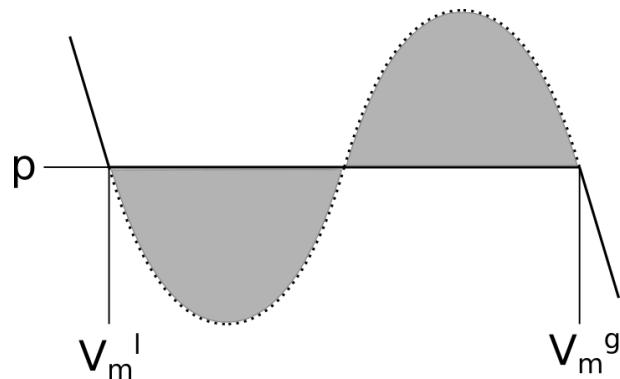


Figure 1.8: An example of Maxwell's equal-area construction. The van der Waals isotherm has spurious behavior, sketched as dotted lines, in the liquid-gas transition part of the  $p$ - $V$  diagram. The van der Waals isotherm is replaced by a straight line in such a way that the area between this line and the isotherm is equal above and below the line.

agreement with experiment can be recovered by replacing these regions with a straight line that covers the zone where the unphysical behavior is located. As we shall see, the most principled way of drawing this straight line is such that the areas under and above the straight line are equal, as shown in Figure 1.8. This is known as the **Maxwell's equal-area construction**, and it will be justified later.

The van der Waals equation of state does not capture the behavior of real gases very accurately, and therefore it is not used very much in practice. If we restrict ourselves to describing a real gas with two parameters, the **Redlich-Kwong** equation of state is a much better alternative:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)T^{1/2}} \quad (1.34)$$

where  $a$  and  $b$  are empirical parameters for each particular gas, with values different from those for the van der Waals equation. Note the Redlich-Kwong is also a cubic polynomial in the volume so it has the same spurious behavior as the van der Waals equation of state in the liquid-gas transition region. Many empirical equations of state for real gases exist, and they are very important in engineering applications in which gases are often subjected to significant pressure under working conditions. More sophisticated equations of state with more adjustable parameters are used in practice.

#### 1.5.4 The Principle of Corresponding States

The location of the critical point predicted by the van der Waals equation of state (Eq. 1.33) can be calculated using the fact that the critical point is an inflection point of the  $p(V)$  curve. Therefore, the first and second derivatives of the  $p(V)$  curve at the critical point must be zero:

$$p_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \quad (1.35)$$

$$\frac{dp}{dV_m} = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \quad (1.36)$$

$$\frac{d^2p}{dV_m^2} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0 \quad (1.37)$$

or:

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \quad (1.38)$$

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4} \quad (1.39)$$

Taking the quotient of both equations and solving for  $V_c$  yields:

$$V_c = 3b \quad (1.40)$$

and substitution of this value into the equations above gives the other two critical properties:

$$T_c = \frac{8a}{27Rb} \quad (1.41)$$

$$p_c = \frac{a}{27b^2} \quad (1.42)$$

These expressions provide a way of determining the van der Waals parameters of a real gas from experimentally measured critical constants.

We now define the **reduced variables** as the ratio between a variable and the corresponding critical variable:

$$T_r = \frac{T}{T_c} \quad p_r = \frac{p}{p_c} \quad V_r = \frac{V}{V_c} \quad (1.43)$$

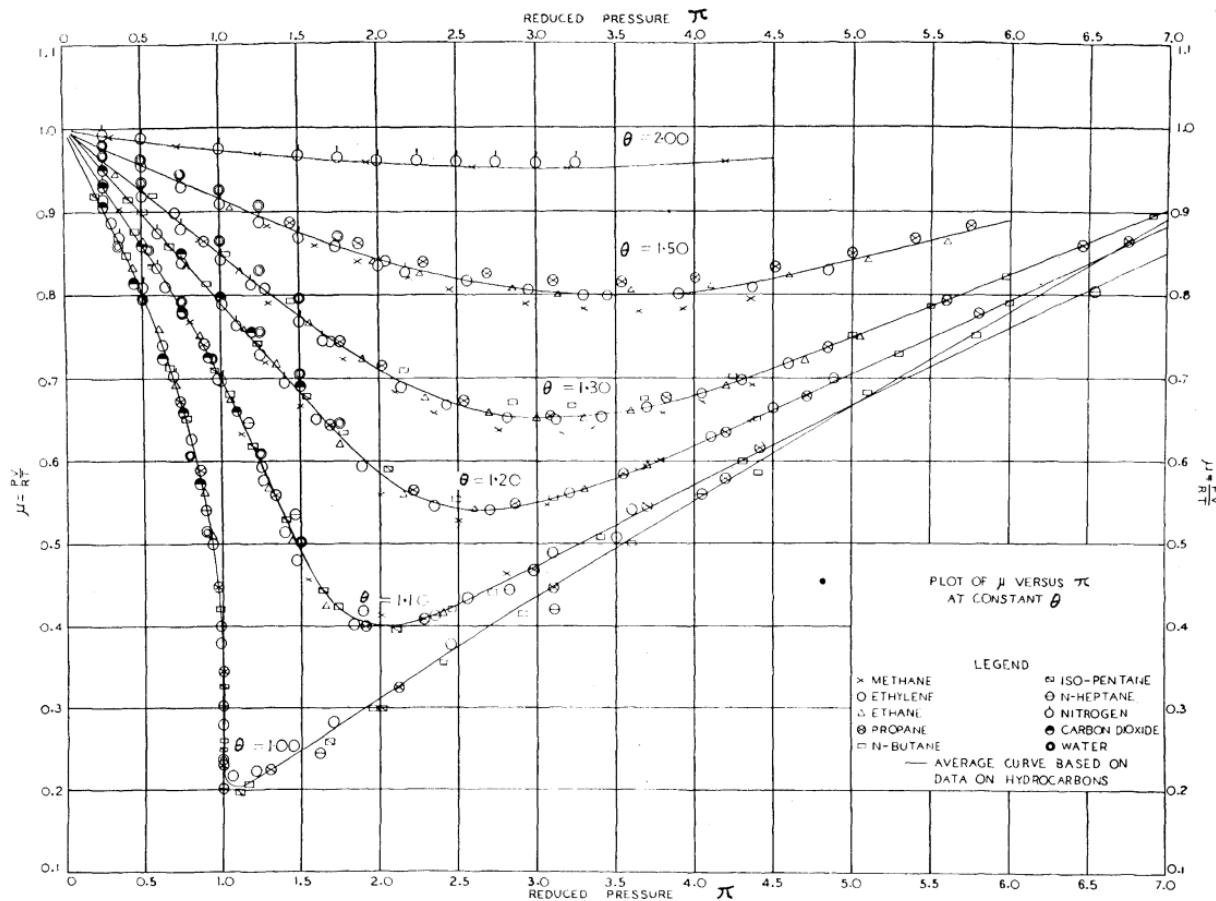


Figure 1.9: Compression factor ( $Z$ ) of several gases as a function of reduced pressure at various temperatures. All gases have similar compression factors in terms of the reduced pressure. Used with permission from G.-J. Su, “Modified law of corresponding states for real gases”, *Ind. Eng. Chem.* **38** 803 (1946).

If we substitute the temperature, pressure, and volume with the corresponding reduced and critical variables in the van der Waals equation of state (Eq. 1.33), we have:

$$p_r p_c = \frac{RT_r T_c}{V_r V_c - b} - \frac{a}{V_r^2 V_c^2} \quad (1.44)$$

And if we apply the formulas we just found for the critical variables:

$$\frac{ap_r}{27b^2} = \frac{8aRT_r}{27Rb(3bV_r - b)} - \frac{a}{9b^2 V_r^2} \quad (1.45)$$

Multiplying both sides by  $27b^2/a$ , we arrive at:

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \quad (1.46)$$

Since only the van der Waals coefficients  $a$  and  $b$  depend on the particular gas under study, Eq. 1.46 must apply to any gas regardless of its chemical nature.

This result is not restricted to van der Waals gases and, in fact, the observation that the equation of state when expressed in terms of reduced variables:

$$p_r = f(T_r, V_r) \quad (1.47)$$

is approximately the same for all real gases is known as the **principle of corresponding states**. This principle is only an approximation, and it fails for non-spherical or very polar

molecules. However for non-polar small molecules the principle of corresponding states is remarkably successful. For instance, Figure 1.9 shows the experimentally determined compression factor as a function of reduced pressure for several gases ( $\text{N}_2$ ,  $\text{CO}_2$ , water, and a number of small hydrocarbons). The value of  $Z$  in terms of  $p_r$  and  $T_r$  is approximately the same for all of them.

## Chapter 2

# The First Law of Thermodynamics

### 2.1 Heat, Work, and Energy

Energy, heat, and work are related quantities that are important in classical thermodynamics. **Work** has the same definition as in classical mechanics. When a force applied on a body ( $\mathbf{F}$ ) causes an infinitesimal displacement ( $d\mathbf{s}$ ), the work exerted is calculated as:

$$dw = \mathbf{F} \cdot d\mathbf{s} \quad (2.1)$$

where  $\cdot$  symbolizes the scalar product between the force ( $\mathbf{F}$ ) and the displacement vectors ( $d\mathbf{s}$ ). If the body moves along a trajectory  $C$  given by the curve  $\mathbf{s}(t)$  between times  $t_0$  and  $t_1$ , the work is calculated by integration of the equation above along the trajectory:

$$w = \int_C \mathbf{F} \cdot d\mathbf{s} = \int_{t_0}^{t_1} \mathbf{F}(\mathbf{s}(t)) \cdot \frac{d\mathbf{s}(t)}{dt} dt \quad (2.2)$$

---

**Example.** We want to lift a box that weighs  $m = 1\text{ kg}$  to a height  $h = 1\text{ m}$  from the ground. The gravitational force on the box is approximately constant and equal to  $F = mg$ , where  $g$  is the gravitational acceleration. The required work is:

$$w = \int_C \mathbf{F} \cdot d\mathbf{s} = mg \int_C d\mathbf{s} = mgh = 1\text{ kg} \times 9.81\text{ m/s}^2 \times 1\text{ m} = 9.81\text{ J}$$

Note that work has units of energy and, in fact, the energy required to lift the box equals its gain in potential energy ( $mgh$ ).

---

In a thermodynamic system, work is done when an external force of any nature (mechanical, electrical, magnetic,...) causes a displacement in the system or in a part of it. For example, if the system consists of a gas chamber fitted with a piston, work can be exerted on the system by applying external pressure on the piston and compressing the gas. Work can also be done by the system on its surroundings. For instance, a battery is a thermodynamic system in which a chemical reaction is taking place that involves the transfer of electrons between reactants. The electric current generated by the battery is used to power devices outside the system. Therefore, the battery is exerting work on the surroundings.

**Energy** is the capacity to do work. When a gas is compressed in a cylinder, or a battery is recharged by running its electron-transfer reaction in reverse, or the mainspring of a clockwork mechanism is wound up, the energy of the system increases and, as a result, it can exert more work on its surroundings. Conversely, when the system does work on its surroundings, it loses energy. Quantitatively, if a system makes a body in its surroundings move against an external

force  $\mathbf{F}$ , the energy the body gains as a result of this work is the same as the energy lost by the system, and both are given by Eq. 2.1 but have opposite signs:

$$dw_{\text{system}} = -dw_{\text{surr}} = \mathbf{F} \cdot d\mathbf{s} \quad (2.3)$$

In the following, we will always adopt the convention that energy gained by the system is positive and energy lost by the system is negative.

The energy of the particles (atoms and molecules) inside the system can be of two kinds: kinetic and potential. The **kinetic energy** ( $T$ ) of a particle is associated with the velocity with which the particle moves:

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} \quad (2.4)$$

where  $p = mv$  is the particle's momentum. The **potential energy** ( $V$ ) of a particle results from its position in the system relative to other particles and any fields external to the system. For instance, a body with mass  $m$  at a height  $h$  from the Earth's surface has potential energy equal to  $mgh$ , where  $g$  is the gravitational acceleration. Two charges  $q_1$  and  $q_2$  a distance  $r$  apart have potential energy equal to  $q_1q_2/(4\pi\epsilon r)$ , where  $\epsilon$  is the permittivity of the medium. As we have seen in the example above, the potential energy of a body equals the work required to move it to its current position, assuming no energy is lost in the process. The **total energy** (or simply the energy) of a particle is the sum of its kinetic and potential energies:

$$E = T + V \quad (2.5)$$

Provided no external forces act on the particle,  $E$  remains constant, although  $T$  and  $V$  individually may vary.

The total energy of a system is the sum of the kinetic and potential energies of its particles. Experimentally, it is known that the energy of a system can be changed by means other than work. Specifically, the energy of a system may be changed as a consequence of a temperature difference with its surroundings. As we have seen, energy transferred in this way is known as **heat** ( $q$ ). From the microscopic point of view, heat is the transfer of energy via random molecular motions, since temperature is related to the average kinetic energy of the particles in a system. When two systems with different temperatures are put in contact, the molecules in the hotter system impact the slower molecules in the colder system, resulting in an energy transfer. This contrasts with the energy transferred as work, where there is an organized motion in the surroundings causing the application of an external force on the system.

Heat, work and energy all have the same units. In the SI, the unit of energy is the joule,  $1\text{ J} = 1\text{ N m} = 1\text{ kg m}^2\text{ s}^{-2}$ . A common alternative unit used in chemical thermodynamics is the calorie, which was originally defined as the amount of energy required to raise the temperature of water by  $1^\circ\text{C}$  at a certain temperature. There have been several different (and incompatible) definitions of the calorie over the years but the one commonly used in chemistry is the **thermochemical calorie**, defined as  $1\text{ cal} = 4.184\text{ J}$  exactly.

A very important point to note is that heat and work refer to types of energy transfer. Heat is energy transfer caused by a temperature difference and work is energy transfer caused by an external force. Systems may have more or less energy but they do not have heat or work, hence terms like “latent heat” or “heat capacity”, which we will use in the rest of the course, are somewhat misleading. The concepts that these terms describe originated at a time when heat was thought to be a fluid substance that was transferred between bodies at different temperatures (the caloric theory). This theory has been debunked, but the language remains. Likewise, for simplicity in the language, we will use terms like “heat transfer” or “heat flow” to mean “energy transferred in the form of heat”.

## 2.2 Internal Energy and the First Law

The **internal energy** ( $U$ ) of a system is the energy contained within it. The internal energy is the total energy of the system (the sum of the kinetic and potential energies of all its particles) excluding the kinetic and potential energies of the system as a whole.

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**Example.** Consider our system is a box full of mechanical springs, for instance, a collection of mechanical toys. We can raise the internal energy of the system by winding up the springs of the mechanisms inside the box. However, the internal energy does not change if we push the box to make it move or if we lift it because the kinetic and potential energies of the box as a whole are not part of  $U$ .

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Since  $U$  is the sum of the energies of the system's particles, if we separate the system into two equal-sized parts, each part receives a fraction of the particles and therefore their internal energy would be only a fraction of the  $U$  in the original system. Therefore, the  $U$  of a system equals the sum of the internal energies of its parts and, consequently, the internal energy is an extensive property. Same as heat and work, the internal energy has units of energy, joules (J) in the SI. Because it is an extensive property, we can define the molar internal energy ( $U_m$ ) as the internal energy of the system divided by the total amount of substance:

$$U_m = \frac{U}{n} \quad (2.6)$$

The molar internal energy is an intensive property, with SI units of joule per mole (J/mol). Far more common units are kJ/mol and kcal/mol.

The **first law of thermodynamics** says that the **internal energy ( $U$ ) is a state function whose change in a closed system equals the energy transferred as heat ( $q$ ) plus the energy transferred as work ( $w$ )**:

$$\Delta U = q + w, \quad \text{for a closed system.} \quad (2.7)$$

The validity of the first law is postulated based on experimental evidence. In order to derive useful thermodynamic relations, we will often consider infinitesimal changes in the internal energy of a system as a response to infinitesimal changes in other properties. The differential statement of the first law is:

$$dU = dq + dw \quad (2.8)$$

where  $dq$  is an infinitesimal heat transfer and  $dw$  is an infinitesimal work. Note that we have considered closed systems only because a closed system can transfer only energy with its surroundings, either in the form of heat or work. An isolated system is a particular type of closed system that exchanges no energy, so  $\Delta U = q = w = 0$ . In an open system, there is mass transfer in addition to energy transfer and the molecules entering and exiting the system carry energy with them, so additional terms are needed in Eq. 2.7 to be valid for open systems (these will be seen later). The signs of heat and work in the first law (Eq. 2.7) are such that energy gained by the system is positive and energy lost by the system is negative.

The first law is a re-statement of the conservation of energy principle for thermodynamic systems. We can always assume the universe (the combination of system plus surroundings) is an isolated system. Combined with the fact that  $U$  is extensive, and therefore

$U_{\text{universe}} = U_{\text{system}} + U_{\text{surroundings}}$ , we have

$$\Delta U_{\text{universe}} = \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0 \quad (2.9)$$

Therefore, the internal energy change for the system equals minus the change in the surroundings:

$$\Delta U_{\text{system}} = -\Delta U_{\text{surroundings}} \quad (2.10)$$

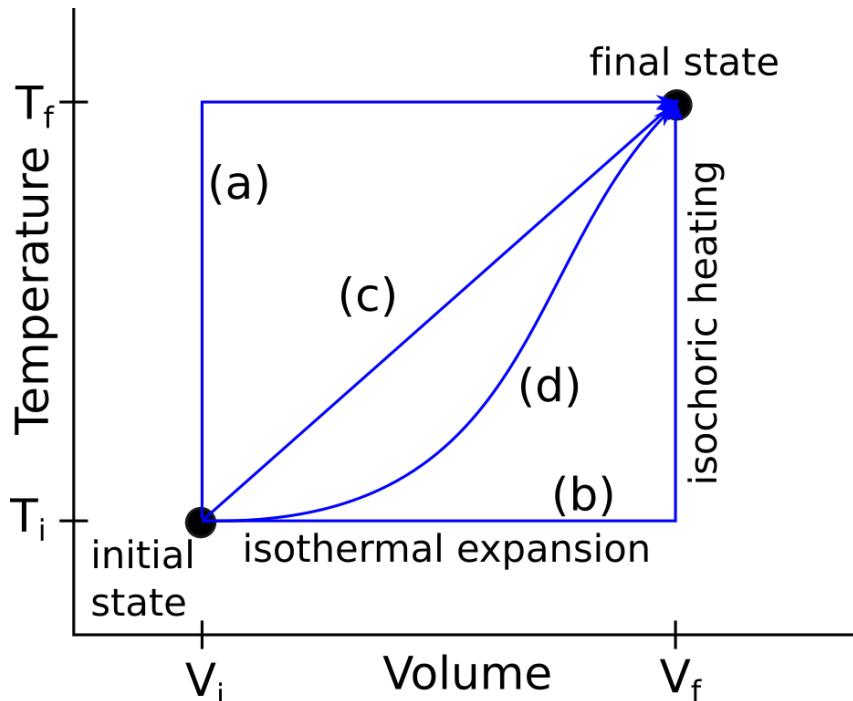


Figure 2.1: Four different processes connecting an initial and a final state in a pure gas.

and, consequently, the energy is conserved. An important consequence of the first law is the impossibility of constructing a “perpetual motion machine” whose only effect is to perform work indefinitely without drawing energy from its surroundings. This would violate the first law, since this machine would be increasing the energy of the universe.

Another important point about the first law is that it posits that work and heat have the same effect on the system, namely, changing its internal energy. The equivalence of heat and work was demonstrated by Joule who showed in 1840 that it is possible to raise the temperature of water in an insulated container by stirring it with a paddle wheel (i.e. by exerting work on it). Joule’s experiment was used to establish the “mechanical equivalent of heat”, the amount of mechanical work required to increase the temperature of one gram water by one degree celsius (4.184 J, what is today known as a calorie) and was a large step towards abandoning caloric theory, because it showed that the hypothetical “caloric” fluid could be created out of nothing by applying mechanical work.

The first law also states that  $U$  is a state function. This means that its value is determined by the thermodynamic state of the system, which in turn is determined by the state variables. Hence,  $U$  can be written as a mathematical function of the state variables. For instance, for a pure gas in a closed system, we can write  $U(V, T)$ , or  $U(p, T)$ , or  $U(p, V)$ , depending on convenience.

In the rest of the course we will consider many examples of thermodynamic processes. A **thermodynamic process** is a change in the system between an initial thermodynamic state at equilibrium ( $i$ ) and a final thermodynamic state also at equilibrium ( $f$ ). In general, there are infinitely many processes that connect a given pair of initial and final states. This is exemplified in Figure 2.1 for a pure gas. If we expand a gas from the thermodynamic state  $(V_i, T_i)$  to the state  $(V_f, T_f)$  with  $V_f > V_i$ , we could use the following two-step process (process a in the figure):

$$(V_i, T_i) \longrightarrow (V_i, T_f) \longrightarrow (V_f, T_f)$$

where an isochoric (constant volume) heating is followed by an isothermal (constant

temperature) expansion. Alternatively, we could expand first and then raise the temperature (process b):

$$(V_i, T_i) \longrightarrow (V_f, T_i) \longrightarrow (V_f, T_f)$$

Or we could make the system go in a straight line from  $(V_i, T_i)$  to  $(V_f, T_f)$  (process c):

$$((1-x)V_i + xV_f, (1-x)T_i + xT_f), \text{ with } x \in [0, 1]$$

Or we could take an entirely arbitrary path like process d in the figure.

Because  $U$  is postulated to be a state function by the first law, its value depends only on the current thermodynamic state of the system and not on its previous history. Therefore, if we consider a process in which the system goes from an initial state  $i$  to a final state  $f$ , the change in internal energy ( $\Delta U$ ) associated with this process depends only on the energies of the initial ( $U_i$ ) and the final states ( $U_f$ ), and not on the path taken between them:

$$\Delta U = U_f - U_i \quad (2.11)$$

In particular, the four processes in Figure 2.1, as well as any other processes between those two states, have the same  $\Delta U$  given by Eq. 2.11. In general, **work and heat are not state functions**. The amount of energy transferred as heat (or work) is different for the different paths in Figure 2.1, and they cannot be calculated from the initial and final states alone.

In the particular case of an ideal gas, molecules do not interact with each other. Consider, for instance, a system composed of a number of classical particles with charge  $q_i$  and mass  $m_i$ . The internal energy of this system is the sum of its kinetic and potential energies:

$$U = T + V = \frac{1}{2} m_i v_i^2 + \frac{1}{4\pi\varepsilon} \sum_{i>j} \frac{q_i q_j}{r_{ij}} \quad (2.12)$$

Now we increase the system's volume at constant temperature (an isothermal expansion). The kinetic energy remains unchanged because the molecular velocities are related to the system's temperature, which does not change in this process. However, the potential energy changes because the particles are now further apart on average, therefore  $U$  also changes. If we now consider the same system with no intermolecular interactions ( $q_i = 0$ ), the second term (the potential energy) vanishes and  $U$  is the same before and after the isothermal expansion. Therefore, if the particles do not interact with each other,  $U$  is independent of the system's volume and depends only on temperature. This result is valid for any system of non-interacting molecules, and therefore **the internal energy of an ideal gas depends only on its temperature**. Later in the course, we will prove this result is a consequence of the ideal gas law (Eq. 1.18). This observation means that the temperature of an ideal gas is a direct measure of its internal energy. For instance, using statistical thermodynamics, it is possible to show that the molar internal energy of a monoatomic ideal gas is:

$$U_m = \frac{3}{2} RT \quad (2.13)$$

The internal energy of an ideal gas is more complicated for polyatomic molecules but it always depends on temperature only.

## 2.3 Mathematical Background and Thermodynamic Notation

In the remainder of the course we will use some mathematical results to develop the theory. Thermodynamics uses a specific notation that may be different from the one used in previous courses. For this reason, the mathematical results we need are summarized here. To avoid clutter, we always assume functions and paths are continuous and sufficiently smooth, and the functions are defined everywhere in the relevant domain.

### 2.3.1 Partial Derivatives and the Differential of a Function

Assume we have a scalar function of several variables  $f : \mathbb{R}^n \rightarrow \mathbb{R}$  that assigns a value to every point,  $f(\mathbf{x}) = f(x_1, \dots, x_n)$ . The **partial derivative** of  $f(\mathbf{x})$  with respect to variable  $x_i$  is the derivative of the function with respect to that variable, holding the other variables constant. In thermodynamics, the following notation is used for a partial derivative:

$$\left( \frac{\partial f}{\partial x_i} \right)_{x_j \neq i} \quad (2.14)$$

For instance, the partial derivative of the internal energy function  $U(V, T)$  with respect to volume is:

$$\left( \frac{\partial U}{\partial V} \right)_T \quad (2.15)$$

This is read as “the derivative of the internal energy with respect to volume at constant temperature”. The fact that the other variables are held constant is implied in the usual notation for a partial derivative but the thermodynamic notation is a convenient way of expressing the whole set of variables on which the function depends. As we have seen,  $U$  for a pure substance in a closed system can also be written as  $U(p, V)$  or  $U(p, T)$ , depending on which quantities we use as state variables. Using the thermodynamic notation circumvents the potential confusion had we considered the volume derivative of  $U(V, p)$ :

$$\left( \frac{\partial U}{\partial V} \right)_p \quad (2.16)$$

which is different from the partial derivative in Eq. 2.15.

The **differential** of a scalar function  $f : \mathbb{R}^n \rightarrow \mathbb{R}$ , denoted by  $df$ , is a  $\mathbb{R}^n \rightarrow \mathbb{R}^n$  vector field whose  $n$  components are the partial derivatives of the function with respect to the variables:

$$df(\mathbf{x}) = \left( \frac{\partial f}{\partial x_1}(\mathbf{x}), \dots, \frac{\partial f}{\partial x_n}(\mathbf{x}) \right) \quad (2.17)$$

The differential, which is very similar to the concept of gradient in differential geometry, represents the slope of the function in every possible direction and, as such, it is a measure of the infinitesimal change in the function as a response of an infinitesimal change in one or more of its variables. For convenience, the differential is commonly written as:

$$df = \left( \frac{\partial f}{\partial x_1} \right) dx_1 + \dots + \left( \frac{\partial f}{\partial x_n} \right) dx_n \quad (2.18)$$

The differentials of composite functions are calculated using rules similar to normal derivatives. For instance, if we have two functions  $f(x, y)$  and  $g(x, y)$  and we consider the differential of the product, we find:

$$\begin{aligned} df(g) &= \left( \frac{\partial(fg)}{\partial x} \right) dx + \left( \frac{\partial(fg)}{\partial y} \right) dy = \left[ \left( \frac{\partial f}{\partial x} \right) g + f \left( \frac{\partial g}{\partial x} \right) \right] dx + \left[ \left( \frac{\partial f}{\partial y} \right) g + f \left( \frac{\partial g}{\partial y} \right) \right] dy \\ &= \left[ \left( \frac{\partial f}{\partial x} \right) dx + \left( \frac{\partial f}{\partial y} \right) dy \right] g + f \left[ \left( \frac{\partial g}{\partial x} \right) dx + \left( \frac{\partial g}{\partial y} \right) dy \right] = df \times g + f \times dg \end{aligned} \quad (2.19)$$

Since the derivatives are calculated component-wise, the rules for calculating differentials are the same as the rules for calculating derivatives. An example of a differential in thermodynamics is:

$$dU = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT \quad (2.20)$$

for the  $U(T, V)$  function.

### 2.3.2 Vector Fields and Path Integrals

A **vector field** is a function  $\mathbf{F} : \mathbb{R}^m \rightarrow \mathbb{R}^n$  that assigns a vector:

$$\mathbf{F}(\mathbf{r}) = (F_1(\mathbf{r}), F_2(\mathbf{r}), \dots, F_n(\mathbf{r})) \quad (2.21)$$

to every position  $\mathbf{r}$ . We define a smooth path  $C$  in  $\mathbb{R}^m$  by a parametrization  $\mathbf{s}(t)$  where  $t \in [a, b]$ . This means that the path starts at  $\mathbf{s}(a)$  and goes continuously to its end at  $\mathbf{s}(b)$ . The **path integral** (or **line integral**) of the vector field along this path is defined as:

$$\int_C \mathbf{F} = \int_C \mathbf{F} \cdot d\mathbf{s} = \int_a^b \mathbf{F}(\mathbf{s}(t)) \cdot \mathbf{s}'(t) dt \quad (2.22)$$

where  $\cdot$  represents the scalar product and  $\mathbf{s}'(t) = \frac{d\mathbf{s}}{dt}$  is the derivative of the curve parametrization, which is a vector tangent to the curve at all points. For instance, if we have a force  $\mathbf{F}$  acting on a body that follows a trajectory  $C$  given by  $\mathbf{s}(t)$ , the work exerted on the body is calculated by integrating Eq. 2.1:

$$w_{\text{body}} = \int_C \mathbf{F} \cdot d\mathbf{s} \quad (2.23)$$

and the path integral is calculated as above. The value of a path integral is independent of the parametrization chosen to represent the path.

For a given vector field  $dg : \mathbb{R}^n \rightarrow \mathbb{R}^n$ , the following four statements are equivalent:

1. The path integral over any closed path is zero:

$$\oint_C dg = 0 \quad (2.24)$$

A closed path is one where the initial and the final points coincide. A path integral over a closed path is sometimes symbolized by putting a circle on the integral symbol, as above, but this is not necessary.

2. All path integrals between any two points A and B have the same value regardless of the path.
3. The vector field  $dg$  is the differential of a function  $g(\mathbf{x})$ :

$$dg = \left( \frac{\partial g}{\partial x_1}, \dots, \frac{\partial g}{\partial x_n} \right) \quad (2.25)$$

4. The crossed second derivatives of  $dg$  are identical:

$$\frac{\partial(dg_i)}{\partial x_j} = \frac{\partial(dg_j)}{\partial x_i} \quad (2.26)$$

for all  $i$  and  $j$ .

When any of these conditions hold, which means all the others also hold because they are equivalent, we say that  $dg$  is an **exact differential**. In other applications,  $dg$  is called a conservative field (for instance, an electric field) and  $g$  is its **potential function** (for instance, the electric potential). A vector field that does not fulfill these conditions is an **inexact differential**. (Sometimes inexact differentials are denoted  $\delta g$  or  $d\bar{g}$  instead of  $dg$ , but we will not use this notation.)

A property of exact differentials that we will use very often is that if C is a path between A and B, the line integral over C of the exact differential  $dg$  is:

$$\begin{aligned}\int_C dg &= \int_a^b dg(\mathbf{x}(t)) \cdot \mathbf{x}'(t) dt = \int_a^b \left( \sum_i \frac{\partial g}{\partial x_i} \frac{\partial x_i}{\partial t} \right) dt = \int_a^b \frac{dg}{dt} dt \\ &= g(\mathbf{x}(b)) - g(\mathbf{x}(a)) = g(B) - g(A)\end{aligned}\quad (2.27)$$

for all paths C that start at A and end at B,  $\mathbf{x}(t)$  being an arbitrary parametrization of the path. The value of the path integral of an exact differential equals the value of the potential function at the final point minus the initial point. This is the statement analogous to the fundamental theorem of calculus, but applied to path integrals.

In thermodynamics, an exact differential always derives from a state function, which acts as its potential function. As discussed above, the internal energy is a state function so it has an exact differential ( $dU$ ), composed of the derivatives of  $U$  with respect to the chosen state variables. In contrast, heat and work are not state functions, so the corresponding vector fields representing the infinitesimal transfer of heat and work as a response to a change in state variables ( $dq$  and  $dw$ ) cannot be written as differentials of a potential function. Therefore, heat and work are inexact differentials, and the heat and work transferred in a process depends on the process itself, not only on the initial and final points.

### 2.3.3 Useful Relations

We now derive a few relations between the derivatives of exact differentials that are useful in thermodynamics. Consider a function  $f(x, y)$  that, in our context, is a state function of the state variables  $x$  and  $y$ . We wish to change the state variables to  $x$  and  $z$ , and so we express  $y$  as a function of the new variables,  $y(x, z)$ . The partial derivative of  $f(x, z)$  with respect to  $x$  must be equal to the total derivative of  $f(x, y(x, z))$  with respect to  $x$  calculated applying the chain rule:

$$\left( \frac{\partial f}{\partial x} \right)_z = \left( \frac{\partial f}{\partial x} \right)_y + \left( \frac{\partial f}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_z \quad (2.28)$$

Note that the same result would have been obtained by starting from the differential of  $f(x, y)$ :

$$df = \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy \quad (2.29)$$

and then “dividing” by  $dx$  and taking the derivatives at constant  $z$ . We will use this shorthand operation in some derivations.

In the function  $y(x, z)$  we consider the  $z$  variable fixed for now. This one-variable function maps values  $x \rightarrow y$ . The corresponding one-variable inverse function maps values of  $y \rightarrow x$ , and is therefore  $x(y, z)$  at the same  $z$ . Since the derivative of the inverse function is the inverse of the function derivative, we have:

$$\left( \frac{\partial y}{\partial x} \right)_z = \frac{1}{\left( \frac{\partial x}{\partial y} \right)_z} \quad (2.30)$$

Equation 2.28 can be applied to the particular case of  $f(x, y) = z(x, y)$ . In this case, the left-hand side of the equation is zero and it reduces to:

$$0 = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_z \quad (2.31)$$

Table 2.1: Types of work.

Name	Factors	$dw$
p–V	External pressure ( $p_{\text{ext}}$ ) and volume ( $V$ )	$-p_{\text{ext}}dV$
Surface expansion	Surface tension ( $\gamma$ ) and surface area ( $\sigma$ )	$\gamma d\sigma$
Extension	Tension ( $f$ ) and length ( $l$ )	$fdl$
Electrical	Charge ( $Q$ ) and electric potential ( $\phi$ )	$\phi dQ$
	Electric potential ( $\phi$ ) and charge ( $Q$ )	$Qd\phi$

Rearranging,

$$\frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y} \quad (2.32)$$

And using Eq. 2.30 we can rewrite it as:

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \quad (2.33)$$

Again, note how this relation could have been derived from the differential of  $x(y, z)$ :

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad (2.34)$$

by first “dividing” by  $dy$  and then taking constant  $x$ , which makes  $dx = 0$ . This shorthand operation is also occasionally useful.

Equation 2.33 is sometimes rearranged using Eq. 2.30 in a more symmetric form:

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \quad (2.35)$$

This relation is known as the **triple product rule** or the **Euler chain relation**.

In summary, the four relations we just derived are:

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \quad (2.36)$$

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\frac{\partial x}{\partial y}\right)_z} \quad (2.37)$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \quad (2.38)$$

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \quad (2.39)$$

These will be used repeatedly throughout the course.

## 2.4 Pressure-Volume (p–V) Work

Depending on the nature of the force exerted on the system, there are several types of work. A few examples of different kinds of work are given in Table 2.1. In chemical systems, an important kind of work is done by the compression or expansion of gases, known as **pressure-volume (p–V) work** or **expansion work**. Many chemical reactions (for instance,

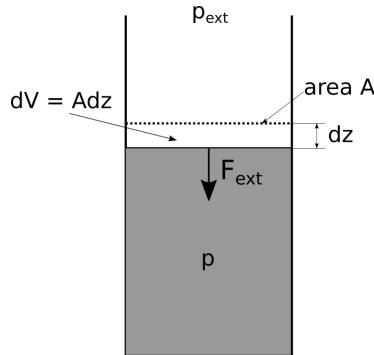


Figure 2.2: An example of a system exerting p–V work. The pressure inside the cylinder ( $p$ ) is greater than the external pressure ( $p_{\text{ext}}$ ) and, as a result, the system expands transferring energy as work to the surroundings.

a combustion) generate gases, and the work done by those gases on the surroundings has to be taken into account when calculating the thermodynamic properties associated with those reactions. Other types of work exist, and we will see some of them later. For now, we denote work that is not p–V as **non-expansion work** or **additional work**. The first law (Eq. 2.8) can be rewritten as:

$$dU = dq + dw = dq + dw_{\text{pv}} + dw_{\text{non-pv}} \quad (2.40)$$

where  $dw_{\text{pv}}$  is the p–V work and  $dw_{\text{non-pv}}$  is the non-expansion work. In the rest of this chapter, and for most of this course, we will assume p–V work only.

A schematic diagram of a system doing p–V work is shown in Figure 2.2. The system has a frictionless movable piston separating it from the surroundings. The pressure inside the system ( $p$ ) is greater than the external pressure ( $p_{\text{ext}}$ ), and consequently the system expands until both pressures equalize and mechanical equilibrium is re-established. The work is being done by the system on the surroundings so, in our sign convention, it has negative value because the system is losing energy. For an infinitesimal displacement of the piston  $dz$ , the work is:

$$dw = -|F_{\text{ext}}|dz \quad (2.41)$$

where  $F_{\text{ext}}$  is the external force on the piston. Pressure is defined as applied force per unit area (Eq. 1.7) so we can rewrite this equation as:

$$dw = -\frac{|F_{\text{ext}}|}{A} \times Adz = -p_{\text{ext}} \times Adz \quad (2.42)$$

but since the volume is the area of the cylinder times its height, the infinitesimal change in the volume of the system is  $dV = Adz$ . Therefore,

$$dw = -p_{\text{ext}}dV \quad (2.43)$$

The total work when the system expands from  $V_i$  to  $V_f$  is calculated by integrating the equation above:

$$w = - \int_{V_i}^{V_f} p_{\text{ext}}dV \quad (2.44)$$

Note that it is the external pressure, not the pressure of the system, what determines the amount of work exerted. This equation also works if the system is compressed. In that case,  $V_f < V_i$  and the work would be positive, which is consistent with the increase in the system's energy. Non-expansion work has similar expressions for the work differential, involving the product of one intensive and one extensive variable (see Table 2.1).

## 2.5 Constant-Volume Heat Capacity

If we consider a thermodynamic process in which the volume of the system does not change (an **isochoric process**), then  $dV = 0$  and:

$$dw = -p_{\text{ext}}dV = 0 \quad (2.45)$$

Therefore, in a constant-volume process the change in internal energy equals the heat transferred:

$$dU = dq = dq_V \quad (2.46)$$

where we used the subscript  $V$  to denote that the heat is transferred at constant volume. If the constant-volume process goes between an initial and a final state, we integrate this equation to find that **the change in internal energy equals the heat transferred in a constant-volume process**:

$$\Delta U = q_V \quad (2.47)$$

Note that we do not write  $\Delta q_V$  because heat, unlike the internal energy, is not a state function, so there is no “initial heat” and “final heat”, just heat transferred during a process.

The change in internal energy in a constant-volume process typically causes a change in the temperature of the system. The relation between the change in the internal energy and the temperature of a system during a constant-volume process is known as the **constant-volume heat capacity**:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (2.48)$$

Since  $\Delta U = q_V$  at constant volume,  $C_V$  measures how much heat is required to raise the temperature of a system that is held at constant volume by a certain amount. A higher  $C_V$  means that more heat is required to raise the system’s temperature, hence the term “heat capacity”. The constant-volume heat capacity is an extensive property because  $U$  is extensive and  $T$  is intensive. Its units are energy divided by temperature, J/K in the SI, although cal/K are common. Very often, heat capacities are reported as intensive quantities, for instance, the **molar constant-volume heat capacity** is the heat capacity per mole of substance:

$$C_{V,m} = \frac{C_V}{n} \quad (2.49)$$

The SI units of the molar heat capacity are J/K/mol. Another common intensive version of the heat capacity is the **specific constant-volume heat capacity** (or simply the **specific heat**), defined as the heat capacity divided by the mass of the system:

$$C_{V,s} = \frac{C_V}{m} \quad (2.50)$$

Its SI unit is J/K/kg but  $1 \text{ J/K/g} = 1 \times 10^{-3} \text{ J/K/kg}$  is more common.

The heat capacity is always positive, indicating that the internal energy increases with increasing temperature. Typical molar constant-volume heat capacities ( $C_{v,m}$ ) are 28.46 J/K/mol ( $\text{CO}_2$ ), 20.8 J/K/mol ( $\text{N}_2$ ), and 74.53 J/K/mol (liquid water). The specific heat capacity of water is about one calorie per kelvin and kilogram at room temperature; this was, in fact, the way the calorie was defined originally. The molar internal energy of a monoatomic ideal gas is (Eq. 2.13)  $3/2RT$ , so its molar constant-volume heat capacity is:

$$C_{V,m} = \left( \frac{\partial U_m}{\partial T} \right)_V = \frac{3}{2}R = 12.47 \text{ J/K/mol} \quad (2.51)$$

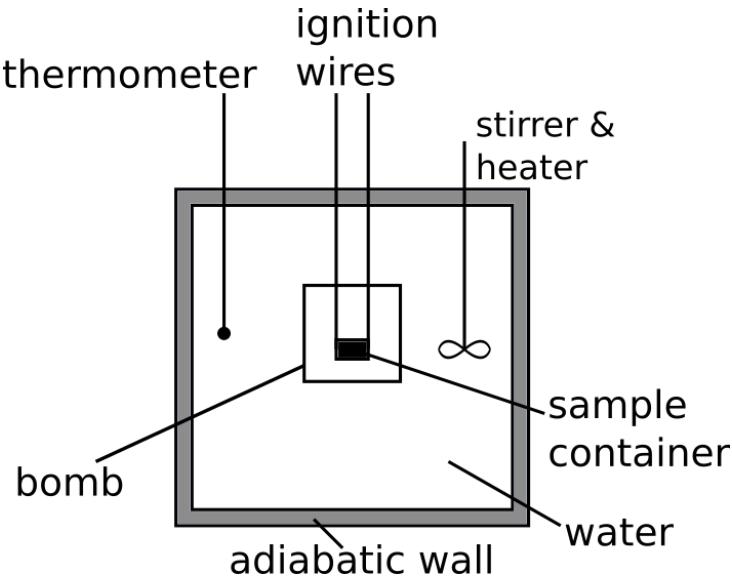


Figure 2.3: Diagram an adiabatic bomb calorimeter.

The heat capacity is itself a function of the thermodynamic state and in particular of temperature although, in general, heat capacities change relatively slowly with temperature.

The relation  $\Delta U = q_V$  (Eq. 2.47) is important because it enables the determination of internal energy differences by means of calorimetric experiments. **Calorimetry** studies the transfer of energy as heat during a chemical process. The device used for this task is a **calorimeter**. In particular, heat transferred at constant volume ( $q_V$ ) can be measured using an **adiabatic bomb calorimeter**, shown schematically in Figure 2.3. The system under study is placed inside a closed container with rigid walls (the “bomb”), which is immersed in a water bath surrounded by adiabatic (thermally insulating) walls. After the calorimeter is set up, the reaction is initiated and we measure the change in temperature  $\Delta T$  of the calorimeter, which is approximately proportional to the amount energy transferred as heat:

$$\Delta U = q_V = C\Delta T \quad (2.52)$$

where  $C$  is the heat capacity of the calorimeter assembly (known as the **calorimeter constant**). This constant is determined beforehand by calibrating the apparatus, either by burning a substance with known properties or by using an electrical resistance to raise its temperature. Bomb calorimeters can also be used to determine the constant-volume heat capacities of substances by measuring the rise in temperature of the calorimeter when a measured amount of energy is transferred into the system, typically by passing a known amount of current through an electrical resistance.

**Example.** A current of 10 A from a 12 V electrical supply is passed for 300 s through an adiabatic bomb calorimeter at room temperature, resulting in a rise of temperature of 5.5 K. The heat capacity of the calorimeter is:

$$C = \frac{\Delta U}{\Delta T} = \frac{IVt}{\Delta T} = \frac{10 \text{ A} \times 12 \text{ V} \times 300 \text{ s}}{5.5 \text{ K}} = 6545.5 \text{ J/K} = 6.5 \text{ kJ/K}$$

Now we carry out a combustion of 2.016 g of glucose at the same temperature. This results in a temperature rise of 3.282 K. The  $\Delta U$  of this particular process is:

$$\Delta U = C\Delta T = 6545.5 \text{ J/K} \times 3.282 \text{ K} = 21\,482.2 \text{ J} = 21.48 \text{ kJ}$$

## 2.6 Enthalpy

Constant pressure conditions are a lot more common in chemistry than constant volume. A simple example is when a chemical reaction produces gases and these are released into the atmosphere. During a process at constant pressure, known as an **isobaric process**, the system may exchange energy both as heat and as work with the surroundings. The natural state function to describe the energy change during an isobaric process is the **enthalpy**, defined as:

$$H = U + pV \quad (2.53)$$

where  $p$  is the system pressure and  $V$  is its volume. Because  $U$ ,  $p$ , and  $V$  are state functions, the enthalpy is also a state function. Same as the internal energy, the enthalpy has units of energy and is an extensive property, so we can define a **molar enthalpy** as:

$$H_m = \frac{H}{n} \quad (2.54)$$

The molar enthalpy itself is an intensive property and has units of energy per mole.

The differential of the enthalpy is:

$$dH = d(U + pV) = dU + pdV + Vdp \quad (2.55)$$

but using the first law (Eq. 2.8), we have:

$$dH = dq + dw + pdV + Vdp \quad (2.56)$$

For an isobaric process,  $dp = 0$ , so:

$$dH = dq + dw + pdV \quad (2.57)$$

Furthermore, the initial and final states of the isobaric process must be at equilibrium and have pressure equal to  $p$ . Since thermodynamic equilibrium implies mechanical equilibrium, this pressure equals the external pressure,  $p = p_{\text{ext}}$  and, since the process is isobaric, this equation is valid at any point during the process. Consequently, Eq. 2.43 becomes:

$$dw = -p_{\text{ext}}dV = -pdV \quad (2.58)$$

Substituting in Eq. 2.57, we have:

$$dH = dq = dq_p \quad (2.59)$$

where the subscript  $p$  is used to indicate that the process is at constant pressure. If we integrate between the initial and the final states:

$$\Delta H = q_p \quad (2.60)$$

so the **change in enthalpy of a system is equal to the heat transferred during a constant-pressure process** (compare to Eq. 2.47).

The enthalpy change can be measured by determining  $\Delta U$  in a bomb calorimeter and then transforming to  $\Delta H$ . If the process involves liquids and solids, where the molar volumes are relatively small and do not change very much, then:

$$\Delta H = \Delta U + p\Delta V \approx \Delta U \quad (2.61)$$

This is not true in processes involving gases. In an isothermal (constant-temperature) process involving ideal gases in which  $\Delta n_g$  moles of gas are generated, we have:

$$\Delta H = \Delta U + p\Delta V = \Delta U + p \times \frac{\Delta n_g RT}{p} = \Delta U + \Delta n_g RT \quad (2.62)$$

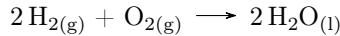
**Example.** The  $\Delta U_m$  of converting the calcite polymorph of  $\text{CaCO}_{3(\text{s})}$  ( $\rho = 2.17 \text{ g/cm}^3$ ) to aragonite ( $\rho = 2.93 \text{ g/cm}^3$ ) at 1 atm and room temperature is 0.21 kJ/mol. The molar change in enthalpy is:

$$\Delta H_m = H_m(\text{a}) - H_m(\text{c}) = U_m(\text{a}) + pV_m(\text{a}) - U_m(\text{c}) - pV_m(\text{c}) = \Delta U_m + p(V_m(\text{a}) - V_m(\text{c}))$$

From Eq. 1.6,  $\rho = M/V_m$ , so at one atmosphere:

$$\begin{aligned}\Delta H_m - \Delta U_m &= pM \left( \frac{1}{\rho(\text{a})} - \frac{1}{\rho(\text{c})} \right) = 101\,325 \text{ Pa} \times 100.09 \text{ g/mol} \times \left( \frac{1}{2.93 \text{ g/cm}^3} - \frac{1}{2.71 \text{ g/cm}^3} \right) \\ &\times \frac{1 \text{ m}^3}{1 \times 10^6 \text{ cm}^3} = -0.28 \text{ J/K/mol}\end{aligned}$$

which is about a thousandth of the  $\Delta U_m$ . In contrast, in the reaction:



we have 3 mol of gas disappearing, so under isothermal conditions at room temperature and assuming ideal behavior of the gases:

$$\Delta H_m - \Delta U_m = -3 \times RT = -3 \times 8.314 \text{ J/K/mol} \times 298.15 \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -7.44 \text{ kJ/mol}$$

Note the difference between enthalpy change and energy change is much larger (kJ/mol instead of J/mol) in the process involving gases.

The change in enthalpy as a response to a change in temperature at constant pressure is the **constant-pressure heat capacity**:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad (2.63)$$

Since  $\Delta H = q_p$  (Eq. 2.59),  $C_p$  measures the heat required to raise the temperature of the system at constant pressure. Apart from this difference,  $C_p$  is entirely analogous to  $C_V$ . It is an extensive property, has the same units, and molar and specific versions of  $C_p$  can be defined:

$$C_{p,m} = \frac{C_p}{n} \quad (2.64)$$

$$C_{p,s} = \frac{C_p}{m} \quad (2.65)$$

The  $C_p$  itself depends on temperature, but in general only mildly. The  $\Delta H$  of a constant-pressure process can be calculated by integrating Eq. 2.63:

$$\Delta H = q_p = \int_{T_i}^{T_f} C_p(T) dT \quad (2.66)$$

Some example molar constant-pressure heat capacities ( $C_{p,m}$ ) are, in J/K/moL: 29.1 ( $\text{N}_2$ ), 36.9 ( $\text{CO}_2$ ), 75.3 (water), 112 (ethanol), 6.115 (diamond), 900 (paraffin wax).

**Example.** Let us calculate the change in the molar enthalpy of  $\text{N}_2$  when heated between 25 °C and 100 °C. Because the temperature range is relatively large, the heat capacity cannot be assumed to be constant. Tabulated values of heat capacities indicate that in this temperature range the heat capacity of  $\text{N}_2$  is given by the expression:

$$C_p(T)/(\text{J/K/mol}) = a + bT + \frac{c}{T^2}$$

where  $a = 28.58$ ,  $b = 3.77 \times 10^{-3} \text{ K}^{-1}$ , and  $c = -0.50 \times 10^5 \text{ K}^2$ . Therefore, the enthalpy change is

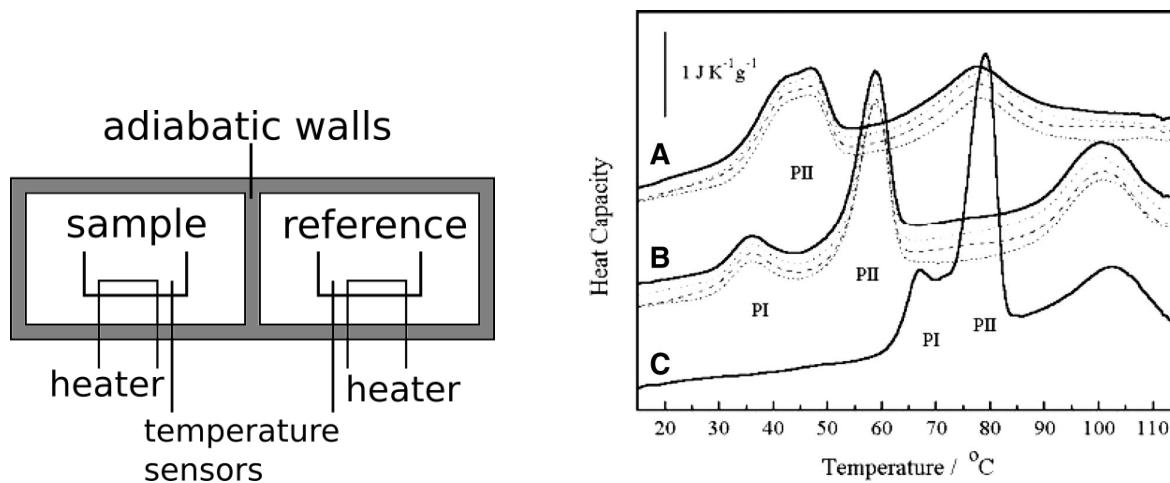


Figure 2.4: Left: diagram of a differential scanning calorimeter. Right: DSC thermogram of the thermal denaturation (unfolding) of a human immunoglobulin protein (hIgG4-A) under several conditions. The peaks indicate the onset of the denaturation process and the  $\Delta H$  can be calculated as the area under the peak (Eq. 2.66). Reproduced with permission from Gill et al. “Differential scanning calorimetry techniques: applications in biology and nanoscience”, *J. Biomol. Tech.* **21** 167 (2010).

given by:

$$\begin{aligned}\Delta H &= \int_{T_i}^{T_f} C_p(T) dT = \left[ aT + \frac{bT^2}{2} - \frac{c}{T} \right]_{T_i}^{T_f} = a(T_f - T_i) + \frac{b}{2}(T_f^2 - T_i^2) - c\left(\frac{1}{T_f} - \frac{1}{T_i}\right) \\ &= 2.20 \text{ kJ/mol}\end{aligned}$$

The experimental determination of  $\Delta H$  can be done using an **isobaric calorimeter** in which the heat evolved in an isobaric process is measured. An alternative is **differential scanning calorimeter** (DSC), shown in Figure 2.4 (left). In a DSC apparatus, two small compartments are heated at a constant rate using a resistance such that the temperature is increased linearly with time. One of the compartments contains the sample and the other contains a reference material which is known to undergo no physical or chemical changes in the studied temperature range. If no chemical change occurs in the sample, the heat transferred is proportional to the change in temperature ( $q_p = C_p \Delta T$ ), and this can be used to measure the constant-pressure heat capacity of the sample. If some chemical or physical change occurs in the sample, the extra heat required to keep the temperature the same as in the reference material,  $q_{p,\text{ex}}$ , is recorded (or, rather, its temperature derivative the extra heat capacity,  $C_{p,\text{ex}}$ ). This measurement is directly related to the  $\Delta H$  involved in those changes. The plot of the extra heat capacity of the sample as a function of temperature produced by DSC is known as a **thermogram**. An example DSC thermogram for the thermal denaturation of a protein is shown in Figure 2.4.

## 2.7 Standard Enthalpy Changes

When a system undergoes a physical or chemical transformation, the  $\Delta H$ , or the change in any other thermodynamic property, refers to the difference between the initial and the final state of the transformation:

$$\Delta H = H_{\text{final}} - H_{\text{initial}} \quad (2.67)$$

For simplicity, enthalpy changes for chemical and physical transformations are often reported and tabulated for processes in which the substances in the initial and the final states are under a certain set of standard conditions, adopted by convention. The **standard enthalpy change**  $\Delta H^\circ$  is the enthalpy of a process in which the substances in the initial and final states are in

their standard state. The **standard state** of a substance, as defined by the IUPAC convention, is:

- If the substance is a gas, the standard state is the hypothetical state in which the gas is pure at a pressure of 1 bar and has ideal gas behavior.
- In the case of liquids and solids, the standard state is the pure substance in the same aggregation state (liquid or solid) and at a pressure of 1 bar.

The definition of standard state applies to pure substances as well as components in mixtures. In the particular case of solutions, we will see additional definitions for the standard state of solvent and solutes later on. The list of all standard states used in this course is given in Appendix A. Note that temperature is not part of the standard state specification so, to be completely defined, a standard enthalpy must be accompanied by the temperatures at the initial and final points. This is usually done by indicating the temperature as a subscript in the case of an isothermal process, for instance,  $\Delta H_{298.15}^\circ$ .

Tables of standard enthalpies typically use room temperature ( $25^\circ\text{C} = 298.15\text{ K}$ ). A pressure of 1 bar is referred to as the **standard pressure**, and denoted by the symbol  $p^\circ$ . The degree symbol ( $^\circ$ ) can be used to indicate that standard quantities other than the enthalpy ( $\Delta U^\circ, \dots$ ). The meaning is the same as with the enthalpy: all substances in their initial and final states of the process are assumed to be in their standard states at the considered temperature. Likewise, the standard internal energy  $U^\circ$  or the standard enthalpy  $H^\circ$  of a substance is the internal energy or enthalpy of that substance under standard conditions.

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**Example.** The standard state of liquid water at  $25^\circ\text{C}$  is pure liquid water at  $25^\circ\text{C}$  and 1 bar. The standard state of water vapor at  $400\text{ K}$  is pure water vapor at that temperature and 1 bar, and in a hypothetical state in which it has ideal gas behavior. The standard state of ice at  $25^\circ\text{C}$  is pure ice at  $25^\circ\text{C}$  and 1 bar.

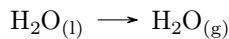
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Note that the standard states for the last two systems in the example refer to hypothetical states that are not experimentally observable. This may seem strange at first but it is done for convenience, because the standard quantities are easier to calculate and this choice of standard state facilitates thermodynamic calculations.

Some enthalpy changes for various physical and chemical transformations are widely utilized, and therefore have specific names. For instance, the molar **enthalpy of vaporization** ( $\Delta_{\text{vap}}H$ , also known as the heat of vaporization) is the molar enthalpy for the transformation of one mole of liquid into one mole of gas. For convenience, tabulated data make use of the standard states: the **standard enthalpy of vaporization** ( $\Delta_{\text{vap}}H^\circ$ ) is the enthalpy of vaporization in which the liquid and the gas are both in their standard states.

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**Example.** The standard enthalpy of vaporization of water is the enthalpy change associated with the transformation:



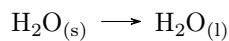
where both the liquid and vapor water are at 1 bar and the water vapor behaves ideally. Its value at  $373\text{ K}$  is  $\Delta H_{\text{vap}}^\circ = 40.66\text{ kJ/mol}$ .

---

Another named enthalpy change is the **standard enthalpy of fusion** ( $\Delta_{\text{fus}}H^\circ$ ), which is associated with the melting of one mole of pure solid into liquid.

---

**Example.** The standard enthalpy of fusion of water corresponds to the transformation:



where the solid and the liquid are pure at 1 bar. Its value at  $273\text{ K}$  is  $\Delta H_{\text{fus}}^\circ = 6.01\text{ kJ/mol}$ .

---

Table 2.2: Named enthalpy changes defined by the IUPAC and in common use. Standard versions of these quantities exist, indicated by the superscript  $^\circ$ , in which the substances in the initial and final states of the transformation are in their standard states.

Enthalpy of...	Process	Symbol
Transition	Phase $\alpha \rightarrow$ Phase $\beta$	$\Delta_{trs}H$
Fusion/Melting	solid $\rightarrow$ liquid	$\Delta_{fus}H$
Vaporization	liquid $\rightarrow$ gas	$\Delta_{vap}H$
Sublimation	solid $\rightarrow$ gas	$\Delta_{sub}H$
Mixing	pure $\rightarrow$ mixture	$\Delta_{mix}H$
Solution	solid solute $\rightarrow$ solution	$\Delta_{sol}H$
Dilution	liquid solute $\rightarrow$ solution	$\Delta_{dil}H$
Hydration	$X_{(g)} \rightarrow X_{(aq)}$	$\Delta_{hyd}H$
Atomization	compound $\rightarrow$ atoms (gas)	$\Delta_{at}H$
Ionization	$X_{(g)} \rightarrow X_{(g)}^+ + e_{(g)}^-$	$\Delta_{ion}H$
Electron gain	$X_{(g)} + e_{(g)}^- \rightarrow X_{(g)}^-$	$\Delta_{eg}H$
Reaction	reactants $\rightarrow$ products	$\Delta_rH$
Combustion	compound + $O_{2(g)}$ $\rightarrow CO_{2(g)} + H_2O_{(l,g)}$	$\Delta_cH$
Formation	elements $\rightarrow$ compound	$\Delta_fH$
Activation	reactants $\rightarrow$ transition state	$\Delta^\ddagger H$

A list of enthalpy changes for common transformations is shown in Table 2.2. The standard version of the quantities shown in the table refers to the process in which the substances in the initial and final states are in their standard state at the chosen temperature.

Because the enthalpy is a state function, the enthalpy change of any transformation depends only on the initial and final states. Consequently, known enthalpy changes can be combined to generate enthalpy changes for other, perhaps unknown, transformations. For instance, assume we want to calculate the standard enthalpy of sublimation of ice water. According to Table 2.2, this refers to the process:



and is denoted  $\Delta_{sub}H^\circ$ . We can consider that this transformation occurs in two steps, first from solid to liquid, and then from liquid to gas:



It takes  $\Delta_{fus}H^\circ$  to go from solid to liquid and  $\Delta_{vap}H^\circ$  to go from liquid to gas. Because the sublimation can be written as fusion followed by vaporization and the enthalpy change depends only on the initial and final states, the enthalpy of sublimation is:

$$\Delta_{sub}H^\circ = \Delta_{fus}H^\circ + \Delta_{vap}H^\circ \quad (2.71)$$

This is correct even though during a sublimation water is never in the liquid state.

Another consequence of the enthalpy being a state function is that the enthalpy change for a transformation is minus the enthalpy change for the reverse transformation. For instance, the standard enthalpy change for the condensation of water:



is minus the standard enthalpy of vaporization,  $-\Delta_{vap}H^\circ$ .

## 2.8 Standard Reaction Enthalpies

An important standard enthalpy change is the **standard reaction enthalpy** ( $\Delta_r H^\circ$ ) the molar enthalpy change associated with the conversion of pure unmixed reactants in their standard states to pure unmixed products in their standard states for a chemical reaction. This quantity is sometimes also known as the **standard enthalpy of reaction** or the **heat of reaction**. For instance, for the reaction:



the standard reaction enthalpy is:

$$\begin{aligned} \Delta_r H^\circ &= 3H_m^\circ(\text{C}) + H_m^\circ(\text{D}) - 2H_m^\circ(\text{A}) - H_m^\circ(\text{B}) \\ &= \sum_{\text{products}} |\nu_B| H_m^\circ(\text{B}) - \sum_{\text{reactants}} |\nu_A| H_m^\circ(\text{A}) \end{aligned} \quad (2.74)$$

where  $H_m^\circ$  is the molar enthalpy of the corresponding substances in their standard states and  $|\nu|$  are the absolute values of the stoichiometric coefficients. A reaction with  $\Delta_r H^\circ < 0$  is known as an **exothermic reaction**. A reaction with  $\Delta_r H^\circ > 0$  is an **endothermic reaction**. Since constant pressure conditions are common in chemistry, and  $\Delta H = q_P$ , exothermic reactions almost always release heat and endothermic reactions absorb heat from the surroundings (hence the name “heat of reaction” for  $\Delta_r H^\circ$ ).

In the rest of the course, we will write a general chemical reaction as:

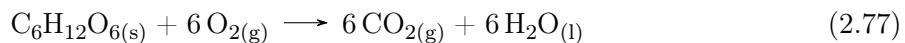


where  $\nu_i$  are the stoichiometric coefficients. The  $\nu_i$  are adimensional quantities that are positive if the species is a product and negative if it is a reactant. For instance, for the reaction in Eq. 2.73,  $\nu_A = -2$ ,  $\nu_B = -1$ ,  $\nu_C = 3$ ,  $\nu_D = 1$ . With this definition, the standard reaction enthalpy can be written as:

$$\Delta_r H^\circ = \sum_i \nu_i H_m^\circ(i) \quad (2.76)$$

where  $i$  runs over all species involved in the reaction (reactants and products). Compare to Eq. 2.74.

The standard reaction enthalpies for some reactions have specific names. For instance, the **standard enthalpy of combustion** (also, **standard heat of combustion**),  $\Delta_c H^\circ$ , refers to the reaction in which a mole of an organic substance is combusted with excess oxygen to give  $\text{H}_2\text{O}$  and  $\text{CO}_2$  (and  $\text{N}_2$ , if N is present in the molecule). For instance, for glucose, the combustion reaction is:



and the standard enthalpy of combustion is  $\Delta_c H^\circ = -2808 \text{ kJ/mol}$ .

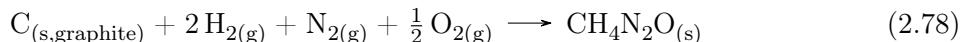
Another important case is the **standard enthalpy of formation** (also, **standard heat of formation**),  $\Delta_f H^\circ$ , which is the standard reaction enthalpy for the formation of a compound from its elements in their reference states. The **reference state** of an element is the standard state of the element in its most stable form at 1 bar and the reaction temperature. (In the particular case of elements that are gases at room temperature and 1 bar, the reference state is conventionally taken as an ideal gas at 1 bar regardless of temperature.)

---

**Example.** At room temperature, the stable form of N<sub>2</sub> is a gas and the stable form of Hg is a liquid. The stable form of C at room temperature is graphite, because at that temperature and 1 bar it is more stable than its allotrope diamond, even though the interconversion between them is extremely slow.

---

Note the difference between the concepts of reference state and standard state. Only elements have reference states and, as discussed above, substances in their standard state need not be stable at the chosen temperature—in fact their existence in the standard state may be completely fictitious, as is the case with gases. With these definitions, the standard formation enthalpy of, for instance, urea at room temperature, corresponds to the reaction:



and its value is  $\Delta_f H^\circ = -333.51 \text{ kJ/mol}$ . Note that, in a formation reaction, the stoichiometric coefficient of the product is always one and all elements are in their stable form (gas for H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> and solid graphite for C). A consequence of the definition is that the standard enthalpy of formation of an element in its reference form is zero at all temperatures.

For reactions in solution involving ionic species, defining the standard enthalpy of formation of the ions poses a problem because it is not possible to prepare a solution with only cations or only anions. To overcome this problem, we adopt the additional convention that the standard enthalpy of formation of H<sup>+</sup> is zero in aqueous solution at all temperatures:

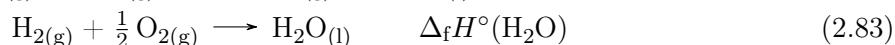
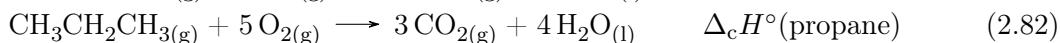
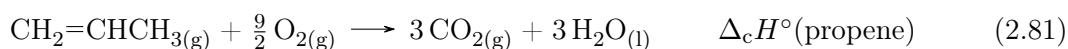
$$\Delta_f H^\circ(\text{H}_{(\text{aq})}^+) = 0 \text{ at any temperature} \quad (2.79)$$

It is possible to calculate the standard enthalpies of formation of any other ion by using this convention and measuring reaction enthalpies involving its salts.

Same as with the other enthalpy changes, standard reaction enthalpies can be combined using the fact that the enthalpy is a state function. For instance, the hydrogenation of propene:



can be thought of as the combination of three reactions, namely the combustion of propene, the combustion of propane, and the formation of water:



The hydrogenation reaction (Eq. 2.80) can be obtained by adding the combustion of propene (Eq. 2.81) and the formation of water (Eq. 2.83), and subtracting the combustion of propane (Eq. 2.82). Therefore, the standard reaction enthalpy for the hydrogenation is:

$$\Delta_r H^\circ(\text{hydrogenation}) = \Delta_c H^\circ(\text{propene}) + \Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_c H^\circ(\text{propane}) \quad (2.84)$$

This is an application of **Hess' law**: the standard reaction enthalpy for a given chemical reaction is the sum of the standard reaction enthalpies of all reactions into which it can be decomposed. Hess' law is applied when the transformation from reactants to products can be achieved via two different paths. For the example reaction above, the corresponding paths are shown in Figure 2.5.

The reactants in a chemical reaction can always be decomposed into their elements, and those elements can always be put back to form the products. Therefore, a corollary of Hess' law is

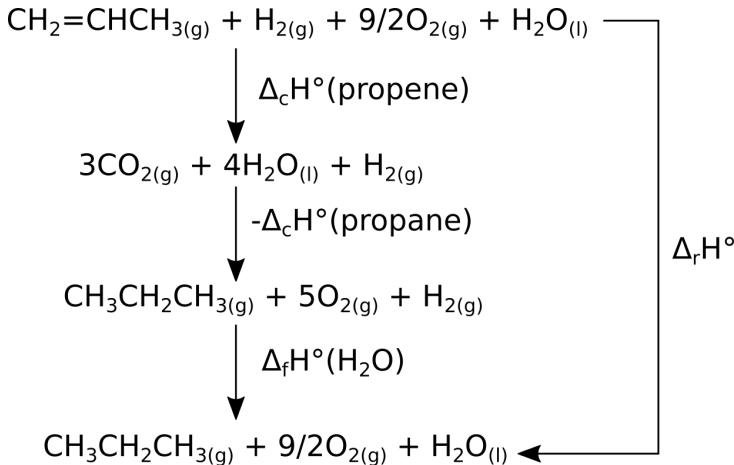


Figure 2.5: Diagram showing the application of Hess' law for the hydrogenation of propene. One can go from reactants to products via the path on the left or the path on the right, so the sum of the enthalpy changes in each path is equal.

that any standard reaction enthalpy can be calculated as a sum of standard formation enthalpies:

$$\Delta_r H^\circ = \sum_i \nu_i \Delta_f H^\circ(i) \quad (2.85)$$

where  $i$  runs over reactants and products and  $\nu_i$  are the stoichiometric coefficients. Similarly, if the reaction involves only organic molecules, we could consider the disaggregation of the reactants into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and the formation of the products back from these molecules. Therefore, in this case, we can also use the combustion enthalpies to calculate the standard reaction enthalpy:

$$\Delta_r H^\circ = \sum_i \nu_i \Delta_c H^\circ(i) \quad (2.86)$$

Lastly, we consider the effect of temperature on standard reaction enthalpies. As mentioned above, standard reaction enthalpies are usually tabulated at a certain temperature, typically at room temperature. If we want a standard reaction enthalpy at a different temperature we can use the fact that in a constant-pressure process:

$$dH = C_p dT \quad (2.87)$$

so the change in enthalpy between an initial ( $T_i$ ) and final ( $T_f$ ) temperatures is:

$$H(T_f) - H(T_i) = \int_{T_i}^{T_f} C_p dT \quad (2.88)$$

If we divide by the number of moles, we find that the same equation applies to the molar quantities:

$$H_m(T_f) - H_m(T_i) = \int_{T_i}^{T_f} C_{p,m} dT \quad (2.89)$$

For the standard reaction enthalpy (Eq. 2.76) we can apply the equation above to each species in the reaction:

$$\Delta_r H^\circ(T_f) = \sum_k \nu_k H_m^\circ(k, T_f) = \sum_k \nu_k \left[ H_m^\circ(k, T_i) + \int_{T_i}^{T_f} C_{p,m}^\circ(k) dT \right] \quad (2.90)$$

$$= \Delta_r H^\circ(T_i) + \int_{T_i}^{T_f} \Delta_r C_{p,m}^\circ dT \quad (2.91)$$

where we defined:

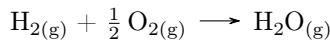
$$\Delta_r C_{p,m}^\circ = \sum_k \nu_k C_{p,m}^\circ(k) \quad (2.92)$$

This is known as **Kirchhoff's law**. Note that by taking the temperature derivative at constant pressure in Eq. 2.90 we also find that:

$$\Delta_r C_{p,m}^\circ = \left( \frac{\partial \Delta_r H^\circ}{\partial T} \right)_p \quad (2.93)$$

which is analogous of the heat-capacity definition (Eq. 2.63) for the standard reaction enthalpy.

**Example.** At 298 K, the  $\Delta_f H^\circ$  of water is  $-241.82 \text{ kJ/mol}$ , and the standard molar heat capacities ( $C_{p,m}^\circ$ ) of the species involved in the formation reaction:



are  $33.58 \text{ J/K/mol}$  ( $\text{H}_2\text{O}_{(\text{g})}$ ),  $28.84 \text{ J/K/mol}$  ( $\text{H}_{2(\text{g})}$ ), and  $29.37 \text{ J/K/mol}$  ( $\text{O}_{2(\text{g})}$ ). If we want to calculate the  $\Delta_f H^\circ$  at  $100^\circ\text{C}$ , we have:

$$\Delta_r C_{p,m}^\circ = C_{p,m}^\circ(\text{H}_2\text{O}) - C_{p,m}^\circ(\text{H}_2) - \frac{1}{2} C_{p,m}^\circ(\text{O}_2) = -9.945 \text{ J/K/mol}$$

Assuming the heat capacities do not change too much in this temperature range,

$$\begin{aligned} \Delta_r H^\circ(373.15 \text{ K}) &= \Delta_r H^\circ(298 \text{ K}) + \int_{T_i}^{T_f} \Delta_r C_{p,m}^\circ(k) dT \approx \Delta_r H^\circ(298 \text{ K}) + \Delta_r C_{p,m}^\circ(k) \times \Delta T \\ &= -241.82 \text{ kJ/mol} + (-9.945 \text{ J/K/mol}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times (373.15 \text{ K} - 298 \text{ K}) \\ &= -242.57 \text{ kJ/mol} \end{aligned}$$

In quantitative work, Kirchhoff's law is applied using empirical temperature relations for  $C_p$ , typically with a form similar to:

$$C_p = a + bT + \frac{c}{T^2} \quad (2.94)$$

## 2.9 Material Properties

### 2.9.1 Derivatives of the Internal Energy

The derivatives of the internal energy and the enthalpy are measurable experimentally and have physical meaning. Most of them are relevant in engineering and technological applications, and are known as **material properties**. Let us consider a closed system (constant  $n$ ) with only one component. The thermodynamic state is determined by two of the three variables  $T$ ,  $V$ , and  $p$ . Therefore, the dependence of  $U$  (and  $H$ ) on the state of the system can be written in three different ways:  $U(V, T)$ ,  $U(V, p)$ , and  $U(p, T)$ .

For now, consider  $V$  and  $T$  are the state variables. The differential of  $U$  is:

$$dU = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT \quad (2.95)$$

The temperature derivative is already known (Eq. 2.48):

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (2.96)$$

and the other derivative is known as the **internal pressure**:

$$\pi_T = \left( \frac{\partial U}{\partial V} \right)_T \quad (2.97)$$

We justified on microscopic grounds, and we will prove later, that in an ideal gas  $U$  is a function of  $T$  only so  $\pi_T = 0$  for an ideal gas. The internal pressure has units of pressure and, in a gas, it can be positive or negative depending on whether intermolecular attraction or repulsion forces dominate.

Using the relation in Eq. 2.36, or dividing Eq. 2.95 by  $dT$  at constant pressure, we can write another derivative of  $U$ :

$$\left( \frac{\partial U}{\partial T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p = C_V + \pi_T \left( \frac{\partial V}{\partial T} \right)_p \quad (2.98)$$

The temperature derivative of the volume on the right is related to the (**volumetric**) **thermal expansion coefficient** ( $\alpha$ ), or **thermal expansivity**, defined as:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad (2.99)$$

The units of  $\alpha$  in the SI are  $K^{-1}$ . The expansion coefficient is a very important quantity in engineering because it determines the expansion of materials when they are heated. Most substances expand with increasing temperature but some contract, a phenomenon known as negative thermal expansion. Some, like invar, a nickel-iron alloy used to construct precision instruments, have near zero thermal expansion. Characteristic values of the thermal expansion coefficient at room temperature are (in  $1 \times 10^{-6} K^{-1}$ ): 750 (ethanol), 207 (water), 36 (steel). The expansion coefficient for a ideal gas is much higher than for liquids and solids:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{pV} = \frac{1}{T} = 3.35 \times 10^{-3} K^{-1} \quad (2.100)$$

at room temperature, and the same can be said in general about real gases.

A quantity similar to the expansion coefficient is the **isothermal compressibility**, defined as:

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \quad (2.101)$$

The compressibility is a measure of the decrease in volume with an increase in pressure. It is always positive and has units of  $\text{Pa}^{-1}$  in the SI. Its inverse is the **isothermal bulk modulus**:

$$B_T = -V \left( \frac{\partial p}{\partial V} \right)_T \quad (2.102)$$

which has units of pressure. The bulk modulus determines the resistance of a material to compression, and is therefore also of great technological importance. For solids and liquids, the bulk modulus is high and their compressibilities are low. Bulk moduli for common materials are (in GPa): 0.82 (methanol), 2.2 (water), 160 (steel), 443 (diamond). The bulk modulus of gases is much lower than solids and liquids. For an ideal gas,

$$B_T = -V \left( \frac{\partial p}{\partial V} \right)_T = -V \left( \frac{-nRT}{V^2} \right) = p = 1 \times 10^{-4} \text{ GPa} \quad (2.103)$$

at 1 bar.

Going back to Eq. 2.98, we can now rewrite the derivative of the internal energy in terms of measurable material properties:

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V + \alpha\pi_T V \quad (2.104)$$

In the particular case of an ideal gas,  $\pi_T = 0$ , so

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V \quad (2.105)$$

and:

$$\begin{aligned} C_p - C_v &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial(U + nRT)}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V \\ &= \left(\frac{\partial U}{\partial T}\right)_p + nR - \left(\frac{\partial U}{\partial T}\right)_V = C_V + nR - C_V = nR \end{aligned} \quad (2.106)$$

For an ideal gas, the difference in the molar heat capacities is equal to  $R$ . As we shall see, this is a particularization for ideal gases of a more general result for  $C_p - C_V$ . Note that  $C_p > C_V$ , which makes sense because if the ideal gas is heated at constant pressure, some of the energy acquired as heat by the system is lost to exerting expansion work on the surroundings.

### 2.9.2 Derivatives of the Enthalpy

Now we consider the material properties obtained as derivatives of the enthalpy. As in the case of the internal energy, we can choose to describe the enthalpy in terms of two out of the three variables  $p$ ,  $V$ , and  $T$ . Choosing  $p$  and  $T$ , the enthalpy differential is:

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \quad (2.107)$$

where we already know that the derivative in the second term is the constant-pressure heat capacity (Eq. 2.63):

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad (2.108)$$

For the derivative in the first term, we use Eq. 2.38 to find:

$$\left(\frac{\partial H}{\partial p}\right)_T = - \left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H = -C_p \mu_{JT} \quad (2.109)$$

where we defined the **Joule-Thomson coefficient** ( $\mu_{JT}$ ) as:

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H \quad (2.110)$$

With this definition, the enthalpy differential is written as:

$$dH = -\mu_{JT} C_p dp + C_p dT \quad (2.111)$$

The Joule-Thomson coefficient is a measure of the change in temperature when a system, typically a gas, is expanded or compressed under isenthalpic (constant enthalpy) conditions. It has SI units of K/Pa, and it can be positive or negative, depending on the gas and the conditions. For instance, for N<sub>2</sub>,  $\mu_{JT} = 0.27$  K/atm and for He,  $\mu_{JT} = -0.062$  K/atm, under ambient conditions.

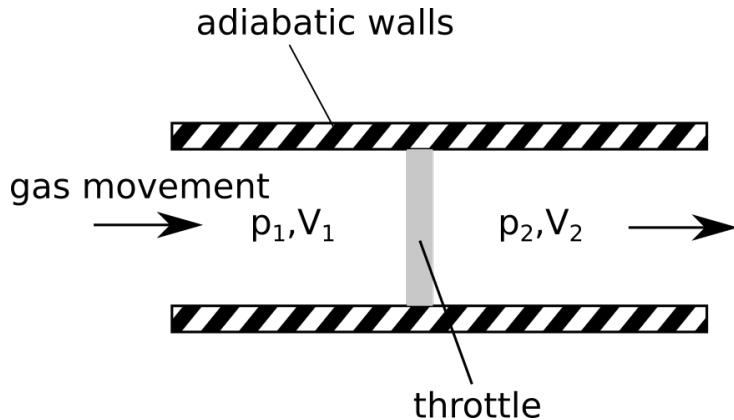


Figure 2.6: A gas throttle. The gas is moving from left to right at high pressure ( $p_1$ ) and encounters a throttle, which can be a constriction valve or a porous membrane that impedes the flow of the gas. After passing the throttle, the gas pressure drops to  $p_2$ .

The Joule-Thomson coefficient is a quantity of fundamental importance in the liquefaction of gases and in refrigeration using compression cycles. Isenthalpic conditions are prevalent in the “throttling” stage of a compression cycle, in which a gas is cooled (and possibly liquefied) by making it pass through a constriction, as shown schematically in Figure 2.6. The gas at high pressure ( $p_1$ ) is forced through a throttle, which could be a constriction in the pipe like a valve, a hole, or a thick porous membrane. We assume a certain volume of gas ( $V_1$ ) is forced into the throttle and compressed to a negligible volume compared to  $V_1$ . The energy gained by the gas in the form of work is:

$$w_1 = -p_1 \times (0 - V_1) = p_1 V_1 \quad (2.112)$$

When the gas clears the throttle, it expands to a volume  $V_2 > V_1$  and the gas after the throttle is at a pressure lower than the original value ( $p_2 < p_1$ ). The work exerted by the gas in the expansion is:

$$w_2 = -p_2 \times (V_2 - 0) = -p_2 V_2 \quad (2.113)$$

The work done in the whole process is:

$$w = w_1 + w_2 = p_1 V_1 - p_2 V_2 \quad (2.114)$$

If the walls of the pipe are adiabatic (they do not allow the transfer of heat with the surroundings), then:

$$\Delta U = U_2 - U_1 = w = p_1 V_1 - p_2 V_2 \quad (2.115)$$

Rearranging, we find:

$$H_2 = U_2 + p_2 V_2 = U_1 + p_1 V_1 = H_1 \quad (2.116)$$

so the throttling process is isenthalpic:

$$\Delta H = H_2 - H_1 = 0 \quad (2.117)$$

Most household refrigerators and freezers use a compression cycle in which the refrigerant fluid at high pressure, typically a hydrofluorocarbon, is forced through a throttle valve causing its temperature to drop under isenthalpic conditions. This is known as the **Joule-Thomson effect**.

Regarding the value of the Joule-Thomson coefficient,  $U$  depends only on temperature in an ideal gas, so the enthalpy of an ideal gas is:

$$H = U + pV = U + nRT \quad (2.118)$$

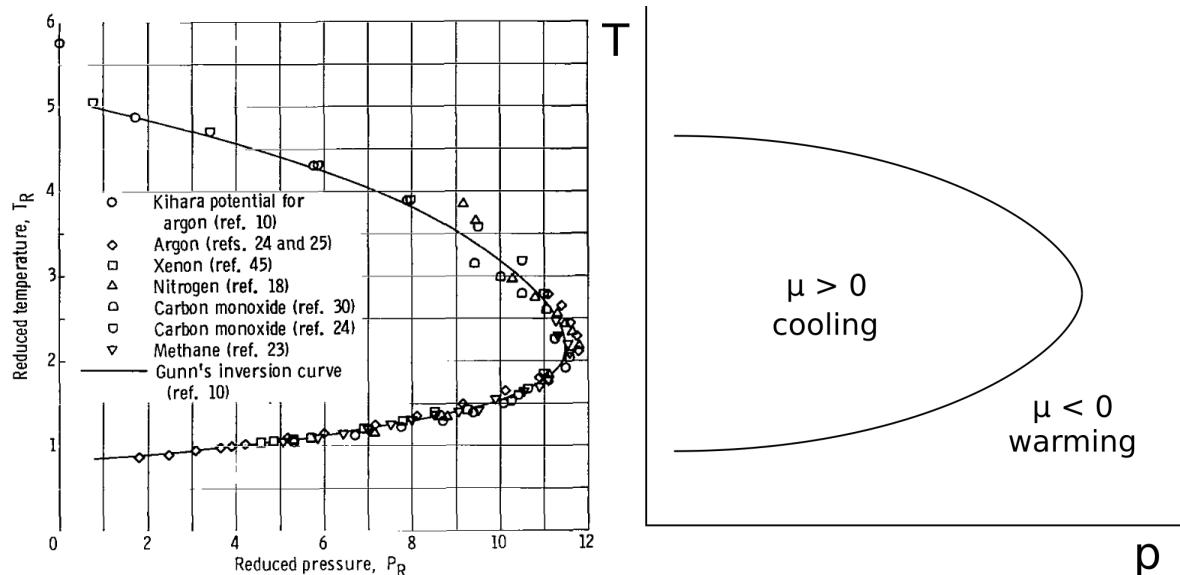


Figure 2.7: Left: Joule-Thomson inversion curves for several gases in terms of their reduced temperature and pressure. (From Robert C. Hendricks et al. “Joule-Thomson inversion curves and related coefficients for several simple fluids”, NASA technical note (1972), in the public domain.) Right: a schematic version of the Joule-Thomson inversion curve for a typical gas.

which is also a function of temperature only. Therefore, the temperature does not change in an isenthalpic process, and the Joule-Thomson coefficient of an ideal gas is zero:

$$\mu_{JT}(\text{ideal gas}) = \left( \frac{\partial T}{\partial p} \right)_H = 0 \quad (2.119)$$

Consequently, the value of  $\mu_{JT}$  in real gases depends on the strength and nature of the intermolecular interactions, which are assumed to be non-existent in an ideal gas.

For real gases  $\mu_{JT}$  is a function of temperature and pressure itself ( $\mu_{JT}(T, p)$ ) and it can be positive or negative depending on the conditions. The  $\mu_{JT}$  of real gases formed by small non-polar molecules depends on pressure and temperature as shown in Figure 2.7, where there is an “inversion curve” corresponding to the points where  $\mu_{JT} = 0$ . The top and the bottom of the curve are sometimes referred to as the “upper inversion temperature” and “lower inversion temperature”. The temperatures and pressures to the left of the inversion curve correspond to  $\mu_{JT} > 0$ , so the gas cools on isenthalpic expansion. To the right of the curve,  $\mu_{JT} < 0$  and isenthalpic expansion warms the gas. As we can see from the figure, the principle of corresponding states applies here as well, and  $\mu_{JT}$  in terms of reduced temperature and pressure is approximately the same for real gases of small non-polar molecules.

The sign of  $\mu_{JT}$  can be understood in terms of the dominance of repulsive or attractive interactions in the gas. The temperature of a gas is related to the average kinetic energy of its component molecules. If attractive interactions are dominant ( $Z < 1$ ), then it costs kinetic energy from the molecules to break away from each other and expand the gas, and therefore the gas cools on expansion ( $\mu_{JT} > 0$ ). If repulsive interactions are dominant ( $Z > 1$ ) then moving the molecules apart from each other increases their kinetic energy and the gas warms on expansion ( $\mu_{JT} < 0$ ).

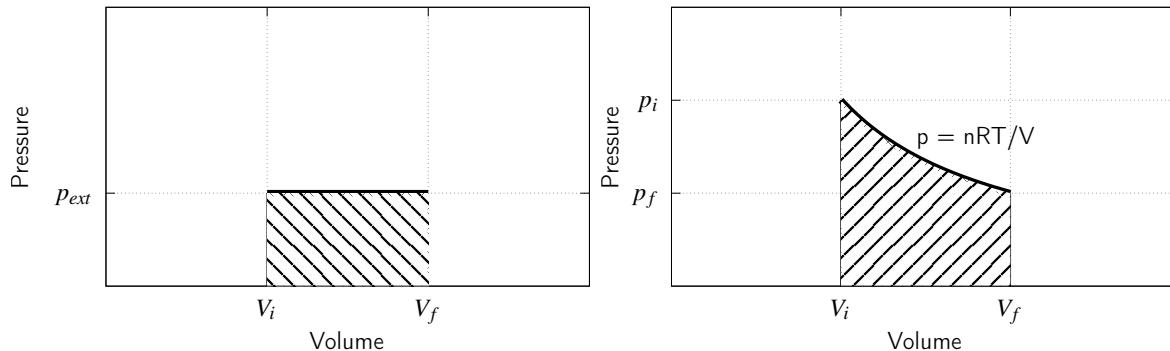


Figure 2.8: The area under the curves is the amount of work exerted by the gas on the surroundings. Left: against a constant external pressure. Right: reversible isothermal expansion.

## 2.10 Thermodynamic Processes in Gases

### 2.10.1 Expansion Against Constant Pressure

Finally, a few simple calculations of thermodynamic properties are shown in this section involving gases, to demonstrate the use of the results in this chapter. In the rest of this section, we consider a closed system composed of a pure gas (sometimes an ideal gas) and only p–V work.

Consider a process in which a gas expands against a constant external pressure  $p_{\text{ext}}$ . For instance, the expansion work against the atmosphere of the gases evolved during a reaction. The work in this process is (Eq. 2.44):

$$w = - \int_{V_i}^{V_f} p_{\text{ext}} dV = -p_{\text{ext}} \int_{V_i}^{V_f} dV = -p_{\text{ext}}(V_f - V_i) = -p_{\text{ext}}\Delta V \quad (2.120)$$

where  $\Delta V = V_f - V_i$  is the change in gas volume. This work is the area under the  $p(V)$  curve, shown on the left in Figure 2.8. A particular case of expansion against a constant external pressure is **free expansion**, where a gas expands in vacuum and  $p_{\text{ext}} = 0$ . In this case,  $w = 0$ , so a gas does no work by expanding in vacuum.

### 2.10.2 Reversible Expansion

A **reversible process** is a process that, under an infinitesimal change in conditions, can be made to go back from the final to the initial state in a way that leaves both the system and the surroundings (i.e. the universe) unchanged.

Consider the example of a gas being compressed by a piston, as in Figure 2.2. If the compression is sudden, the movement of the piston creates vortices in the gas, which destroys equilibrium because there are unbalanced forces in the system. These vortices also dissipate some of the work as friction, which means that more work is necessary for the compression to take place than if they had not been present. As we shall see in the next chapter, this results in an increase in the entropy of the universe (to be defined later), and therefore this process is not reversible. If the same compression happens slowly, and the pressure of the gas is approximately equal to the applied external pressure, the friction from those vortices is smaller. In the limit of infinitely slow compression, the vortices disappear and the gas pressure is at all times equal to the external pressure, meaning that the system is always in equilibrium. In this limit, the process is reversible because an infinitesimal increase or decrease in the external pressure can make the system either compress or expand without destroying equilibrium.

In general, a **reversible process happens through an infinite sequence of equilibrium states**. Since the system has to be in thermodynamic equilibrium at all times, a reversible

process is **quasistatic**, meaning that it is infinitely slow. A reversible process is therefore only an idealization that can only be approximately realized in the limit of infinitely slow processes. A process that is not reversible is known as **irreversible**.

Reversible processes are very useful for the calculation of thermodynamic properties. Because a system undergoing a reversible process is always at equilibrium, its thermodynamic state is always defined (see Section 1.2.3), which means we can consider how its properties (pressure, temperature, internal energy,...) evolve as it progresses from the initial to the final state. If, for instance, a system undergoing a reversible process is in contact with its surroundings via a movable wall, then  $p = p_{\text{ext}}$  because thermodynamic equilibrium implies mechanical equilibrium. Therefore, the work in a reversible expansion is given by:

$$dw_{\text{rev}} = -p_{\text{ext}}dV = -pdV \quad (2.121)$$

Reversible processes are great importance in the rest of the course because the fact that all thermodynamic properties are defined throughout the process simplifies the calculation of changes in state functions. Given an initial and final state, we assume that the transformation between them happens reversibly and then calculate the change in the state function of interest. Because changes in state functions depend only on the initial and the final states and not on the process, the state function change calculated using a reversible process is valid for any process between those specific initial and final states, regardless of whether the process is reversible or irreversible.

### 2.10.3 Isothermal Reversible Expansion of an Ideal Gas

We now consider the expansion of an ideal gas at constant temperature (an **isothermal process**) that is carried out reversibly. Because the process is reversible and the gas is ideal,

$$p_{\text{ext}} = p = \frac{nRT}{V} \quad (2.122)$$

From this, we can calculate the work as:

$$w = - \int_{V_i}^{V_f} pdV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \ln \left( \frac{V_f}{V_i} \right) \quad (2.123)$$

Note that if the process is a compression,  $V_f < V_i$  and  $w > 0$  and if the process is an expansion,  $V_f > V_i$  and  $w < 0$ . This is consistent with our sign convention that energy gained by the system is positive and energy lost by the system is negative. We justified the internal energy of an ideal gas depends only on temperature, so we can anticipate that in an isothermal expansion  $\Delta U = 0$  and the work exerted equals the heat absorbed,  $q = -w$ .

Figure 2.8 compares the expansion of a gas against a constant pressure with an isothermal reversible expansion. The amount of work performed by the system on its surroundings, given by the area under the curve, depends on the path chosen between the initial and final states because work and heat are not state functions. The work performed by the system in a reversible expansion is greater than when the gas expands (irreversibly) against a constant external pressure, when  $p > p_{\text{ext}}$  except at the final state. Because the system pushes harder than necessary, some energy is lost to friction and the amount of work in an expansion against constant pressure is not as high as it would be had the expansion been reversible. In fact, the work exerted in a reversible expansion is greater than in any other expansion since the reversible expansion  $p(V)$  curve in Figure 2.8 (right) is the maximum possible external pressure against which the system can expand. Next chapter, we will show that this is a general result based on the second law of thermodynamics.

### 2.10.4 Reversible Adiabatic Expansion of an Ideal Gas

Lastly, we consider an ideal gas undergoing adiabatic expansion. An **adiabatic process** is one in which no heat is exchanged between the system and its surroundings ( $q = 0$ ). Let us first calculate the change in internal energy ( $\Delta U$ ) between the initial conditions (volume  $V_i$  and temperature  $T_i$ ) and the final conditions (volume  $V_f$  and temperature  $T_f$ ). Because this is an ideal gas,  $U$  depends on temperature only and therefore:

$$dU = C_V dT \quad (2.124)$$

Because the process is reversible, we have  $p = p_{\text{ext}}$  at every intermediate step and  $dw = -pdV$ , so:

$$dw = -pdV = -\frac{nRT}{V} dV \quad (2.125)$$

By the first law and because the process is adiabatic ( $dq = 0$ ):

$$dU = dq + dw = dw \quad (2.126)$$

Combining the equations above, we have:

$$C_V dT = -\frac{nRT}{V} dV \quad (2.127)$$

This is a separable differential equation, which we can rearrange to give:

$$\frac{C_V}{T} dT = -\frac{nR}{V} dV \quad (2.128)$$

Integrating between the initial and the final conditions:

$$\int_{T_i}^{T_f} \frac{C_V}{T} dT = \int_{V_i}^{V_f} -\frac{nR}{V} dV \quad (2.129)$$

Assuming  $C_V$  is approximately constant in the temperature range, we can integrate both sides of the equation to find:

$$C_V \ln \left( \frac{T_f}{T_i} \right) = -nR \ln \left( \frac{V_f}{V_i} \right) \quad (2.130)$$

$$\ln \left( \frac{T_f}{T_i} \right)^c = \ln \left( \frac{V_i}{V_f} \right) \quad (2.131)$$

where:

$$c = \frac{C_v}{nR} = \frac{C_{v,m}}{R} \quad (2.132)$$

Eliminating the logarithms we arrive at:

$$\left( \frac{T_f}{T_i} \right)^c = \left( \frac{V_i}{V_f} \right) \quad (2.133)$$

$$T_f^c V_f = T_i^c V_i \quad (2.134)$$

Therefore, in the adiabatic reversible expansion of an ideal gas,  $VT^c$  is constant.

Using the ideal gas law, the relation between pressure and volume can be derived as well. From the last equation:

$$\frac{V_i}{V_f} = \left( \frac{T_f}{T_i} \right)^c = \left( \frac{\frac{p_f V_f}{nR}}{\frac{p_i V_i}{nR}} \right)^c = \left( \frac{p_f V_f}{p_i V_i} \right)^c \quad (2.135)$$

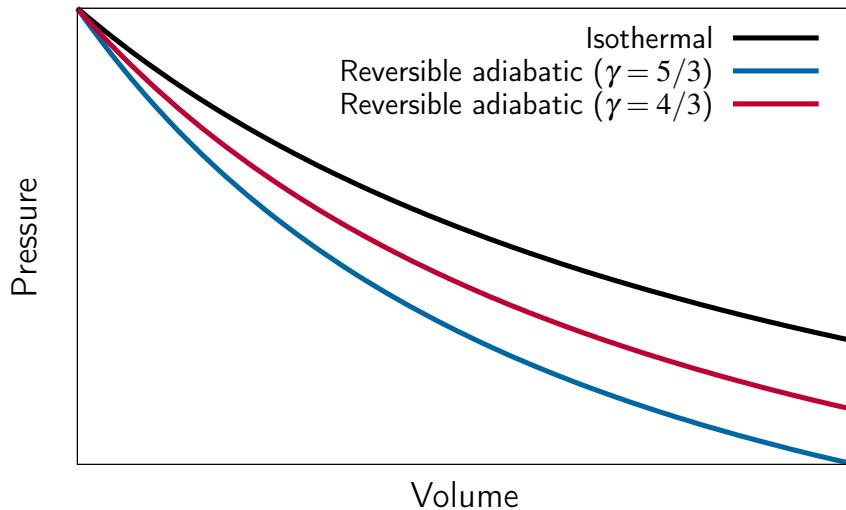


Figure 2.9: Pressure-volume curves for the isothermal expansion (isotherms) and adiabatic reversible expansion (adiabats) of an ideal gas. The two adiabats correspond to a monoatomic ( $\gamma = 5/3$ ) and a non-linear polyatomic ( $\gamma = 4/3$ ) gas.

Rearranging, we have:

$$p_i^c V_i^{c+1} = p_f^c V_f^{c+1} \quad (2.136)$$

$$p_i V_i^\gamma = p_f V_f^\gamma \quad (2.137)$$

$$(2.138)$$

where:

$$\gamma = 1 + \frac{1}{c} = 1 + \frac{nR}{C_V} = \frac{C_V + nR}{C_V} = \frac{C_p}{C_v} \quad (2.139)$$

since  $C_p = C_V + nR$  for an ideal gas (Eq. 2.106). Therefore, for the adiabatic reversible expansion of an ideal gas,  $pV^\gamma$  is constant.

For a monoatomic ideal gas (Eq. 2.13),  $C_{v,m} = 3/2R$  and  $\gamma = 5/3$ . For a small-molecule non-linear polyatomic ideal gas, it can be shown using statistical thermodynamics that  $C_{v,m} \approx 3R$  and  $\gamma \approx 4/3$ . Figure 2.9 compares the pressure-volume curves for these reversible adiabatic expansions (these curves are known as **adiabats**) against the isothermal expansion  $p(V) \propto 1/V$  curves of an ideal gas (its **isotherms**). In an isothermal expansion, heat flows into the system as the gas expands in order to maintain the temperature constant, and therefore the pressure does not fall so steeply. In an adiabatic expansion, the gas cools as it expands and the pressure drops faster than in the isothermal case.

## Chapter 3

# The Second Law of Thermodynamics

### 3.1 Heat Engines and the Second Law of Thermodynamics

The first law is a restatement of the conservation of energy law for thermodynamic systems. Experience shows that not all processes for which the first law holds are equally likely. For instance, if you drop a rubber ball from a height, it falls and eventually comes to a stop as its kinetic energy dissipates as heat due to friction with air and with the ground. We know intuitively that the opposite process, a ball at rest on the ground that gathers energy from its surroundings and leaps upwards, is not possible. The second law of thermodynamics states that some processes, like the ball falling from a height, are spontaneous while others are not. In addition, the second law allows us to define a new state function called the entropy to quantify the spontaneity of a physical or chemical transformation. A given process, like a chemical reaction, is spontaneous if it is thermodynamically allowed to occur. However, this does not mean that the reaction in question will occur because it could be so slow that, effectively, it does not take place. An example of this is the conversion from diamond to graphite, graphite being the thermodynamically stable form of carbon at ambient conditions.

A **cyclic process** is a process in which the initial and the final state of the system are the same. Because the internal energy and the enthalpy are state functions, we have that for a cyclic process:

$$\Delta U = \Delta H = 0 \quad (3.1)$$

And using the first law (Eq. 2.7):

$$q = -w \quad (3.2)$$

Therefore, for a cyclic process, the amount of heat exchanged with the environment equals minus the amount of work exerted. A cyclic process either absorbs heat from the environment and performs work or the surroundings exert work on the system and it releases heat. We already know from experience that a cyclic process in which the surroundings exert work and the system releases the same amount of energy as heat is feasible and easy to carry out. For instance, in the Joule experiment a paddle wheel is stirred in a vat of water and the mechanical energy applied as work to the paddle is transferred as heat into the water. The water is then allowed to cool down to room temperature by releasing heat to the surroundings, completing a cyclic process in which we transformed work into heat. Another example is a household electric heater that draws work from the surroundings in the form of electrical energy (work) to raise the temperature of a room by emitting heat to the surroundings.

We are normally interested in the opposite exchange, namely whether and to what extent it is possible to draw heat from the surroundings and convert it into work. For instance, we want to convert heat from the sun into usable electrical energy that can be used to exert useful work. A

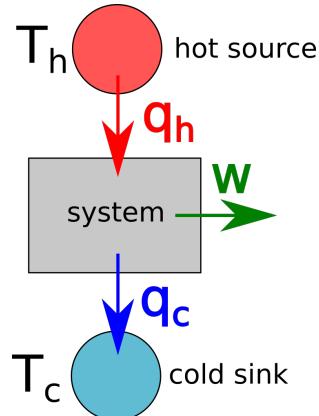


Figure 3.1: A heat engine. The system undergoes a cyclic process whose only effects are: draw  $q_h > 0$  energy from a hot source (with temperature  $T_h$ ) as heat, transfer  $q_c < 0$  to the cold sink (with temperature  $T_c < T_h$ ) also as heat, and exert work  $w < 0$  on the surroundings.

**heat engine** is a system that undergoes a cyclic process that converts heat into work. A schematic representation of a heat engine is shown in Figure 3.1. A heat engine is connected to a “hot source”, which we assume to be at temperature  $T_h$ , from where it draws an amount of energy  $q_h$  as heat. Since the process in a heat engine is cyclic,  $\Delta U = 0$ , and the first law states that the energy entering the system equals the energy released from it. The energy escaping the system can do so in two ways: either as heat transferred to a “cold sink” ( $q_c$ ) at temperature  $T_c < T_h$ , or as work exerted on the surroundings  $w$ . The heat and work are related by:

$$\Delta U = q + w = q_c + q_h + w = 0 \quad (3.3)$$

Note that, with our sign convention, energy gained by the system is positive and energy lost by the system is negative, so  $q_h > 0$ ,  $q_c < 0$ , and  $w < 0$ .

There are many examples of engineering processes of industrial relevance that can be represented by heat engines. For instance, in a steam engine or in a thermal power plant, the system (the working fluid, usually water) draws heat from the boiler (the hot source) and transforms it into work by evaporating and pushing a piston or a turbine. The low-pressure vapor is released to the atmosphere (the cold sink) whereby it is cooled down and liquefied and returns to the system as liquid water.

Heat engines can also be made to work in reverse. In this case, the arrows in Figure 3.1 are reversed and heat is absorbed from the cold reservoir ( $q_c > 0$ ) and work is exerted by the surroundings on the system ( $w > 0$ ). The system then releases an equivalent amount of heat ( $q_h < 0$ ) to the hot reservoir. The three quantities are also related by Eq. 3.3. This is what is known as a **heat pump**. A practical example of such a machine is a refrigerator, where the refrigerant fluid transfers heat from the inside of the fridge to the outside, while work is exerted on the fluid by the compressor.

The **second law of thermodynamics** states that **it is impossible to have a cyclic process whose only effect is to absorb heat from a source and perform the same amount of work on the surroundings**. This is the **Kelvin statement** of the second law. In a heat engine (Figure 3.1) the second law states that it is necessary to transfer part of the heat absorbed from the hot source to the cold sink, that is,  $q_c$  cannot be zero. An alternative is the **Clausius statement** of the second law, which says that **it is impossible to have a cyclic process whose only effect is to absorb heat from a cold reservoir and release an equal amount of heat to a hot reservoir**. In Figure 3.1, such a process would have the directions of  $q_c$  and  $q_h$  reversed and  $w = 0$ .

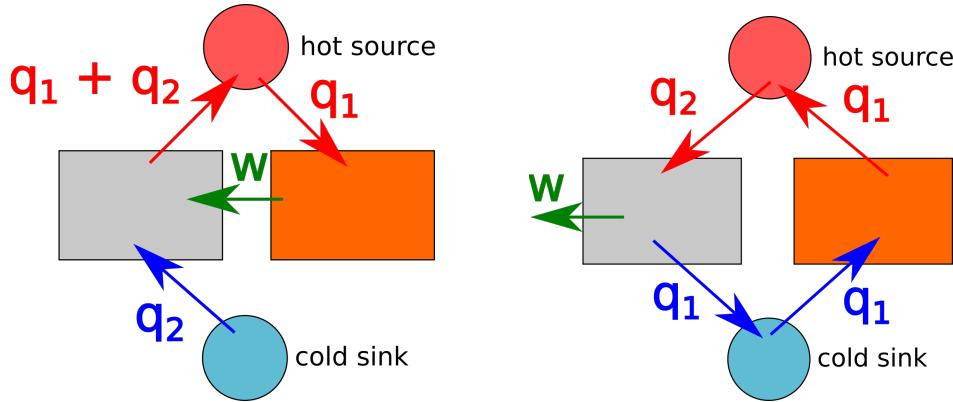


Figure 3.2: Heat engines that illustrate violations of the second law. Left: the orange system violates the Kelvin statement and the combination of the two heat engines violates the Clausius statement. Right: the orange system violates the Clausius statement and the combination of the two heat engines violates the Kelvin statement.

The equivalence of the Clausius (C) and Kelvin (K) statements of the second law can be proven by contradiction. To show that the Clausius statement implies the Kelvin statement ( $C \Rightarrow K$ ), we assume that K is violated and show that this implies a violation of C. If K is violated, then a heat engine exists whose only effect is to convert heat into work. Figure 3.2 (left) shows a schematic representation of this heat engine. The orange engine violates K and, since the net effect of the combined engine is to draw  $q_2$  from the cold reservoir and deposit  $q_2$  into the hot reservoir, it violates C. Conversely, if C is violated, a heat engine exists whose only effect is a heat flow from the cold to the hot reservoir. Figure 3.2 (right) shows that we can combine this heat engine, shown in orange, with another regular heat engine to give a combined engine whose net effect is to draw  $q_2 > q_1$  heat from the hot source and transform it into work, thus violating the Kelvin statement.

## 3.2 Carnot's Principle

We define the **efficiency** ( $e$ ) of a heat engine as the fraction of the input energy that is converted into work. The second law as stated above says that the efficiency of a heat engine can never be 100%. As we now prove, the theoretical efficiency limit of a heat engine is lower, and depends only on the temperatures of the hot and the cold reservoirs. Using the notation in Figure 3.1, the efficiency of a heat engine is calculated as:

$$e = \frac{-w}{q_h} = \frac{|w|}{q_h} = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h} \quad (3.4)$$

Note that  $w < 0$ ,  $q_c < 0$ , and  $|q_c| < |q_h|$ , so  $e$  is a positive quantity between 0 and 1. In addition, the second law ensures that there is some heat transferred to the cold sink, so  $q_c$  cannot be zero, which means that the efficiency can never be 100% ( $e < 1$ ).

The heat engine in Figure 3.1 operates between the temperatures of the hot and cold reservoirs,  $T_h$  and  $T_c$ , respectively. The **Carnot principle** states that **any heat engine has efficiency lower than a reversible heat engine operating between the same two temperatures**:

$$e \leq e_{\text{rev}} \quad (3.5)$$

The Carnot principle, which is a consequence of the second law, implies that the maximum amount of work that can be performed by a heat engine is a fraction of the energy drawn from the hot reservoir, and this fraction is given by the efficiency of a reversible heat engine.

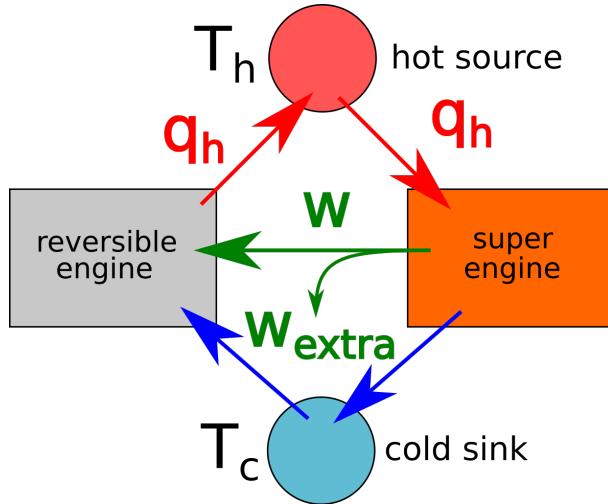


Figure 3.3: Diagram for proving Carnot's principle. The heat engine on the left is reversible and acts as a heat pump. The heat engine on the right has efficiency higher than the reversible engine. Both engines work between the temperature of the hot source ( $T_h$ ) and the temperature of the cold sink ( $T_c$ ).

To prove Carnot's principle, we first assume the existence of a super-engine that violates the principle and show that this violates the second law. The efficiency of the super-engine is higher than that of a reversible engine ( $e_{rev} < e_{super}$ ). Consider a super-engine that draws  $q_h$  heat from the hot source and exerts  $w_{super} = -e_{super}q_h$  work, as shown in Figure 3.3. We combine this super-engine with a reversible heat engine that draws  $q_h$  from the hot source and exerts  $w_{rev} = -e_{rev}q_h$  on the surroundings. Because this engine is reversible, we can reverse its cyclic process and make it act as a heat pump with the same heat and work being transferred to and from the surroundings, but with opposite signs. This reversible heat pump is combined with the super-engine as shown in Figure 3.3. The amount of work required by the reversible heat engine is less than the work provided by the super-engine because:

$$|w_{rev}| = e_{rev}|q_h| < e_{super}|q_h| = |w_{super}| \quad (3.6)$$

Therefore, there is an extra amount of work:

$$|w_{extra}| = |w_{super}| - |w_{rev}| \quad (3.7)$$

that is left-over from the operation of the combined engine in Figure 3.3. Since the super-engine draws the same energy from the hot source as the energy deposited by the reversible engine, the hot source transfers no net energy to the engine. Applying the first law, this means that the net effect of the combined heat engine in the figure is to draw heat from the cold sink and convert it into work, which violates the Kelvin statement of the second law.

A consequence of the Carnot principle is that the efficiency of any reversible heat engine operating between the same two temperatures is  $e_{rev}$ , regardless of the substance used in its construction. If we have two reversible engines (A and B) that are constructed differently, Carnot's principle (Eq. 3.5) can be applied by considering either of them as the reversible engine on the left of Figure 3.3, so  $e_A \leq e_B$  and  $e_B \leq e_A$  and therefore  $e_A = e_B$ .

Another corollary of the Carnot principle is that the efficiency of a reversible engine depends only on the two working temperatures  $T_c$  and  $T_h$ . We now find this dependence. Since any reversible engine has the same efficiency, we can construct a reversible engine using a substance whose behavior is known, such as an ideal gas doing p-V work, and the result will be valid for all reversible engines regardless of their construction. This system is shown Figure 3.4 and is known as the **Carnot cycle**. The Carnot cycle consists of four steps:

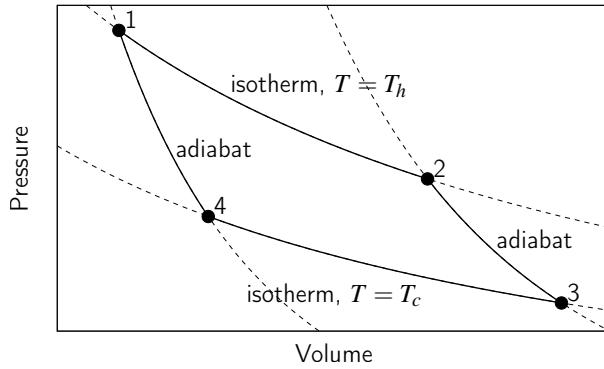


Figure 3.4: A schematic diagram of a Carnot cycle. The  $1 \rightarrow 2$  and  $3 \rightarrow 4$  paths are reversible isothermal ( $p = nRT/V$ ) and the  $2 \rightarrow 3$  and  $4 \rightarrow 1$  are reversible adiabatic ( $pV^\gamma = \text{constant}$ ).

1. Reversible isothermal expansion at temperature  $T_h$  ( $1 \rightarrow 2$ ).
2. Reversible adiabatic expansion from  $T_h$  to  $T_c$  ( $2 \rightarrow 3$ ).
3. Reversible isothermal compression at temperature  $T_c$  ( $3 \rightarrow 4$ ).
4. Reversible adiabatic compression from  $T_c$  to  $T_h$  ( $4 \rightarrow 1$ ).

Since the whole process is reversible ( $p = p_{\text{ext}}$ ), we can write the internal energy as:

$$dU = dq + dw = dq - pdV \quad (3.8)$$

and because this is an ideal gas,  $U$  depends only on temperature, so  $dU = C_V dT$  and:

$$C_V dT = dq - pdV = dq - \frac{nRT}{V} dV \quad (3.9)$$

Now we do the path integral of these differentials over the whole cycle. In order to simplify the calculation, we divide the whole equation by the temperature first:

$$\frac{C_V}{T} dT = \frac{dq}{T} - \frac{nR}{V} dV \quad (3.10)$$

Integrating over the Carnot cycle gives:

$$\oint \frac{C_V}{T} dT = \oint \frac{dq}{T} - nR \oint \frac{dV}{V} \quad (3.11)$$

The path integral on the left hand side can be written as the path integral over the four paths that compose the cycle (Figure 3.4):

$$\oint \frac{C_V}{T} dT = \int_1^2 \frac{C_V}{T} dT + \int_2^3 \frac{C_V}{T} dT + \int_3^4 \frac{C_V}{T} dT + \int_4^1 \frac{C_V}{T} dT \quad (3.12)$$

The system is an ideal gas, so  $U$  depends on  $T$  only and, since  $C_V$  is its temperature derivative,  $C_V$  depends on  $T$  only as well. Therefore, these four path integrals reduce to one-dimensional integrals between the initial and the final temperatures of each step:

$$\oint \frac{C_V}{T} dT = \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{T_2}^{T_3} \frac{C_V}{T} dT + \int_{T_3}^{T_4} \frac{C_V}{T} dT + \int_{T_4}^{T_1} \frac{C_V}{T} dT \quad (3.13)$$

Using the properties of integrals:

$$\int_a^b f(x) dx = - \int_b^a f(x) dx \quad (3.14)$$

$$\int_a^b f(x) dx + \int_b^c f(x) dx = \int_a^c f(x) dx \quad (3.15)$$

the right hand side of Eq. 3.12 cancels out to find:

$$\oint \frac{C_V}{T} dT = 0 \quad (3.16)$$

Likewise, the integrand of the second term on the right hand side of Eq. 3.11 is the exact differential of the state function  $\ln V$ , so:

$$nR \oint \frac{dV}{V} = nR \oint d\ln V = 0 \quad (3.17)$$

Putting both results together, we find:

$$\oint \frac{dq}{T} = 0 = \int_1^2 \frac{dq}{T} + \int_2^3 \frac{dq}{T} + \int_3^4 \frac{dq}{T} + \int_4^1 \frac{dq}{T} \quad (3.18)$$

The paths  $2 \rightarrow 3$  and  $4 \rightarrow 1$  correspond to adiabatic transformations, so  $dq = 0$ . The other two are isothermal, and the temperature comes out of the integral. Path  $3 \rightarrow 4$  corresponds to the system at temperature  $T_c$  and the heat exchanged with the surroundings (cold sink) is  $q_c$ . Path  $1 \rightarrow 2$  corresponds to the system at temperature  $T_h$  and the heat exchanged with the surroundings (hot source) is  $q_h$ . Therefore:

$$\frac{q_h}{T_h} + \frac{q_c}{T_c} = 0 \quad (3.19)$$

$$\frac{q_c}{q_h} = -\frac{T_c}{T_h} \quad (3.20)$$

so the efficiency of the Carnot cycle is (Eq. 3.4):

$$e_{\text{rev}} = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} = \frac{T_h - T_c}{T_h} \quad (3.21)$$

and, since all reversible heat engines have the same efficiency, this result is valid for any reversible heat engine regardless of its nature. (In fact, the efficiency of a reversible heat engine can be used to define a temperature scale that does not depend on any substance, identical to the thermodynamic temperature scale we are already using.)

The maximum efficiency of any heat engine working between temperatures  $T_c$  and  $T_h$  is given by Eq. 3.21, and this result applies to any engine. For instance, power plants that operate on steam (coal, natural gas) have boiler temperatures of about  $550^\circ\text{C}$ . The condenser (for instance, a cooling tower) may be at  $40^\circ\text{C}$ . The maximum efficiency of a heat engine between those two temperatures is:

$$e = \frac{823.15\text{ K} - 313.15\text{ K}}{823.15\text{ K}} = 0.62 \quad (3.22)$$

At most a fraction of 62% of the heat generated by the combustion of coal or gas ends up converted into electrical work. The existence of friction in the various components as well as energy loss to the surroundings causes irreversible behavior in the heat engine, which makes the actual efficiency lower than the theoretical value, about 40%. The efficiency in the generation of electricity can be increased substantially by using the exhaust steam to power additional heat engines (the so-called combined cycle power plants), although it can never go above the Carnot limit.

### 3.3 Entropy

#### 3.3.1 Definition and Properties

Equation 3.18 shows the differential  $\frac{dq}{T}$  is zero over any closed Carnot cycle. In fact, this result can be generalized to any reversible cyclic process, as shown in Figure 3.5. Consider the

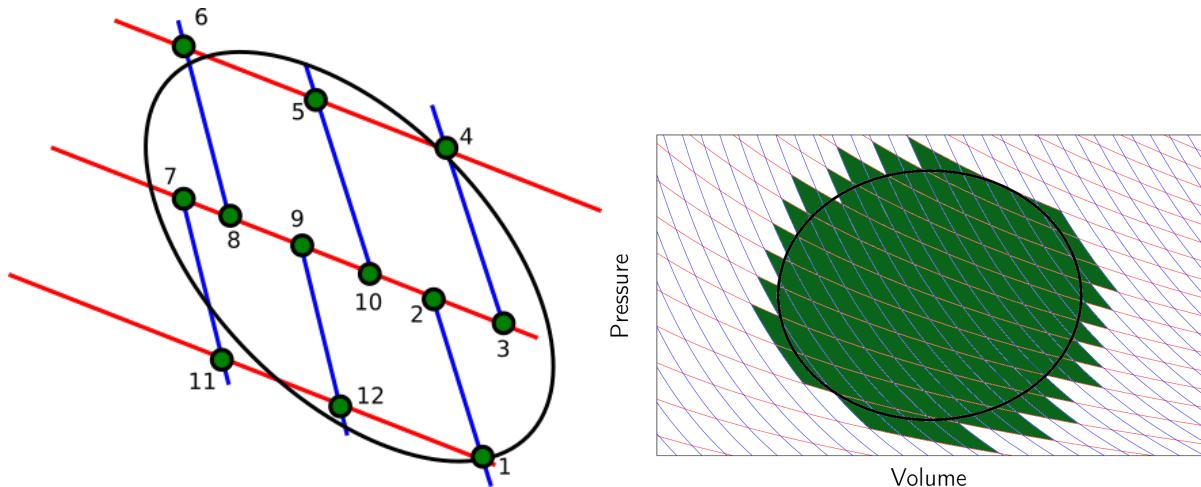


Figure 3.5: Left: an arbitrary reversible cyclic process ( $1 \rightarrow 1$ , black curve) approximated by four Carnot cycles. Right: Another reversible cyclic process approximated by many small Carnot cycles. Red lines are isotherms and blue lines are adiabats. The black cycle can be approximated as the sum of all the Carnot cycles in green. If we consider even more isotherms and adiabats, the green region converges to the cycle in black.

reversible cycle on the left of the figure, in which the initial and the final state are the point 1. This cycle can be approximated by the combination of four Carnot cycles, determined by the shown isotherms (red) and adiabats (blue). The process following the Carnot cycles that approximates the black curve is:  $1 \rightarrow 2 \rightarrow 10 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 10 \rightarrow 5 \rightarrow 6 \rightarrow 8 \rightarrow 10 \rightarrow 7 \rightarrow 11 \rightarrow 12 \rightarrow 9 \rightarrow 12 \rightarrow 1$ . Note that, if you follow this path, every interior segment is traversed twice in opposite directions. Because the process is reversible, the heat and work from these interior segments cancel out and the resulting heat and work from the cycle comes only from the contributions of the outer segments. If we consider even more isotherms and adiabats and more numerous but smaller Carnot cycles, we can approximate the reversible process with as much accuracy as we want. For instance, Figure 3.5 (right) shows the same reversible cyclic process approximated by the combination of Carnot cycles shaded in green. If we consider infinitely many isotherms and adiabats, the green region can be made to coincide with the interior of the cycle. Therefore, we can represent this cycle, or any other reversible cycle, by a combination of Carnot cycle steps and consequently:

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \quad (3.23)$$

for any arbitrary reversible cycle, where we used the label “rev” to emphasize that the cyclic process is reversible. Since this equation is valid for any closed cycle, by the result in Section 2.3.2, a state function exists whose exact differential is  $dq_{\text{rev}}/T$ . We call this state function the **entropy** ( $S$ ):

$$dS = \frac{dq_{\text{rev}}}{T} \quad (3.24)$$

To calculate the change in entropy between an initial state  $i$  and a final state  $f$ , we consider a reversible process between those two states, and calculate the corresponding path integral:

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} \quad (3.25)$$

The entropy difference calculated in this way is correct even if the process leading from the initial to the final state is irreversible, because  $S$  is a state function and therefore  $\Delta S$  depends only on the initial and the final states, and not on the path followed by the system.

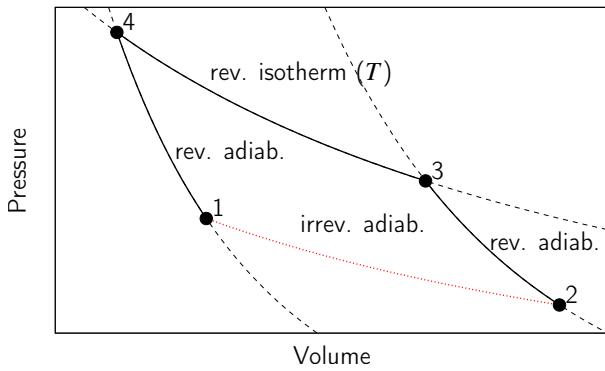


Figure 3.6: The red path is an irreversible adiabatic transformation between states 1 and 2. This transformation occurs via non-equilibrium states of the system, so the path shown in the figure is only for guidance since  $V$  and  $p$  may not be defined except at 1 and 2. The same transformation can be done reversibly using a combination of reversible adiabatic and isothermal paths (in black).

The entropy has units of energy divided by temperature, J/K in the SI although cal/K are also used. The entropy is extensive because the reversible heat transferred depends on the size of the system. Same as for the other extensive quantities, we can define a **molar entropy** as:

$$S_m = \frac{S}{n} \quad (3.26)$$

with units of J/K/mol or cal/K/mol, which is itself intensive. In addition, we can also define a **standard entropy** ( $S^\circ$ ) as the entropy of a substance in its standard state, and the **standard molar entropy** ( $S_m^\circ$ ) as the standard entropy divided by the amount of substance. Like temperature, entropy is a statistical property—only macroscopic systems have entropy.

To understand the physical meaning of the entropy, consider a reversible transformation in a closed system. The heat absorbed by the system is the same as the heat released by the surroundings but with opposite sign  $dq_{\text{syst}} = -dq_{\text{surr}}$  and, since the transformation is reversible, system and surroundings are in equilibrium at all times, so  $T_{\text{syst}} = T_{\text{surr}}$ . Therefore the change of entropy of the universe brought about by the reversible transformation is:

$$dS_{\text{univ}} = dS_{\text{syst}} + dS_{\text{surr}} = \frac{dq_{\text{syst}}}{T_{\text{syst}}} + \frac{dq_{\text{surr}}}{T_{\text{surr}}} = \frac{dq_{\text{syst}}}{T_{\text{syst}}} - \frac{dq_{\text{syst}}}{T_{\text{syst}}} = 0 \quad (3.27)$$

Consequently, the entropy of the universe does not change when a reversible process takes place:

$$\Delta S_{\text{univ}} = 0 \text{ (reversible process)} \quad (3.28)$$

Now let us consider an adiabatic irreversible process occurring in a closed system, such as the one shown in red in Figure 3.6. To calculate the  $\Delta S = S_2 - S_1$  for this process, we build a reversible process comprising a reversible adiabatic compression ( $1 \rightarrow 4$ ), a reversible isothermal expansion ( $4 \rightarrow 3$ ), and a reversible adiabatic expansion ( $3 \rightarrow 2$ ). Since  $S$  is a state function, the  $\Delta S$  for this reversible process is the same as for the irreversible process:

$$\Delta S = S_2 - S_1 = \int_1^4 \frac{dq}{T} + \int_4^3 \frac{dq}{T} + \int_3^2 \frac{dq}{T} = \frac{q_{4 \rightarrow 3}}{T} \quad (3.29)$$

where we used that  $dq = 0$  in an adiabatic process and that  $T$  is constant in an isothermal process. For the cyclic process consisting of the  $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$ ,

$$\oint dU = 0 = q + w \quad (3.30)$$

But all steps other than  $3 \rightarrow 4$  are adiabatic so  $q = q_{3 \rightarrow 4}$ :

$$\oint dU = 0 = q_{3 \rightarrow 4} + w \quad (3.31)$$

and step  $3 \rightarrow 4$  is reversible, so  $q_{3 \rightarrow 4} = -q_{4 \rightarrow 3}$ . Rearranging:

$$w = q_{4 \rightarrow 3} \quad (3.32)$$

If  $w < 0$ , then  $q_{4 \rightarrow 3} < 0$  and  $q_{3 \rightarrow 4} > 0$ , so the only effects of cyclic process  $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$  would be to draw heat from the source at temperature  $T$  in step  $3 \rightarrow 4$  and convert it into work, which is exerted on the surroundings. This would violate the Kelvin statement of the second law of thermodynamics. Therefore it must be that  $w \geq 0$ ,  $q_{4 \rightarrow 3} \geq 0$ . Substituting in Eq. 3.29:

$$\Delta S \geq 0 \quad (3.33)$$

for any adiabatic process in a closed system. If the process  $1 \rightarrow 2$  is reversible, then:

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = 0 \quad (3.34)$$

because  $1 \rightarrow 2$  is also adiabatic, and therefore  $\Delta S = q = w = 0$  corresponds to the case when the  $1 \rightarrow 2$  process is reversible.

Since all processes in an isolated system are adiabatic, the equation above is also applicable to any process in an isolated system, so **the entropy in an isolated system always increases**. An isolated system may undergo several irreversible transformations, each of them increasing its entropy. Once the maximum entropy of the isolated system has been reached, no further spontaneous transformations are possible. Therefore, **an isolated system is at thermodynamic equilibrium when its entropy is maximized**. The universe is an isolated system, so any process must increase the entropy of the universe. Because  $S$  is an extensive property, this means that:

$$dS_{\text{univ}} = dS_{\text{syst}} + dS_{\text{surr}} \geq 0 \quad (3.35)$$

Now let us consider a closed system that is in thermal equilibrium with its surroundings and undergoes an isothermal process. Whenever an isothermal process is considered, we can assume that the surroundings act as a thermal reservoir. A **thermal reservoir** is an idealized system with constant temperature  $T$  and infinite heat capacity and thermal conductivity, such that it is able to transfer any heat to or from the system instantly, without changing its temperature or losing its internal thermal equilibrium. In the lab, a thermal reservoir may be approximated by a large water bath at controlled temperature. Lakes and oceans are example of thermal reservoirs in nature.

As a consequence of being in contact with a thermal reservoir, our system is undergoing an isothermal process in which it is exchanging heat with its surroundings  $dq_{\text{syst}} = -dq_{\text{surr}}$  at constant temperature  $T$ , perhaps as a consequence of an irreversible process occurring in the system (for instance, a chemical reaction). Because the surroundings are always in thermal equilibrium at the same temperature, they undergo isothermal reversible change and therefore:

$$dS_{\text{surr}} = \frac{dq_{\text{surr,rev}}}{T} = \frac{dq_{\text{surr}}}{T} = -\frac{dq_{\text{syst}}}{T} \quad (3.36)$$

Note, in passing, that if the surroundings act as a thermal reservoir then  $T_{\text{surr}}$  do not change during the process, and therefore:

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} \quad (3.37)$$

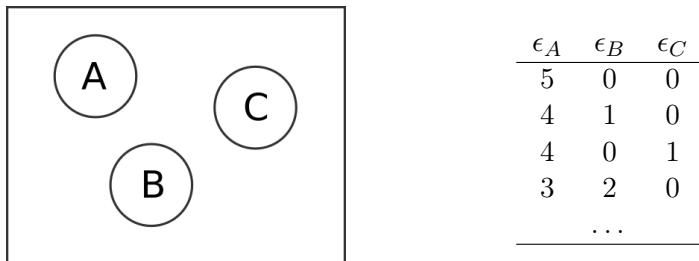


Figure 3.7: Left: a system of three distinguishable non-interacting particles has an internal energy  $U = 5$ . Right: each row in the table is a possible microstate of the system in which the 5 units of energy are distributed among the energies ( $\epsilon$ ) of the three molecules.

which allows the calculation of the entropy change in the surroundings for an isothermal process.

Substituting Eq. 3.36 in Eq. 3.35, we find:

$$dS_{\text{syst}} - \frac{dq_{\text{syst}}}{T} \geq 0 \quad (3.38)$$

Rearranging and dropping the subindices:

$$dS \geq \frac{dq}{T} \quad (3.39)$$

This is known as the **Clausius inequality**, valid for a closed system in thermal equilibrium with its surroundings. The equality of  $dS$  and  $dq/T$  happens only in the case of a reversible process (Eq. 3.24), as shown before. For an irreversible process, entropy is created relative to  $dq/T$ . This inequality will be very important when we examine the spontaneity of chemical reactions.

### 3.3.2 Interpretation

Microscopically, the entropy is a measure of the number of microscopic states (**microstates**) available to the system in its current thermodynamic state. An example illustrating the concept of microstate is shown in Figure 3.7. This system contains only three distinguishable non-interacting molecules (A, B, and C) that can only have integer energies  $\epsilon = 0, 1, 2, \dots$ . The total energy of the system is  $U = 5$ , and this energy can be distributed in different ways over the available molecular energy levels, as shown in the table. Each of these distributions is a different microstate compatible with the thermodynamic state of the system ( $U = 5$ ).

In statistical thermodynamics, the entropy of an isolated system is given by the **Boltzmann equation**:

$$S = k_B \ln \Omega \quad (3.40)$$

where  $k_B = R/N_A$  is **Boltzmann's constant** and  $\Omega$  is the number of microstates compatible with the current thermodynamic state of the system. In the example shown in Figure 3.7,  $\Omega$  would be the number of rows in the table, corresponding to the number of ways in which 5 can be written as a sum of three non-negative integers. As can be seen in the example, there are many microstates for a given thermodynamic state. In a system with a realistic number of molecules,  $\Omega$  is much, much larger.

Going back to the Boltzmann equation (Eq. 3.40), the fact that an isolated system achieves thermodynamic equilibrium when its entropy is maximized means that the system tends to occupy the thermodynamic state with most microstates available. This can be also justified on statistical grounds with a few simple examples.

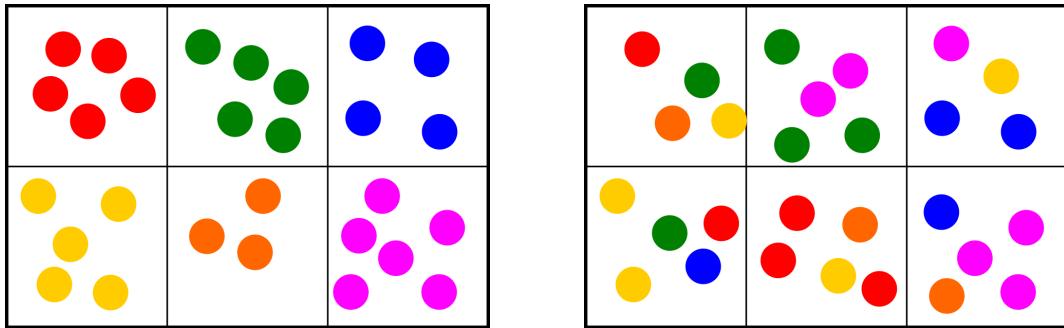


Figure 3.8: Left: a compartmentalized box with ordered buttons. Right: the same set of buttons after shaking the box.

First, consider a box with differently colored buttons separated in compartments, as shown on the left in Figure 3.8. If we take this box and shake it in such a way that the buttons may move between compartments, then a distribution of the buttons like the one on the right of the figure may be obtained. It is very unlikely that if we shake the box we will obtain a perfectly ordered distribution of buttons. This is not because any of the disordered button arrangements is more likely than any of the ordered ones; it is simply because there are many more ways to arrange the buttons in a disordered than in an ordered fashion. In this analogy, our system has two thermodynamic states: ordered and disordered. The disordered thermodynamic state has more microstates (different arrangements of the buttons) than the ordered state. Therefore, the equilibrium state of the system is the disordered state. If we want the system to be in the ordered state, we have to exert work on the system by ordering the buttons ourselves. In other words, the process of shaking the box is irreversible because it leads to an increase in entropy.

A more physical example is provided by the isothermal entropy of mixing of two ideal gases, illustrated in Figure 3.9. In the initial state (top left), two gases A (red) and B (green) with amounts  $n_a$  and  $n_b$  and volumes  $V_a$  and  $V_b$  are at the same pressure ( $p$ ) and temperature ( $T$ ) and separated by an impermeable wall. Now we remove the wall and the two gases expand and mix with each other irreversibly and isothermally, such that the final state has the same pressure and temperature but now the two gases occupy a volume  $V_a + V_b$  (top right). To calculate the entropy change in this process, we consider an equivalent reversible process in two steps. Assume the wall is actually composed of two semipermeable walls, shown as red and green in Figure 3.9. The red wall is permeable to A and the green wall is permeable to B. In the first step, we reversibly move the red wall to the right, allowing A to expand to the whole the box. In the second step, we move the green wall reversibly to the left, allowing B to expand and reaching the final state.

Since the gases are ideal, their molecules do not interact with each other and therefore the entropy change in both reversible steps corresponds to the isothermal reversible expansion of each gas to a volume of  $V = V_a + V_b$ . For an isothermal reversible expansion, the work for gas A in the first step is (Eq. 2.123):

$$w_{\text{rev}} = n_a RT \ln \left( \frac{V_a}{V_a + V_b} \right) \quad (3.41)$$

and, since  $U$  depends only on  $T$  in an ideal gas and the expansion is isothermal,  $dU = 0$ , so:

$$q_{\text{rev}} = -w = n_a RT \ln \left( \frac{V_a + V_b}{V_a} \right) \quad (3.42)$$

The entropy change for the expansion of gas A is (Eq. 3.25)

$$\Delta S_A = \int_i^f \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T} = n_a R \ln \left( \frac{V_a + V_b}{V_a} \right) \quad (3.43)$$

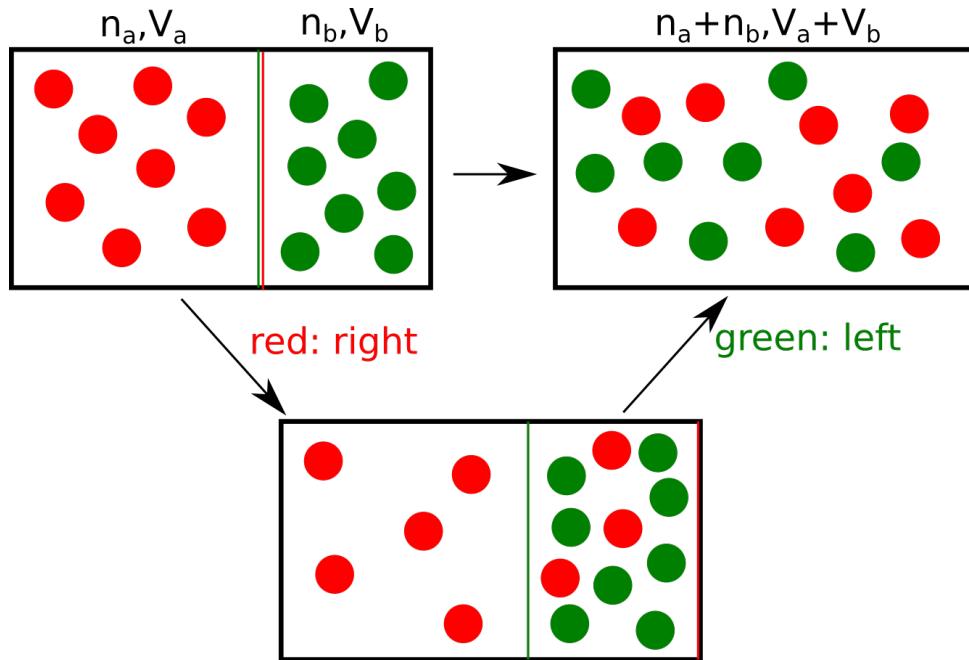


Figure 3.9: Mixing of two ideal gases. Left: two ideal gases at the same pressure ( $p$ ) and temperature ( $T$ ) are separated by an impermeable wall, and the whole system is in thermal contact with a heat bath at temperature  $T$ . Right: the gases are mixed and at the same temperature and pressure. A reversible process between the same initial and final states can be set up by considering there are two walls: one permeable only to gas A (red) and one permeable only to gas B (green). First, we move the red wall reversibly to the right, which allows A to occupy the whole box. Then, we move the green wall reversibly to the left, reaching the final state.

and likewise for gas B:

$$\Delta S_B = n_b R \ln \left( \frac{V_a + V_b}{V_b} \right) \quad (3.44)$$

so the entropy associated with the mixing of the gases is:

$$\Delta_{\text{mix}}S = \Delta S_A + \Delta S_B = n_a R \ln \left( \frac{V_a + V_b}{V_a} \right) + n_b R \ln \left( \frac{V_a + V_b}{V_b} \right) \quad (3.45)$$

Because the gases are ideal,

$$pV_a = n_a RT \quad (3.46)$$

$$p(V_a + V_b) = (n_a + n_b)RT \quad (3.47)$$

$$\frac{V_a}{V_a + V_b} = \frac{n_a}{n_a + n_b} = x_a \quad (3.48)$$

and the equivalent expression applies to gas B. Therefore, the entropy of mixing (Eq. 3.45) is:

$$\Delta_{\text{mix}}S = -n_a R \ln x_a - n_b R \ln x_b \quad (3.49)$$

Note that for any mole fraction other than 0 and 1 (i.e. pure gases), the change in entropy is positive. As in the case of the box with buttons, this indicates that the system has more microstates available in the final than in the initial state. In fact, all microstates of the initial state are possible microstates of the final state, corresponding to a situation in which each of the two gases separates spontaneously into either of the two halves of the container. Being ideal gases, this does not violate the first law but it is extremely unlikely to occur because there are overwhelmingly many more microstates in which the two gases are mixed and molecules of either gas are spread over the whole container.

The last two examples illustrate why entropy is commonly understood as a measure of “disorder” in the system. This is somewhat correct but disorder is ill-defined and not quantifiable. It is best to think of entropy as a measure of the number of microscopic configurations available to a system in its current thermodynamic state, as given by the Boltzmann equation (Eq. 3.40). Note also that the second law of thermodynamics is probabilistic in nature. The entropy of an isolated system could in principle decrease spontaneously but this is extremely unlikely.

Because the universe is an isolated system, the entropy of the universe must always increase. The creation of entropy in the universe is one of the few physical phenomena that is not invariant with respect to a time reversal. For instance, if we drop a ball from a height, it will bounce until all its kinetic energy is dissipated due to friction. Nothing in Newton’s equations or the first law prevents the reverse movement from happening. The ball could acquire energy from the surroundings by collisions with air and ground molecules and bounce up to its original position, then remain at rest. We consider this event impossible because it would decrease the entropy of the universe. The fact that entropy increases constantly with time gives time a direction, allowing the distinction between cause and effect and between past and future events.

### 3.4 Calculation of Entropy Changes

The definition of entropy is (Eq. 3.24):

$$dS = \frac{dq_{\text{rev}}}{T} \quad (3.50)$$

To calculate the change in entropy for a particular process, we first consider a reversible process between the same initial and final states. The entropy change can be calculated as a path integral over the exact differential:

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} \quad (3.51)$$

and, since  $S$  is a state function and  $\Delta S$  depends only on the initial and the final states, this result is valid for any process, reversible or irreversible, between those two states. We have seen an example of this procedure in the last section when we calculated the entropy of mixing of two gases by considering a reversible mixing. A few more examples follow.

**Cyclic process.** For a cyclic process, the initial and final states are the same, so  $\Delta S = 0$ .

**Reversible process.** In a reversible process,  $dq = dq_{\text{rev}}$ , so:

$$\Delta S = \int_1^2 \frac{dq}{T} \quad (3.52)$$

In the case of an adiabatic reversible process,  $dq = 0$  and  $\Delta S = 0$ . For a reversible isothermal process,  $T$  is constant, and the equation above reduces to:

$$\Delta S = \frac{q}{T} \quad (3.53)$$

As discussed above, the entropy of the surroundings can always be calculated in this way if the system is kept at constant temperature because we assume that the surroundings behave as a thermal reservoir, and therefore always undergo reversible isothermal change.

**Ideal gas.** In a pure ideal gas, the thermodynamic state is determined by two variables, for instance by  $V$  and  $T$ . For a process between  $(V_1, T_1)$  and  $(V_2, T_2)$ , we first assume the process is reversible, so:

$$dq_{\text{rev}} = dU - dw_{\text{rev}} = C_V dT + pdV = C_V dT + \frac{nRT}{V} dV \quad (3.54)$$

where we used that  $U$  is a function of  $T$  only, the definition of constant-volume heat capacity (Eq. 2.48), that in a reversible process  $p = p_{\text{ext}}$ , and the ideal gas law. The entropy differential is:

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_V}{T} dT + \frac{nR}{V} dV \quad (3.55)$$

and integrating, we find:

$$\begin{aligned} \Delta S &= \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \frac{nR}{V} dV = \int_{T_1}^{T_2} \frac{C_V}{T} dT + nR \ln \left( \frac{V_2}{V_1} \right) \\ &\approx C_V \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right) \end{aligned} \quad (3.56)$$

where in the last step we assumed  $C_V$  is approximately constant in the considered temperature range. (It is possible to turn the path integral into two separate one-dimensional integrals because the function accompanying  $dT$  depends on  $T$  only and the function with  $dV$  depends on  $V$  only.) This result shows that increasing the volume or the temperature of an ideal gas increases its entropy. In particular, note that in an adiabatic free expansion of an ideal gas against vacuum  $q = w = \Delta U = \Delta H = 0$  but  $\Delta S > 0$ , and this process is irreversible.

**Heating with no phase change.** If the system is heated and no phase change takes place, then  $\Delta S$  can be calculated from the heat capacity. For instance, if the heating is at constant pressure, we assume it is reversible, so  $dq_{\text{rev}} = dq_p = dH = C_p dT$  and:

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_p dT}{T} \quad (3.57)$$

so the constant-pressure heat capacity is:

$$C_p = T \left( \frac{\partial S}{\partial T} \right)_p \quad (3.58)$$

Integrating the equation above, we calculate the entropy change as:

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{C_p}{T} dT \approx C_p \ln \left( \frac{T_2}{T_1} \right) \quad (3.59)$$

where in the last equation we assumed  $C_p$  is approximately constant with temperature.

If the heating occurs at constant volume, then  $dq_{\text{rev}} = dq_p = dU = C_V dT$  and:

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_V dT}{T} \quad (3.60)$$

so the constant-volume heat capacity is:

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V \quad (3.61)$$

and the entropy change is:

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{C_V}{T} dT \approx C_V \ln \left( \frac{T_2}{T_1} \right) \quad (3.62)$$

**Phase transitions at constant temperature and pressure.** In pure substances, phase transitions at constant pressure also occur at a constant temperature. The **normal transition temperature** is the temperature at which the two phases are in equilibrium at 1 atm and the similar **standard transition temperature** is the temperature at which they are in equilibrium at 1 bar.

As before, the entropy change can be calculated by assuming the phase transition is reversible. Since it also happens at constant pressure,  $dq_{\text{rev}} = dq_p = \Delta_{\text{trs}}H$  and because it happens at constant temperature as well:

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{\Delta_{\text{trs}}H}{T} \quad (3.63)$$

Therefore, a phase change increases the entropy of the system if it is endothermic (e.g. melting a solid or evaporating a liquid) and decreases the entropy if it is exothermic (condensation and freezing).

---

**Example.** The entropy for the melting of 5.0 g of ice (with  $\Delta_{\text{fus}}H = 79.7 \text{ cal/g}$ ) at 0 celsius and 1 atm is:

$$\Delta S = \frac{\Delta_{\text{fus}}H}{T} = \frac{(79.7 \text{ cal/g}) \times (5.0 \text{ g})}{273 \text{ K}} = 1.46 \text{ cal/K}$$


---

In the particular case of the entropy of vaporization, it has been empirically determined that the  $\Delta_{\text{vap}}S_m$  of many liquids at their normal boiling point is approximately the same, and equal to  $10.5R = 87.3 \text{ J/K/mol}$ . This is known as **Trouton's rule**, and comes from the fact that all gases have approximately the same molar volume. It does not work very well for polar liquids (for instance, water has  $\Delta_{\text{vap}}S_m = 109.1 \text{ J/K/mol}$ ) and for liquids with a very low or very high boiling point, and more accurate generalizations exist. Note that because of Eq. 3.63 we have that  $\Delta_{\text{vap}}H = T\Delta_{\text{vap}}S(T_{\text{vap}})$ , and therefore Trouton's rule also says that the enthalpy of vaporization of a liquid is  $\Delta_{\text{vap}}H = 10.5RT_{\text{vap}}$  where  $T_{\text{vap}}$  is the normal boiling point. The  $\Delta_{\text{vap}}H$  is a measure of the strength of the intermolecular interactions in the liquid, and typically has values between 20 and 50 kJ/mol at the normal boiling point for substances that are liquids at room temperature.

### 3.5 The Third Law of Thermodynamics and Conventional Entropies

Within classical thermodynamics, there is no way of assigning an absolute value for the entropy since the entropy is defined by its differential (Eq. 3.24), so the entropy is only known up to an arbitrary constant and only entropy differences ( $\Delta S$ ) can be calculated. However, it is customary to define conventional entropies by assigning a more or less arbitrary value to certain systems. The convention used is based on two principles: Boltzmann's equation and Nernst's heat theorem.

Using Boltzmann's equation (Eq. 3.40) it is possible to calculate the entropy of any system in a given thermodynamic state by computing the number of associated microstates. In the particular case when temperature tends to zero  $T \rightarrow 0$ , the system does not have enough thermal energy to populate anything other than the lowest-energy state (the **ground state**). In the limit of  $T = 0$ , atoms and molecules crystallize in an ordered lattice corresponding to a single ground-state, so  $\Omega = 1$  and  $S = 0$ . (Although  $\Omega = 1$  at  $T = 0$  for most substances, an exception occurs when the ground state has more than one microstate associated with it if, for instance, there are several energy-equivalent arrangements in the crystalline state. For example, the protons in ice can jump between both sides of the hydrogen bond even at  $T = 0$ , resulting in a residual molar entropy of  $3.4 \text{ J/K/mol}$ . This is why in the following we require that the substances are perfectly ordered.)

The second observation we need to define conventional entropies is **Nernst's heat theorem**, which states that the  $\Delta S$  of any isothermal process tends to zero as  $T \rightarrow 0$ , provided all substances involved are perfectly ordered. Nernst's heat theorem is an empirical result based on low-temperature calorimetric experiments.

Putting together Nernst's heat theorem and Boltzmann's equation suggests the convention that the standard entropy of all elements in their reference state at  $T = 0$  is zero:

$$S_0^\circ(\text{element, reference state}) = 0 \quad (3.64)$$

Remember that the reference state of an element is the pure element in its most stable form at 1 bar and, in this case, at  $T = 0$ . All elements under those conditions are ordered crystalline solids except for He, which is a liquid.

For a given substance, we can always consider the process in which the compound is formed from the corresponding elements in their reference states at zero temperature. Nernst's heat theorem ensures that the entropy change for this process, which is the standard formation entropy at zero temperature ( $\Delta_f S_0^\circ$ ), is zero. The formation can be written as:

$$\Delta_f S_0^\circ = S_0^\circ(\text{compound}) - \sum_i^{\text{elements}} \nu_i S_0^\circ(i, \text{reference state}) = S_0^\circ(\text{compound}) \quad (3.65)$$

because by convention  $S_0^\circ(i, \text{reference state}) = 0$ . Therefore,  $S_0^\circ(\text{compound}) = \Delta_f S_0^\circ = 0$  by application of Nernst's heat theorem.

All compounds are solids or liquids at zero temperature and, for solids and liquids, the standard superscript ( $\circ$ ) means that they are pure and at 1 bar. Consider the process in which we change the pressure of the substance at  $T = 0$ . Nernst's theorem also applies to this change, and therefore  $\Delta S = 0$  and the entropy of a compound at zero temperature and any pressure is also zero, so we can drop the standard superscript. In summary, all substances with perfectly ordered structures at zero temperature have zero entropy:

$$S_0(\text{compound}) = 0 \quad (3.66)$$

which is the statement of the **third law of thermodynamics**.

The convention regarding the value of the entropy at absolute zero allows the determination of **conventional entropies**. The calculation of the conventional entropy of a compound at temperature  $T$  is carried out by starting with the compound at  $T = 0$ , at which  $S = 0$  and then using (Eq. 3.59):

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p}{T} dT \quad (3.67)$$

for temperature ranges where there is no phase change and (Eq. 3.63):

$$\Delta_{\text{trs}} S = \Delta S(T_{\text{trs}}) = \frac{\Delta_{\text{trs}} H}{T} \quad (3.68)$$

for the change in entropy during a phase transition.

Standard conventional molar entropies ( $S_m^\circ$ ), often called simply standard molar entropies, are extensively reported in thermodynamic tables. For instance, the  $S_m^\circ$  of a few substances at room temperature are, in J/K/mol: 5.7 (graphite), 2.4 (diamond), 69.9 (water), 186.3 (methane), 213.7 (CO<sub>2</sub>). Diamond has the lowest standard molar entropy at room temperature of any known substance.

As in the case of the standard enthalpies of formation in the previous chapter, the experimental determination of conventional entropies of ions is difficult because a solution of only cations or

only anions cannot be prepared. For the conventional entropies of ions, we make the additional convention that the standard conventional entropy of protons in aqueous solution is zero at all temperatures:

$$S^\circ(\text{H}^+, \text{aq}) = 0 \quad (3.69)$$

With this convention, the entropies of the various ions can be positive or negative, depending on whether they give more or less structure to the solvent around them. For instance,  $S_m^\circ(\text{Cl}^-, \text{aq}) = 57 \text{ J/K/mol}$  and  $S_m^\circ(\text{Mg}^{2+}, \text{aq}) = -128 \text{ J/K/mol}$ , indicating that the water molecules around the  $\text{Cl}^-$  anion are less structured (less ordered) than around a proton and the water molecules around a  $\text{Mg}^{2+}$  cation are more structured than around a  $\text{H}^+$  cation. Small, highly charged ions in solution induce more structuring of the solvent than large, singly charged ions, and they have correspondingly lower entropies.

## 3.6 Reaction Entropies

Lastly, we define reaction entropies in exactly the same way we did for reaction enthalpies. For a chemical reaction:



the **standard reaction entropy** is the difference between the conventional molar entropies of the pure products and the pure reactants separated and in their standard states:

$$\Delta_r S^\circ = \sum_i \nu_i S_m^\circ(i) \quad (3.71)$$

Almost always,  $\Delta_r S^\circ > 0$  if there is a net generation of gases in the reaction and  $\Delta_r S^\circ < 0$  if there is a net consumption of gases in the reaction. As in the case of the reaction enthalpies and internal energies, we can use Hess' law to calculate the reaction entropy from other known reaction entropies. For instance:

$$\Delta_r S^\circ = \sum_i \nu_i \Delta_f S^\circ(i) = \sum_i \nu_i \Delta_c S^\circ(i) \quad (3.72)$$

where  $\Delta_f S^\circ(i)$  are the standard formation entropies and  $\Delta_c S^\circ(i)$  are the standard combustion entropies.

The dependence of the standard reaction entropy with temperature can be calculated by substituting Eq. 3.59 in the definition (Eq. 3.71):

$$\Delta_r S^\circ(T_2) = \Delta_r S^\circ(T_1) + \int_{T_1}^{T_2} \frac{\Delta_r C_{p,m}^\circ}{T} dT \approx \Delta_r S^\circ(T_1) + \Delta_r C_{p,m}^\circ \ln\left(\frac{T_2}{T_1}\right) \quad (3.73)$$

where in the last step we assumed the heat capacities are approximately constant in the considered temperature range. Note the similarity between this result and Kirchhoff's law.

# Chapter 4

## Material Equilibrium

### 4.1 Phase and Reaction Equilibrium

The second law states that any process that decreases the entropy of the universe is impossible:

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} \geq 0 \quad (4.1)$$

In order to find conditions for spontaneous change and equilibrium in chemical systems, we would like to express this principle in terms of system quantities, so we do not need to consider the entropy of the surroundings. In the rest of this chapter, we consider closed systems doing p-V work only and at mechanical and thermal equilibrium with their surroundings, so their pressures and temperatures are defined.

A system is in **material equilibrium** if the amount of each substance in each of its phases does not change with time. Material equilibrium occurs when the following two types of equilibria happen at the same time:

- **Phase equilibrium:** the amount of each component does not change as a result of matter being transported between different phases in the system.
- **Reaction equilibrium:** the amount of each component does not change as a result of a chemical reaction.

Our system is closed and in thermal equilibrium so the Clausius inequality (Eq.3.39) applies to any process happening in it:

$$dS \geq \frac{dq}{T} \quad (4.2)$$

where the equality corresponds to a reversible process (because  $dq = dq_{\text{rev}}$ ) and the  $\geq$  symbol corresponds to an irreversible process. Substituting in the first law equation we have that the change in internal energy is:

$$dU = dq + dw \leq TdS + dw \quad (4.3)$$

with equality only for a reversible process.

### 4.2 Helmholtz Free Energy

Let us first consider a process at constant temperature ( $dT = 0$ ) and constant volume ( $dV = 0$ ), perhaps a chemical reaction or a phase change occurring under those conditions. In this case,

$$dw = -p_{\text{ext}}dV = 0 \quad (4.4)$$

and from the equation above we have:

$$dU \leq TdS = TdS + SdT - SdT \quad (4.5)$$

$$dU - TdS - SdT = d(U - TS) \leq -SdT \quad (4.6)$$

and since  $dT = 0$  as well,

$$dA = d(U - TS) \leq 0 \quad (4.7)$$

where we defined the **Helmholtz free energy** ( $A$ ) as:

$$A = U - TS \quad (4.8)$$

This property is also known as the **Helmholtz energy** or the **work function** (sometimes  $F$  is used to denote this quantity instead of  $A$ ).

The Helmholtz free energy is a state function because  $U$ ,  $T$ , and  $S$  are state functions. In addition, Equation 4.7 shows that the Helmholtz free energy of a closed system always decreases when it undergoes a process at constant temperature and volume, with  $dA = 0$  corresponding to the particular case of a reversible process. In other words, **a process in a closed system at constant  $T$  and  $V$  is spontaneous only if it decreases  $A$** . A consequence of this is that **a closed system held at constant  $T$  and  $V$  is at equilibrium if and only if  $A$  is at a minimum**.

The name “work function” for  $A$  originates from the following result. We can write  $dA$  as:

$$\begin{aligned} dA &= dU - SdT - TdS \\ &= dq + dw - SdT - TdS \\ &\leq TdS + dw - SdT - TdS = dw - SdT \end{aligned} \quad (4.9)$$

Therefore, for an isothermal process ( $dT = 0$ ):

$$dA \leq dw \quad (4.10)$$

Integrating these differentials along the considered isothermal process, we have:

$$w_{\text{by}} = -w \leq -\Delta A \quad (4.11)$$

where  $w_{\text{by}}$  is the work done by the system, which in our sign convention is equal to  $-w$ . The work done by the system is at most equal to the  $\Delta A$  (in absolute value) of the process and the equality happens only if the process is reversible. Consequently, the change in Helmholtz free energy in an isothermal process is the maximum amount work a closed system can exert on its surroundings during that process, and the maximum work is only achieved if the process is reversible.

### 4.3 Gibbs Free Energy

We now consider a process at constant temperature and pressure, which are more common conditions in chemical practice than constant temperature and volume. In this case, because our system is assumed to be in mechanical equilibrium ( $p = p_{\text{ext}}$ ), Eq. 4.3 becomes:

$$dU = dq + dw \leq TdS + dw = TdS - pdV \quad (4.12)$$

$$d(U - TS + pV) = dU - TdS - SdT + pdV + Vdp \leq -SdT + Vdp \quad (4.13)$$

We define the **Gibbs free energy** ( $G$ , also known simply as **Gibbs energy**) as:

$$G = U - TS + pV = H - TS = A + pV \quad (4.14)$$

The Gibbs free energy is a state function because  $H$ ,  $T$ , and  $S$  are state functions. At constant temperature ( $dT = 0$ ) and constant pressure ( $dp = 0$ ), the Eq. 4.13 reduces to:

$$dG \leq 0 \quad (4.15)$$

Therefore, the Gibbs free energy of a closed system always decreases when it undergoes a process at constant  $T$  and  $p$ , with  $dG = 0$  corresponding to the case when the process is reversible. This means that **a process in a closed system at constant temperature and pressure is spontaneous only if it decreases  $G$** . The consequence is that **a closed system held at constant temperature and pressure is at equilibrium if and only if  $G$  is at a minimum**. This is a very important result for the study of chemical reactions and phase equilibria. A chemical reaction at constant pressure and temperature will occur spontaneously in the direction in which  $G$  decreases. In addition, we can use the condition  $dG = 0$  to determine the criteria for material equilibrium. For instance, the reactant and product concentrations at which  $G$  is a minimum ( $dG = 0$ ) corresponds to the equilibrium composition of a chemical reaction.

Same as in the case of  $A$ , the  $\Delta G$  of a given process can be interpreted in terms of the work done by the system. The change in Gibbs free energy can be written as:

$$dG = d(A + pV) = dA + pdV + Vdp \quad (4.16)$$

Using Eq. 4.9, we have:

$$dG \leq dw - SdT + pdV + Vdp \quad (4.17)$$

If we momentarily drop the requirement that only p–V work is done by the system, we have:

$$dG \leq dw_{pV} + dw_{\text{non}-pV} - SdT + pdV + Vdp \quad (4.18)$$

If we assume the process is at constant temperature ( $dT = 0$ ) and pressure ( $dp = 0$ ):

$$dG \leq dw_{pV} + dw_{\text{non}-pV} + pdV \quad (4.19)$$

and if we further assume that the p–V work is done in a mechanically reversible way ( $p = p_{\text{ext}}$ ), we have  $dw_{pV} = -pdV$  and:

$$dG \leq dw_{\text{non}-pV} \quad (4.20)$$

Integrating:

$$\Delta G \leq w_{\text{non}-pV} \quad (4.21)$$

Therefore, the non-p–V work done by the system is:

$$w_{\text{by},\text{non}-pV} = -w_{\text{non}-pV} \leq -\Delta G \quad (4.22)$$

The maximum non-p–V work that can be exerted by a closed system on the surroundings at constant temperature and pressure (assuming reversible p–V work) is given by  $-\Delta G$ , and this maximum is reached only if the process is reversible. This result and the calculation of  $\Delta G$  for a chemical reaction is very important in the field of electrochemistry, fuel cells, and batteries. For instance, the  $\Delta G$  of a redox reaction is a measure of the maximum amount of usable energy that can be extracted from a battery based using that reaction.

The two results:

- A process in a closed system at constant  $T$  and  $V$  decreases  $A$ .
- A process in a closed system at constant  $T$  and  $p$  decreases  $G$ .

are re-statements of the second law, the fact that the entropy of the universe always increases, but written in terms of system quantities only, which is more useful for chemical calculations. For instance, if a closed system undergoes a chemical reaction at constant temperature and pressure, the change in entropy of the surroundings is (Eq. 3.37):

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = -\frac{q_{\text{syst}}}{T} = -\frac{\Delta H_{\text{syst}}}{T} \quad (4.23)$$

where we used that  $q = q_p = \Delta H$ . Therefore, the entropy change of the universe is:

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{syst}} = -\frac{\Delta H_{\text{syst}}}{T} + \Delta S_{\text{syst}} = -\frac{\Delta H_{\text{syst}} - T\Delta S_{\text{syst}}}{T} = -\frac{\Delta G_{\text{syst}}}{T} \quad (4.24)$$

so the entropy change in the universe is positive if and only if the  $\Delta G$  of the system is negative. Hence, saying that  $\Delta S_{\text{univ}}$  increases is equivalent to saying that  $\Delta G$  decreases for a process under these conditions. In a closed system at constant  $T$  and  $p$  an increase in  $G$  equates to an increase in the entropy of the universe, which violates the second law.

## 4.4 Standard Free Energies

The Gibbs and Helmholtz free energies,  $G$  and  $A$ , are state functions and, as such, can be calculated whenever the system is in a well-defined thermodynamic state, in other words, when meaningful values for all thermodynamic variables exist. Same as  $U$  and  $H$ , both quantities have units of energy and are extensive. The corresponding intensive molar quantities can be defined by dividing by the amount of substance:

$$G_m = \frac{G}{n} \quad (4.25)$$

$$A_m = \frac{A}{n} \quad (4.26)$$

where  $G_m$  is the **molar Gibbs free energy** and  $A_m$  is the **molar Helmholtz free energy**. Likewise, we can define the corresponding standard quantities.  $G^\circ$  is the Gibbs free energy of a substance in its standard state at the chosen temperature and  $G_m^\circ = G^\circ/n$  is the standard molar Gibbs free energy. Equivalent definitions apply to  $A^\circ$  and  $A_m^\circ$ .

The **standard Gibbs energy of formation** ( $\Delta_f G^\circ$ ) is the change in Gibbs free energy when one mole of compound in its standard state is formed from its elements in their reference states, all at the considered temperature. This definition is entirely analogous to the standard enthalpy of formation (Eq. 2.8). Example values at room temperature in kJ/mol are: 2.9 (diamond), 124.3 (benzene),  $-50.7$  (methane),  $-394.4$  ( $\text{CO}_2$ ), and  $-384.1$  ( $\text{NaCl}$ ). In addition, there is another convention for the standard Gibbs energy of formation of ions in solution. Namely, the Gibbs free energy of formation of the proton in aqueous solution is zero at any temperature:

$$\Delta_f G^\circ(\text{H}_{\text{(aq)}}^+) = 0 \text{ at any temperature} \quad (4.27)$$

This convention is the equivalent of those for the enthalpy (Section 2.8) and for the entropy (Section 3.5), and allows the experimental determination of formation free energies of individual ions, circumventing the fact that cations and anions cannot exist alone in solution.

The **standard Gibbs energy of reaction** (also known as the standard reaction Gibbs energy,  $\Delta_r G^\circ$ ) is defined as the difference between the standard molar Gibbs free energies of pure, separated reactants and products. For the chemical reaction:



the standard Gibbs energy of reaction is:

$$\Delta_r G^\circ = \sum_i \nu_i G_m^\circ(i) \quad (4.29)$$

Because the standard Gibbs energy of each species is:

$$G_m^\circ(i) = H_m^\circ(i) - TS_m^\circ(i) \quad (4.30)$$

we can express the standard Gibbs energy of reaction in terms of the standard reaction enthalpy and entropy:

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \quad (4.31)$$

In addition, using Hess' law, we can also write it in terms of the free energies of formation of reactants and products:

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ(i) \quad (4.32)$$

and also in terms of any other combination of free energies for suitable reactions like, for instance, standard combustion free energies:

$$\Delta_r G^\circ = \sum_i \nu_i \Delta_c G^\circ(i) \quad (4.33)$$

in the case of reactions between organic substances.

Standard Gibbs free energies of reaction are very important because they determine whether a given reaction is spontaneous or not. However, note that in an actual reaction, reactants and products need not be in their standard states. We will see how the free energy of a substance and combinations of free energies for various substances, such as  $\Delta_r G$ , depend on  $T$  and  $p$ . The  $\Delta_r G^\circ$  for a particular reaction can be determined from calorimetric experiments by measuring the corresponding  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  and combining them using Eq. 4.31. Standard Gibbs energies for reactions can also be obtained from measurements of equilibrium constants, electrochemical experiments and spectroscopic measurements because, as we shall see, the  $\Delta_r G^\circ$  of a reaction is directly linked to its equilibrium constant. Also, using statistical thermodynamics, it is also possible to calculate  $\Delta_r G^\circ$  for some reactions from quantum mechanical calculations of the microscopic properties of the component molecules.

## 4.5 The Gibbs Equations and the Maxwell Relations

### 4.5.1 Derivation

For a reversible process in a closed system with only p–V work,

$$dq_{\text{rev}} = TdS \quad (4.34)$$

$$dw_{\text{rev}} = -pdV \quad (4.35)$$

so the first law can be written as:

$$dU = TdS - pdV \quad (4.36)$$

This equation is valid for a reversible process only but, since  $U$  is a state function, any integral of  $dU$  between two states yields the correct  $\Delta U$  between those two states, because the internal energy change depends only on the initial and the final state and not on the path connecting them. Therefore, the  $\Delta U$  calculated by integrating this equation is also correct for any irreversible processes going between the same initial and final states as the reversible path.

Using a reversible process for the  $\Delta U$  calculation is more convenient than an irreversible process, because in the latter  $TdS$  does not equal the heat exchanged ( $dq < dq_{\text{rev}} = TdS$ ) and  $pdV$  does not equal the work ( $dw > dw_{\text{rev}} = -pdV$ ). In fact, an irreversible process may go through states of the system in which some or all of the system's thermodynamic properties are ill-defined, for instance, if the temperature or the pressure is not uniform throughout the system. If, on the other hand, the system is in thermal equilibrium ( $T$  is defined, and the same as the surroundings if the walls are diathermal) and in mechanical equilibrium ( $p$  is defined, and equal to  $p_{\text{ext}}$  if the walls are nonrigid), then:

$$dU \leq TdS - pdV \quad (4.37)$$

with equality only at material equilibrium. Expressions like this will serve to establish the conditions for chemical and phase equilibrium in the following.

Relations similar to Eq. 4.36 can be derived for the other energy functions undergoing a reversible process. Namely,

$$dH = d(U + pV) = dU + pdV + Vdp = TdS - pdV + pdV + Vdp = TdS + Vdp \quad (4.38)$$

$$dA = d(U - TS) = dU - TdS - SdT = TdS - pdV - TdS - SdT = -SdT - pdV \quad (4.39)$$

$$dG = d(H - TS) = dH - TdS - SdT = TdS + Vdp - TdS - SdT = -SdT + Vdp \quad (4.40)$$

so, in summary:

$$dU = TdS - pdV \quad (4.41)$$

$$dH = TdS + Vdp \quad (4.42)$$

$$dA = -SdT - pdV \quad (4.43)$$

$$dG = -SdT + Vdp \quad (4.44)$$

These four equations are very important, and they are known as the **fundamental thermodynamic relations** (also **Gibbs equations**). Their importance lies in the fact that they can be used to derive relations between the various thermodynamic properties of a system at equilibrium in order to write thermodynamic properties of interest in terms of other more easily measurable properties.

We can derive a few of these relations by identifying the quantities appearing in the fundamental relations with the corresponding derivatives from the state function differential. For instance, for the internal energy, using  $V$  and  $S$  as state variables we have:

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \quad (4.45)$$

Identifying the derivatives that accompany  $dS$  and  $dV$  with the corresponding properties in Eq. 4.41, we have:

$$\left( \frac{\partial U}{\partial S} \right)_V = T \quad \left( \frac{\partial U}{\partial V} \right)_S = -p \quad (4.46)$$

The first relation ( $(\frac{\partial U}{\partial S})_V = T$ ) can, in fact, be used as the thermodynamic definition of temperature.

For the other energies, the corresponding exact differentials are:

$$dH = \left( \frac{\partial H}{\partial S} \right)_p dS + \left( \frac{\partial H}{\partial p} \right)_S dp \quad (4.47)$$

$$dA = \left( \frac{\partial A}{\partial T} \right)_V dT + \left( \frac{\partial A}{\partial V} \right)_T dV \quad (4.48)$$

$$dG = \left( \frac{\partial G}{\partial T} \right)_p dT + \left( \frac{\partial G}{\partial p} \right)_T dp \quad (4.49)$$

and, comparing to the corresponding fundamental relations (Eqs. 4.42, 4.43, and 4.44) we get:

$$\left(\frac{\partial H}{\partial S}\right)_p = T \quad \left(\frac{\partial H}{\partial p}\right)_S = V \quad (4.50)$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -p \quad (4.51)$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \left(\frac{\partial G}{\partial p}\right)_T = V \quad (4.52)$$

Another way of finding relations between thermodynamic properties is by noting that the crossed second derivatives of an exact differential are equal. For instance, for the internal energy:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad (4.53)$$

the crossed second derivatives of the differential must be identical:

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} \quad (4.54)$$

Substituting Eq. 4.46, we have:

$$\left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial p}{\partial S}\right)_V \quad (4.55)$$

Applying the same procedure to the other differentials we find:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (4.56)$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad (4.57)$$

$$\left(\frac{\partial V}{\partial T}\right)_p = - \left(\frac{\partial S}{\partial p}\right)_T \quad (4.58)$$

These are known as **Maxwell's relations**, and some of them involve quantities that are experimentally measurable like, for instance, the thermal expansion coefficient ( $\alpha$ , Eq. 2.99) in Eq. 4.58.

### 4.5.2 Some Applications

We now apply the results above to obtain some important thermodynamic relations.

**Internal pressure.** We have seen that the internal pressure (Eq. 2.97) is related to the strength of the intermolecular interactions in a gas. Dividing the  $dU$  in terms of  $S$  and  $V$  (Eq. 4.53) by  $dV$  at constant  $T$  (i.e. applying Eq. 2.36), the internal pressure can be rewritten as:

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S \quad (4.59)$$

The first derivative on the right-hand side of this equation is equal to  $T$  (Eq. 4.46), the second derivative is equal to  $\left(\frac{\partial p}{\partial T}\right)_V$  (Eq. 4.57), and the third derivative is equal to  $-p$  (Eq. 4.46).

Therefore:

$$\pi_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad (4.60)$$

Since the right-hand side depends only on pressure, temperature, and volume, this expression is known as the **thermodynamic equation of state**. For an ideal gas, taking the derivative of the ideal gas law ( $pV = nRT$ ) and substituting gives:

$$\pi_T = T \times \frac{nR}{V} - p = p - p = 0 \quad (4.61)$$

Therefore, since  $\pi_T$  is the volume derivative of  $U(V, T)$ , we have shown that the internal energy of an ideal gas depends on temperature only, something that was justified earlier but not proven.

Using Eqs. 2.38 and 2.37, we have:

$$\left( \frac{\partial p}{\partial T} \right)_V = - \left( \frac{\partial p}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p = - \frac{\left( \frac{\partial V}{\partial T} \right)_p}{\left( \frac{\partial V}{\partial p} \right)_T} = \frac{\alpha}{\kappa} \quad (4.62)$$

where we have used the definitions of the expansion coefficient ( $\alpha$ , Eq. 2.99) and the isothermal compressibility ( $\kappa$ , Eq. 2.101). Substituting in Eq. 4.60, the internal pressure is:

$$\pi_T = \frac{\alpha T}{\kappa} - p \quad (4.63)$$

so the internal pressure can be expressed in terms of other more easily measurable quantities ( $p, T, \alpha$ , and  $\kappa$ ).

**Joule-Thomson coefficients.** The Joule-Thomson coefficient (Eq. 2.110) measures the temperature change with pressure in an isenthalpic process:

$$\mu_{JT} = \left( \frac{\partial T}{\partial p} \right)_H \quad (4.64)$$

We have seen that the Joule-Thomson coefficient is zero for an ideal gas and can be positive or negative, depending on the conditions, in real gases. Using Eqs. 2.38 and 2.37:

$$\mu_{JT} = \left( \frac{\partial T}{\partial p} \right)_H = - \left( \frac{\partial T}{\partial H} \right)_p \left( \frac{\partial H}{\partial p} \right)_T = - \frac{\left( \frac{\partial H}{\partial p} \right)_T}{\left( \frac{\partial H}{\partial T} \right)_p} = - \frac{1}{C_p} \left( \frac{\partial H}{\partial p} \right)_T \quad (4.65)$$

where we substituted  $C_p$  for its definition (Eq. 2.63). The derivative in the right-hand side of this equation is calculated by dividing the fundamental relation for the enthalpy (Eq. 4.42) by  $dp$  at constant temperature:

$$\left( \frac{\partial H}{\partial p} \right)_T = T \left( \frac{\partial S}{\partial p} \right)_T + V \quad (4.66)$$

Applying the Maxwell's relations (Eq. 4.58) and the definition of the expansion coefficient (Eq. 2.99):

$$\left( \frac{\partial H}{\partial p} \right)_T = -T \left( \frac{\partial V}{\partial T} \right)_p + V = -VT\alpha + V \quad (4.67)$$

And substituting this result in Eq. 4.65,

$$\mu_{JT} = \frac{V}{C_p} (\alpha T - 1) \quad (4.68)$$

Note that for an ideal gas,

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{pV} = \frac{1}{T} \quad (4.69)$$

so  $\alpha T - 1 = 0$ . Therefore  $\mu_{JT} = 0$  for an ideal gas, in agreement with our previous results.

**Heat capacities.** The constant-volume heat capacity is defined in Eq. 2.48. Using the chain rule:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial U}{\partial S} \right)_V \left( \frac{\partial S}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V \quad (4.70)$$

where we applied Eq. 4.46 to the first derivative on the right-hand side. In turn, the constant-pressure heat capacity is:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial H}{\partial S} \right)_p \left( \frac{\partial S}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p \quad (4.71)$$

where Eq. 4.50 was used. These results were obtained previously in a different way (Eq. 3.58 and 3.61) and show that the heat capacities are related to the temperature-derivative of the entropy under the corresponding conditions: constant pressure for  $C_p$  and constant volume for  $C_V$ .

We showed before (Eq. 2.106) that the value of  $C_p - C_V$  for an ideal gas is  $nR$ . The relations above allow deriving the same result for any type of system:

$$C_p - C_V = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V \quad (4.72)$$

At constant pressure, since  $H = U + pV$ :

$$\left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p \quad (4.73)$$

so:

$$C_p - C_V = \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V \quad (4.74)$$

If we take the differential of  $U(T, V)$ :

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (4.75)$$

and divide by  $dT$  at constant pressure, we find:

$$\left( \frac{\partial U}{\partial T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \quad (4.76)$$

(This is equivalent to using Eq. 2.36.) Substituting in the heat capacity difference and using the definition of the internal pressure  $\pi_T$  (Eq. 4.60) and  $\alpha$  (Eq. 2.99):

$$C_p - C_V = \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p = \left( \frac{\partial V}{\partial T} \right)_p (\pi_T + p) = V\alpha (\pi_T + p) \quad (4.77)$$

The expression for the internal pressure in Eq. 4.63 can be substituted to find:

$$C_p - C_V = V\alpha \left[ \frac{\alpha T}{\kappa} - p + p \right] = \frac{TV\alpha^2}{\kappa} \quad (4.78)$$

It is easy to verify that the heat capacity difference for an ideal gas ( $nR$ , Eq. 2.106) is obtained using the ideal gas law and the corresponding values of  $\alpha$  ( $1/T$ , Eq. 2.100) and  $\kappa$  ( $1/p$ , Eq. 2.103) in this equation. This result also shows that  $C_p - C_V \rightarrow 0$  as  $T \rightarrow 0$  as well as that  $C_p \geq C_V$ , since  $\kappa$  can be shown to be always positive. The heat capacity difference is relatively small for solids but large for liquids and, particularly, for gases.

**Changes in State Functions.** The thermodynamic relations above can be used to write the differentials of state functions in terms of measurable quantities so they are easier to integrate. This implicitly assumes that the process is reversible, otherwise the measurable quantities may not even be defined along the process. However, as previously mentioned, the change in a state function depends only on the initial and the final states and not on the particularities of the process, so the calculated state function change is correct for any irreversible process between the same initial and final states.

For instance, assume we want to calculate the entropy change associated with a process that goes between an initial state  $(p_1, T_1)$  and a final state  $(p_2, T_2)$ . The corresponding differential can be written as:

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \quad (4.79)$$

but using Eq. 4.71:

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \quad (4.80)$$

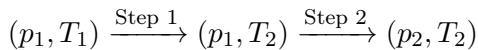
and using Maxwell's relations (Eq. 4.58) and the definition of the expansion coefficient (Eq. 2.99):

$$\left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p = -V\alpha \quad (4.81)$$

so the entropy differential is:

$$dS = \frac{C_p}{T} dT - \alpha V dp \quad (4.82)$$

Because  $S$  is a state function, we can choose any reversible path we want between the initial and the final states. In particular, we can consider a reversible isobaric temperature change followed by a reversible isothermal change of pressure:



The path integrals for each of these steps involve only one term of the differential and therefore reduce to one-dimensional integrals:

$$\Delta S_1 = \int_{T_1}^{T_2} \frac{C_p}{T} dT \quad (4.83)$$

$$\Delta S_2 = \int_{p_1}^{p_2} -\alpha V dp \quad (4.84)$$

where the first step is calculated at constant  $p = p_1$  and the second step at constant  $T = T_2$ . The entropy change for the whole process is the sum of the changes for two steps:

$$\Delta S = \Delta S_1 + \Delta S_2 = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{p_1}^{p_2} \alpha V dp \quad (4.85)$$

However, note that if the system suffers a phase transition, there will be an additional contribution to the entropy given by Eq. 3.63.

Likewise, if we want to calculate the change in enthalpy ( $\Delta H$ ) along the same path, we have:

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \quad (4.86)$$

The first derivative is  $C_p$  by definition and the second derivative is given by Eq. 4.67:

$$dH = C_p dT + V(1 - T\alpha) dp \quad (4.87)$$

Same as above, we assume first a reversible isobaric change in temperature followed by a reversible isothermal change in pressure to give:

$$\Delta H = \int_{T_1}^{T_2} C_p dT + \int_{p_1}^{p_2} V(1 - T\alpha) dp \quad (4.88)$$

And, again, there may be additional contributions to the enthalpy change if the system undergoes any phase change.

## 4.6 Properties of the Gibbs Free Energy

Calculating changes in the Gibbs free energy due to varying experimental conditions is essential in chemistry because  $dG = 0$  is the equilibrium condition for a closed system at constant temperature and pressure, which are common conditions in experimental chemistry. The dependence of  $G$  with temperature at constant pressure is given by (Eq. 4.52):

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad (4.89)$$

This equation can be rewritten as:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2} = \frac{-G - TS}{T^2} = -\frac{H}{T^2} \quad (4.90)$$

This is the **Gibbs-Helmholtz equation**. The Gibbs-Helmholtz equation is particularly useful when applied to the calculation of the temperature dependence of Gibbs free energy changes. For instance:

$$\left(\frac{\partial(\Delta_r G^\circ/T)}{\partial T}\right)_p = \sum_i \nu_i \left(\frac{\partial(G_m^\circ(i)/T)}{\partial T}\right)_p = -\sum_i \nu_i \frac{H_m^\circ(i)}{T^2} = -\frac{\Delta_r H^\circ}{T^2} \quad (4.91)$$

Therefore, the temperature dependence of the standard reaction Gibbs energy is given by the standard reaction enthalpy, that is, by whether the reaction is exothermic or endothermic.

The dependence of  $G$  with pressure is given by (Eq. 4.52):

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad (4.92)$$

For an isothermal process between  $p_1$  and  $p_2$ :

$$G_m(p_2) = G_m(p_1) + \int_{p_1}^{p_2} V_m dp \quad (4.93)$$

Solids and liquids are mostly incompressible so their molar volumes are approximately constant in a reasonable pressure range (up to hundreds to thousands of atmospheres) so  $V_m$  can be assumed to be constant. In addition, molar volumes of liquids and solids are relatively small, so:

$$G_m(p_2) - G_m(p_1) \approx V_m(p_2 - p_1) \approx 0 \quad (4.94)$$

Therefore, the Gibbs free energy of a solid or a liquid is not significantly affected by changes in pressure, up to hundreds to thousands of atmospheres. Pressures in the geological scale, such as those prevailing in the interior of the Earth, can go up to hundreds of GPa (1 GPa = 10 000 atm). In that case, the dependence of  $G$  with  $p$  is very important and the integral in Eq. 4.93 has to be calculated without the approximations above. We will not consider this case in the rest of the course.

In the case of gases, the pressure dependence of  $G$  is reasonably approximated by the behavior of an ideal gas. The molar volume of an ideal gas is:

$$V_m = \frac{RT}{p} \quad (4.95)$$

and therefore the integration of Eq. 4.93 gives:

$$G_m(p_2) = G_m(p_1) + RT \ln \left( \frac{p_2}{p_1} \right) \quad (4.96)$$

If we take  $p_1 = p^\circ = 1 \text{ bar}$  and  $p_2 = p$ , we have:

$$G_m(p) = G_m^\circ + RT \ln \left( \frac{p}{p^\circ} \right) \quad (4.97)$$

In an ideal gas,  $G$  increases logarithmically with pressure. Note we used that  $G_m(p^\circ) = G_m^\circ$  because an ideal gas at 1 bar and the considered temperature is in its standard state.

In a closed one-component system, if the Gibbs free energy is known as a function of pressure and temperature, then all thermodynamic properties of the system can be calculated. One could calculate the entropy:

$$\left( \frac{\partial G}{\partial T} \right)_p = -S \quad (4.98)$$

and the volume:

$$\left( \frac{\partial G}{\partial p} \right)_T = V \quad (4.99)$$

directly as derivatives of  $G(p, T)$ . This last equation establishes a relation between volume, pressure, and temperature, so it constitutes the equation of state. Once  $S$  and  $V$  are known, the enthalpy:

$$H = G + TS = G - T \left( \frac{\partial G}{\partial T} \right)_p \quad (4.100)$$

the Helmholtz free energy:

$$A = G + pV = G + p \left( \frac{\partial G}{\partial p} \right)_T \quad (4.101)$$

the internal energy:

$$U = H + pV = G - T \left( \frac{\partial G}{\partial T} \right)_p + p \left( \frac{\partial G}{\partial p} \right)_T \quad (4.102)$$

can also be obtained from  $G(p, T)$  and its derivatives. From these, all the other thermodynamic properties follow. In general, a state function whose knowledge in terms of its **natural variables** completely determines all thermodynamic properties in a system is known as a **thermodynamic potential**. The Gibbs free energy is a thermodynamic potential in terms of its natural variables  $T$  and  $p$ . The natural variables of a thermodynamic potential are those appearing in the corresponding fundamental relations (Eqs. 4.41 to 4.44). The natural variables also appear in the corresponding statement of the second law in terms of a particular thermodynamic potential; for instance, a process in a closed system at constant  $T$  and  $p$  decreases  $G$ .  $U(V, S)$ ,  $F(V, T)$ , and  $H(p, S)$  are also thermodynamic potentials in closed one-component systems.

## 4.7 Chemical Potential

The fundamental equations (Eq. 4.41 to 4.44) are not applicable to open systems. We consider now a system whose composition is changing either because a chemical reaction is happening or because a mass transfer inside the system, or between the system and its surroundings, is occurring.

**Homogeneous system.** Consider a homogeneous (one-phase) system of any kind (open or closed) with  $k$  components that undergoes a chemical reaction or is exchanging matter with its surroundings. We assume the system is in mechanical and thermal equilibrium, so the pressure and temperature in the system are well defined. The system's thermodynamic state is given by  $T$ ,  $p$ , and the amount of each component,  $n_1, \dots, n_k$ . Since the Gibbs free energy is a state function, it must be a function of all these variables,  $G(T, p, n_1, \dots, n_k)$ . The differential of  $G$  is:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \sum_{i=1}^k \left(\frac{\partial G}{\partial n_i}\right)_{T,n_j \neq i} dn_i \quad (4.103)$$

For the first two partial derivatives, the fact that we are taking constant  $n_i$  for every component  $i$  means we are considering a constant composition. This means that the system behaves like a closed system in material equilibrium, which is also in thermal and mechanical equilibrium by our previous hypotheses. Therefore, the temperature and pressure derivative of  $G$  are given by Eq. 4.52 for a reversible process:

$$\left(\frac{\partial G}{\partial T}\right)_{p,n_i} = -S \quad (4.104)$$

$$\left(\frac{\partial G}{\partial p}\right)_{T,n_i} = V \quad (4.105)$$

Substituting:

$$dG = -SdT + Vdp + \sum_{i=1}^k \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j \neq i} dn_i \quad (4.106)$$

We define the **chemical potential** of component  $i$  as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j \neq i} \quad (4.107)$$

With this definition,  $dG$  can be written as:

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i \quad (4.108)$$

This equation, which is fundamental in chemical thermodynamics, is valid for a homogeneous system in thermal and mechanical equilibrium undergoing p–V work only. In particular, note that this equation is valid even if the system is not in material equilibrium, in other words, if there is a chemical reaction or exchange of matter inside the system or between the system and its surroundings.

Using the definition of the Gibbs free energy (Eq. 4.14),

$$G = U - TS + pV \quad (4.109)$$

$$dG = dU - TdS - SdT + pdV + Vdp \quad (4.110)$$

and substituting in Eq. 4.108 gives:

$$dU = TdS - pdV + \sum_i \mu_i dn_i \quad (4.111)$$

Doing the same thing for the enthalpy (Eq. 2.53) and the Hemlholtz free energy (Eq. 4.8) gives:

$$dH = TdS + Vdp + \sum_i \mu_i dn_i \quad (4.112)$$

$$dA = -SdT - pdV + \sum_i \mu_i dn_i \quad (4.113)$$

But the total differential of  $U$  can also be written as:

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V,n_i} dS + \left( \frac{\partial U}{\partial V} \right)_{S,n_i} dV + \sum_{i=1}^k \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_j \neq i} dn_i \quad (4.114)$$

Identifying the terms in this equation with those in Eq. 4.111, we have that the chemical potential can also be expressed as a derivative of the internal energy at constant  $S$  and  $V$ :

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_j \neq i} \quad (4.115)$$

Doing the same for the other state functions we find:

$$\mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n_j \neq i} = \left( \frac{\partial H}{\partial n_i} \right)_{S,p,n_j \neq i} = \left( \frac{\partial A}{\partial n_i} \right)_{T,V,n_j \neq i} = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq i} \quad (4.116)$$

The chemical potential of component  $i$  is always the derivative with respect to  $n_i$  of a suitable thermodynamic potential, but the derivative has to be taken with the potential's corresponding natural variables constant. The natural variables are given by the corresponding fundamental equation (Eqs. 4.41 to 4.44).

**Heterogeneous system.** Now we generalize Equation 4.108 by considering a heterogeneous system of any kind (open or closed), where several different phases exist. In a heterogeneous system, the composition is given by the amount of each component in each phase. We label phases with lowercase Greek letters ( $\alpha, \beta, \dots$ ). In this system, the thermodynamic state is determined by  $T, p$ , and the amounts of all components in all phases ( $n_1^\alpha, \dots, n_k^\alpha, n_1^\beta, \dots, n_k^\beta, \dots$ ), where  $n_i^\alpha$  is the amount of component  $i$  in phase  $\alpha$ .

The Gibbs free energy is extensive, so its value for the whole system equals the sum of the Gibbs energy for each phase:

$$G = \sum_{\alpha} G^{\alpha} \quad (4.117)$$

Consequently, the change in the free energy of the system equals the sum of the changes for each phase:

$$dG = \sum_{\alpha} dG^{\alpha} \quad (4.118)$$

Applying Eq. 4.108 to each phase individually, we have:

$$dG = \sum_{\alpha} -S^{\alpha}dT + V^{\alpha}dp + \sum_i \mu_i^{\alpha} dn_i^{\alpha} \quad (4.119)$$

$$= -SdT + Vdp + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha} \quad (4.120)$$

where we used that the entropy and the volume are also extensive properties ( $S = \sum_{\alpha} S^{\alpha}$  and  $V = \sum_{\alpha} V^{\alpha}$ ). Note that comparing this equation to the  $dG$  of the heterogeneous system, we can generalize the definition of chemical potential to a heterogeneous system as:

$$\mu_i^{\alpha} = \left( \frac{\partial G}{\partial n_i^{\alpha}} \right)_{T,p,n_j^{\beta} \neq n_i^{\alpha}} \quad (4.121)$$

where all amounts are fixed except for  $n_i^{\alpha}$ .

**Properties of the chemical potential.** The chemical potential,  $\mu_i^\alpha$ , is a derivative of  $G$  and, therefore,  $\mu_i^\alpha$  is a state function. Its units are energy divided by amount, J/mol in the SI. Since the chemical potential is the derivative of a extensive quantity with respect to another extensive quantity,  $\mu_i^\alpha$  is intensive. Because it does not depend on the total amount of substance in the system ( $n$ ), the chemical potential can be written as a function of  $T$ ,  $p$ , and the mole fractions of all the components:

$$\mu_i(T, p, x_1^\alpha, \dots) \quad (4.122)$$

The set of intensive thermodynamic properties that determine the state of the system except for its total amount  $n$  is known as the **intensive state** of the system. In this case, the intensive state is determined by  $T$ ,  $p$ ,  $x_1^\alpha$ , etc. We will see this again later.

As we shall see, the chemical potential is a measure of the escaping tendency of component  $i$  from phase  $\alpha$ . The higher the value of  $\mu_i^\alpha$ , the more the component wants to escape from the phase. An important point to note is that if the system is a pure substance (if there is only one component in the system), then the Gibbs free energy for the system is:

$$G = n_i G_{m,i} \quad (4.123)$$

and consequently:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p} = G_{m,i} \quad (4.124)$$

Therefore, in a pure substance, the chemical potential equals the molar Gibbs free energy. However, in mixtures this is no longer the case.

## 4.8 Material Equilibrium

### 4.8.1 Conditions for Equilibrium and Change

For a closed system with p–V work only and in thermal and mechanical equilibrium, but not necessarily in material equilibrium, we have (Eq. 4.13):

$$dG \leq -SdT + Vdp \quad (4.125)$$

where the equality corresponds to a reversible process. The  $dG$  from Eq. 4.120 is valid for this kind of system, and substitution leads to:

$$\sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha \leq 0 \quad (4.126)$$

where, again, the  $<$  sign corresponds to an irreversible process and equality is valid for a reversible process. At thermodynamic equilibrium, equivalent to material equilibrium in this case because we already assumed the system is in mechanical and thermal equilibrium, no further irreversible processes are possible, and:

$$\sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha = 0 \quad (4.127)$$

This is the general condition for material equilibrium in a closed system. In a closed system not in material equilibrium, the sum on the left-hand side of Eq. 4.126 must decrease. At equilibrium the equality in Eq. 4.127 holds. We now apply these conditions to two particularly important cases: phase equilibria and chemical reactions.

### 4.8.2 Phase Equilibrium

Consider a system that has one component  $i$  and two phases  $\alpha$  and  $\beta$ . For instance, ice in contact with liquid water at the normal melting point and 1 atm. The general equilibrium condition (Eq. 4.127) reduces to:

$$\mu_i^\alpha dn_i^\alpha + \mu_i^\beta dn_i^\beta = 0 \quad (4.128)$$

Component  $i$  can move only between phase  $\alpha$  and  $\beta$  so the amount of  $i$  gained by  $\alpha$  equals the amount lost by  $\beta$ :

$$dn_i^\alpha = -dn_i^\beta \quad (4.129)$$

Substitution in the equation above gives:

$$\mu_i^\alpha dn_i^\alpha + \mu_i^\beta dn_i^\beta = \mu_i^\alpha dn_i^\alpha - \mu_i^\beta dn_i^\alpha = (\mu_i^\alpha - \mu_i^\beta)dn_i^\alpha = 0 \quad (4.130)$$

At equilibrium, this equation must hold for any  $dn_i^\alpha$  so the equilibrium condition for this system becomes:

$$\mu_i^\alpha = \mu_i^\beta \quad (4.131)$$

Therefore, **two phases are in material equilibrium when their chemical potentials are equal.**

If the chemical potentials of the two phases are not equal, then substitution of Eq. 4.129 in Eq. 4.126 gives:

$$\mu_i^\alpha dn_i^\alpha + \mu_i^\beta dn_i^\beta = \mu_i^\alpha dn_i^\alpha - \mu_i^\beta dn_i^\alpha = (\mu_i^\alpha - \mu_i^\beta)dn_i^\alpha < 0 \quad (4.132)$$

If  $\mu_i^\alpha > \mu_i^\beta$ , then  $\mu_i^\alpha - \mu_i^\beta > 0$  and a spontaneous transfer of component  $i$  must have  $dn_i^\alpha < 0$ . Therefore, if the chemical potential of phase  $\alpha$  is greater than that of  $\beta$ ,  $\alpha$  loses component  $i$  to  $\beta$  spontaneously. Conversely, if  $\mu_i^\alpha < \mu_i^\beta$  then  $\mu_i^\alpha - \mu_i^\beta < 0$  and  $dn_i^\alpha > 0$  so if the chemical potential is higher in the  $\beta$  phase, then it spontaneously transfers component  $i$  to the  $\alpha$  phase.

It is possible to show that the chemical potential of a component in a phase always increases with the mole fraction of component:

$$\left( \frac{\partial \mu_i^\alpha}{\partial x_i^\alpha} \right)_{T,p,n_j^\alpha \neq i} > 0 \quad (4.133)$$

Therefore, as the transfer of component happens, the phase with higher chemical potential loses substance and its chemical potential decreases, while the other phase and increases in chemical potential. When the chemical potentials of the two phases equalize, the mass transfer stops and material equilibrium is reached (Eq. 4.131). In summary, **if two phases have different chemical potentials, mass is transferred from the phase with higher potential to the phase with lower potential until their chemical potentials equalize.**

---

**Example.** Consider a slightly soluble salt in contact with water. The chemical potential in the solid is constant and equal to its molar Gibbs free energy because the solid is a pure phase. The chemical potential of the salt in the liquid is at first very low and, as the salt dissolves, it increases. Once enough salt has dissolved, the chemical potentials of the solid and the dissolved salt in the liquid equalize and material equilibrium is reached.

---

The chemical potential behaves with respect to the amount of substance in the same way as pressure and temperature do regarding volume and heat flow. If we put two systems with different temperatures in contact via a thermally conducting wall, heat flows from the hotter to the colder system. If two systems with different pressures are put in contact via a movable wall, the system with the highest pressure expands and the other contracts. In the same way, if two phases are in contact via a permeable wall, mass is transferred from the phase with higher

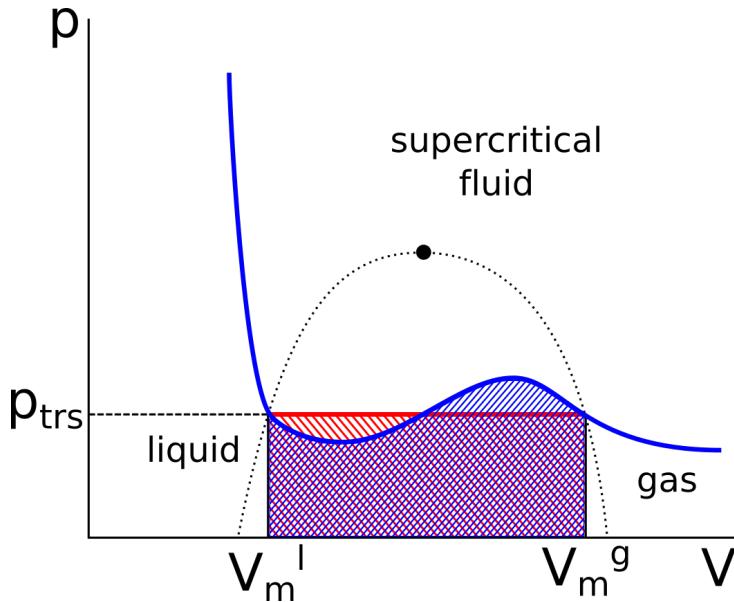


Figure 4.1: Area under the van der Waals isotherm (blue) and under the real system's isotherm (red), corresponding to the change in Helmholtz energy in the liquid-gas phase transition.

chemical potential to the phase with lower chemical potential until both equalize. An exception to this is when one of the components is missing from a phase. In that case, equilibrium can also be reached when the chemical potential of the phase where the component is absent is higher than the phase where it is present. In the example above, if the salt is completely insoluble the chemical potential of the salt in solution is higher than in the solid. Since there is no salt in solution, it cannot be transferred to the solid, so the system is at equilibrium with  $\mu_i^s < \mu_i^l$ .

The phase equilibrium condition in Eq. 4.131 can be applied to justify the Maxwell's equal-area construction used to rectify the spurious behavior of the van der Waals equation of state in the liquid-gas transition region (the van der Waals loops, Figure 1.8). In the transition region, we have:

$$\mu^g = G_m^g = G_m^l = \mu^l \quad (4.134)$$

Rearranging and using that the pressure of the liquid and the gas in the transition region is equal ( $p_{trs}$ ):

$$A_m^l + p_{trs}V_m^l = A_m^g + p_{trs}V_m^g \quad (4.135)$$

$$A_m^g - A_m^l = -p_{trs}(V_m^g - V_m^l) \quad (4.136)$$

At constant temperature,  $dA_m = -pdV_m$  (Eq. 4.43), so the molar Helmholtz free energy change between the liquid and the gas can also be written as:

$$A_m^g - A_m^l = \int_l^g dA_m = - \int_{V_m^l}^{V_m^g} p(V_m) dV_m \quad (4.137)$$

where  $p(V_m)$  is the isotherm pressure. Equating the two:

$$p_{trs}(V_m^g - V_m^l) = \int_{V_m^l}^{V_m^g} p(V_m) dV_m \quad (4.138)$$

The left hand side of this equation is the red area under the straight line in Figure 4.1, corresponding to the  $\Delta A$  for the gas to liquid transformation from the real system's isotherm,

which is simply a horizontal line. The right hand side of the equation is the blue area under the van der Waals isotherm, and corresponds to the  $\Delta A$  for the same transformation calculated for the van der Waals gas. If we want to find the transition pressure  $p_{trs}$ , arguably the most principled approach is to impose that the  $\Delta A$  for the liquefaction of the gas predicted by the van der Waals gas is the same as the experimental value. This requirement is met if the areas under the straight line (red) and the van der Waals isotherm (blue) are equal. Therefore, the areas above and below the straight line (red) up to van der Waals isotherm (blue) must be equal. Compare to Figure 1.8.

### 4.8.3 Reaction Equilibrium

Consider a chemical reaction:



in a homogeneous closed system with only p–V work and in thermal and mechanical equilibrium, but not necessarily in material equilibrium. If we consider some initial amount of each species  $n_i^0$  then, after some time has passed, the amount is:

$$n_i = n_i^0 + \nu_i \xi \quad (4.140)$$

where  $\xi$  is the **extent of the reaction**, a quantity with amount units (moles) that measures how far the reaction has progressed. Taking differentials:

$$dn_i = \nu_i d\xi \quad (4.141)$$

This equation and Eq. 4.140 reflect that the changes in the amount of substance for all species involved in a reaction is controlled by the stoichiometric coefficients. For instance, in the reaction:



for every mole of  $\text{O}_2$  consumed, two moles of  $\text{H}_2$  are consumed and two moles of  $\text{H}_2\text{O}$  are generated.

In a homogeneous system, the material equilibrium condition (Eq. 4.127) reads:

$$\sum_i \mu_i dn_i = 0 \quad (4.143)$$

where we dropped the phase superscripts for simplicity, since we are considering a one-phase system. Substituting the differential from Eq. 4.141:

$$\sum_i \mu_i dn_i = \left( \sum_i \nu_i \mu_i \right) d\xi = 0 \quad (4.144)$$

and since this equation must be valid for any  $d\xi \neq 0$ , the reaction equilibrium condition becomes:

$$\sum_i \nu_i \mu_i = 0 \quad (4.145)$$

For instance, in the water formation reaction above (Eq. 4.142), the equilibrium condition in terms of the chemical potentials of reactants and products is:

$$2\mu(\text{H}_2\text{O}) - 2\mu(\text{H}_2) - \mu(\text{O}_2) = 0 \quad (4.146)$$

or:

$$2\mu(\text{H}_2\text{O}) = 2\mu(\text{H}_2) + \mu(\text{O}_2) \quad (4.147)$$

For equilibrium to be reached in a chemical reaction, the sum of the chemical potentials of the reactants must equal the sum of the chemical potentials of the products, weighed with their stoichiometric coefficients. Note how this condition is very similar to the phase equilibrium condition in Eq. 4.131.

Furthermore, application of the same procedure to the equation for material change (Eq. 4.126) gives that for a spontaneous reaction:

$$\sum_i \mu_i dn_i = \left( \sum_i \nu_i \mu_i \right) d\xi < 0 \quad (4.148)$$

Since the stoichiometric coefficients for the reactants are negative and for those for the products are positive, the factor in parentheses can be written as:

$$\sum_i \nu_i \mu_i = \sum_i^{\text{products}} |\nu_i| \mu_i - \sum_i^{\text{reactants}} |\nu_i| \mu_i \quad (4.149)$$

If the chemical potential of the reactants outweighs that of the products, then:

$$\sum_i \nu_i \mu_i = \sum_i^{\text{products}} |\nu_i| \mu_i - \sum_i^{\text{reactants}} |\nu_i| \mu_i < 0 \quad (4.150)$$

and in order to fulfill the condition in Eq. 4.148 we must have  $d\xi > 0$ , and the reaction progresses in the forward direction (to the right, generating products). Conversely, if the chemical potential of reactants is lower than that of products, then

$$\sum_i \nu_i \mu_i = \sum_i^{\text{products}} |\nu_i| \mu_i - \sum_i^{\text{reactants}} |\nu_i| \mu_i > 0 \quad (4.151)$$

and we must have  $d\xi < 0$  and the reaction goes in the reverse direction (to the left, generating reactants). Once the chemical potentials of reactants and products equalize, or one of the reactants or products is exhausted, equilibrium is reached. The same observation regarding absent components in phase equilibria applies to reactions as well. Equilibrium can be reached when  $\mu_{\text{reactants}} > \mu_{\text{products}}$  if one or more of the reactants are absent from the system, perhaps because it has been consumed completely.

It is important to note that these equations, and in general any equilibrium criteria based on thermodynamic properties, control the spontaneity of a chemical or physical transformation, but not its velocity. For a chemical reaction to happen at all, the condition in Eq. 4.151 must be met. However, even if this condition is met the reaction may be so slow that, for all purposes, it will never happen. One example is the formation of ammonia from N<sub>2</sub> and H<sub>2</sub>, which is spontaneous but so slow that it does not happen unless catalyzed. The same observation applies to phase equilibria. For instance, at ambient conditions the graphite allotrope of carbon is more stable than the diamond allotrope, but the transformation between them is so slow that it is not observable.

## 4.9 Ideal Gas Mixtures

### 4.9.1 Chemical Potential

For a pure ideal gas, the chemical potential equals the molar Gibbs free energy ( $G_m = \mu$ ) so Eq. 4.97 can also be written as:

$$\mu(T, p) = \mu^\circ(T) + RT \ln \left( \frac{p}{p^\circ} \right) \quad (4.152)$$

where  $\mu^\circ$  depends only on temperature because it corresponds to the same ideal gas at a pressure of  $p^\circ = 1$  bar. An **ideal gas mixture** is a gas mixture in which the ideal gas equation of state ( $pV = nRT$  with  $n = \sum_i n_i$ , Eq. 1.18) holds, and therefore Dalton's law ( $p_i = n_i RT/V$ , Eq. 1.24, where  $p_i = x_i p$  is the partial pressure of component  $i$ ) also applies. In an ideal gas mixture, each component behaves as if it were alone in the container, so the thermodynamic properties of a given component  $i$  are the same as the pure component at the same temperature and pressure  $p_i$ . In particular, the chemical potential of any component in an ideal gas mixture is:

$$\mu_i(T, p, x_1, \dots) = \mu_i^*(T, p_i) = \mu_i^\circ(T) + RT \ln \left( \frac{p_i}{p^\circ} \right) \quad (4.153)$$

In a mixture, the \* symbol is used to represent that a thermodynamic property (the chemical potential in this case) refers to the corresponding pure component. The standard state of a gas in an ideal gas mixture is the same as for a pure ideal gas, namely the pure ideal gas at 1 bar and temperature  $T$ .

Equation 4.153 can be taken as the definition of an ideal gas mixture because, as we shall see, all thermodynamic properties of the mixture can be derived from it. In fact, complete knowledge of the chemical potentials of all components in any mixture completely determines its thermodynamic behavior, for the same reason that complete knowledge of  $G(T, p)$  in a one-component closed system allows the calculation of all the other thermodynamic properties. In particular, it is possible to show that any extensive thermodynamic property of an ideal gas mixture can be written as the sum of the corresponding properties of the pure ideal gases at their partial pressures and the same temperature.

#### 4.9.2 Chemical Reactions

Consider a chemical reaction:



happening between gases in an ideal gas mixture at constant temperature and pressure. The standard reaction Gibbs free energy is:

$$\Delta_r G^\circ = \sum_i \nu_i G_{m,i}^\circ = \sum_i \nu_i \mu_i^\circ \quad (4.155)$$

because the  $\Delta_r G^\circ$  refers to the conversion of reactants to products separated and in their standard states. If reactants and products are separated, they are pure substances, and therefore  $G_{m,i} = \mu_i$ . The equilibrium condition for this reaction is (Eq. 4.145):

$$\sum_i \nu_i \mu_i = 0 \quad (4.156)$$

Substitution of the chemical potentials for the components of an ideal gas mixture (Eq. 4.153) gives:

$$0 = \sum_i \nu_i \left[ \mu_i^\circ + RT \ln \left( \frac{p_i^{\text{eq}}}{p^\circ} \right) \right] = \sum_i \nu_i \mu_i^\circ + \sum_i \nu_i RT \ln \left( \frac{p_i^{\text{eq}}}{p^\circ} \right) \quad (4.157)$$

where we used the “eq” superscript to denote the partial pressures at equilibrium. In the last equation, the first term on the right hand side is  $\Delta_r G^\circ$  (Eq. 4.155), so we can rewrite it as:

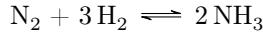
$$\Delta_r G^\circ = -RT \sum_i \nu_i \ln \left( \frac{p_i^{\text{eq}}}{p^\circ} \right) = -RT \ln \prod_i \left( \frac{p_i^{\text{eq}}}{p^\circ} \right)^{\nu_i} = -RT \ln K_p^\circ \quad (4.158)$$

where  $K_p^\circ$  is the **standard (pressure) equilibrium constant**, defined as:

$$K_p^\circ = \prod_i \left( \frac{p_i^{\text{eq}}}{p^\circ} \right)^{\nu_i} \quad (4.159)$$

The standard equilibrium constant is an adimensional quantity that relates the partial pressures at equilibrium of all species involved in a reaction between gases in an ideal gas mixture at constant temperature and pressure. Since  $\nu_i$  is positive for products and negative for reactants, it has the familiar law of mass action form.

**Example.** For the synthesis of ammonia reaction:



the standard equilibrium constant is:

$$K_p^\circ = \frac{\left( \frac{p_{\text{NH}_3}^{\text{eq}}}{p^\circ} \right)^2}{\left( \frac{p_{\text{H}_2}^{\text{eq}}}{p^\circ} \right)^3 \left( \frac{p_{\text{N}_2}^{\text{eq}}}{p^\circ} \right)}$$

Because the partial pressures are positive,  $K_p^\circ$  is a positive quantity. If  $K_p^\circ$  is very large, the numerator is much greater than the denominator, so the partial pressures of products are much higher than those of reactants, and the equilibrium is shifted to the right. Conversely, if  $K_p^\circ$  is close to zero, the denominator is much greater than the numerator, the partial pressures of reactants are higher than the products, and the equilibrium is shifted to the left.

Equation 4.158 gives the relation between the standard equilibrium constant and the free energy of reaction:

$$K_p^\circ = \exp \left( -\frac{\Delta_r G^\circ}{RT} \right) \quad (4.160)$$

We can see that if  $\Delta_r G^\circ \ll 0$ ,  $K_p^\circ \gg 1$  and the equilibrium is shifted to the products.

Conversely, if  $\Delta_r G^\circ \gg 0$ ,  $K_p^\circ \ll 1$  and the equilibrium is shifted to the reactants. Note that the  $RT$  in the denominator of the exponential is  $0.59 \text{ kcal/mol} = 2.48 \text{ kJ/mol}$  at room temperature, which is a relatively small energy. A change of as little as  $1.7 \text{ kJ/mol}$  in the  $\Delta_r G^\circ$  results in  $K_p^\circ$  doubling its value at that temperature. Commonly, equilibrium constants of reactions are calculated using  $\Delta_r G^\circ$  obtained by combining the formation free energies ( $\Delta_f G^\circ$ , Eq. 4.32) of reactants and products, which are in turn obtained from thermodynamic tables. Because of the sensitivity to errors in  $\Delta_r G^\circ$ , very accurate formation energy data is required to obtain reliable  $K_p^\circ$ . Often, reliable formation energy data is not available, because typical experimental errors in the formation energies and enthalpies are in the order of tenths to a few  $\text{kJ/mol}$ .

In an ideal gas mixture, the standard chemical potentials ( $\mu_i^\circ(T)$ ) are functions of temperature only because the standard state is set at a pressure of 1 bar. Therefore, the standard Gibbs free energy of reaction ( $\Delta_r G^\circ$ ) is also a function of temperature only and, because of Eq. 4.160, so is  $K_p^\circ(T)$ . In particular,  $K_p^\circ$  is independent of the total pressure of the mixture and of the individual component concentrations. However, note that this applies only to ideal gas mixtures, and only to real gas mixtures in the limit of zero pressure.

A reaction is **exergonic** (or **exoergic**) if  $\Delta_r G^\circ < 0$  and it is **endergonic** (or **endoergic**) if  $\Delta_r G^\circ > 0$ . An exergonic reaction is spontaneous in the sense that, in general, as it progresses towards equilibrium, products are generated from reactants, since  $K_p^\circ > 1$ . In an endergonic reaction, in general, reactants are formed from products, since  $K_p^\circ < 1$ . If we are interested in whether a given reaction can be used to synthesize a particular product, a  $\Delta_r G^\circ < 0$  is a necessary condition because otherwise products will not be significantly generated. However,

$\Delta_r G^\circ < 0$  does not guarantee that a reaction will happen because the standard equilibrium constant and  $\Delta_r G^\circ$  do not carry any information about the rate of a reaction. A reaction may be spontaneous but so slow that products are never formed.

Lastly, the standard reaction Gibbs free energy can be written in terms of the standard reaction enthalpy and entropy:

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad (4.161)$$

At room temperature,  $\Delta_r H^\circ$  usually dominates so exothermic reactions are often spontaneous. At higher temperatures, the entropy term dominates, and the reaction may become spontaneous at increasing temperature if  $\Delta_r S^\circ > 0$ . In reactions involving gases,  $\Delta_r S^\circ > 0$  happens if there is a net generation of gas molecules in the reaction:

$$\Delta\nu = \sum_i \nu_i > 0 \quad (4.162)$$

This is why decomposition reactions are favored at high temperature. For instance, the decomposition of N<sub>2</sub>:



is very endothermic because the triple bond in N<sub>2</sub> is very strong. However, it is spontaneous at several thousand kelvin because  $\Delta\nu = 2 - 1 = 1 > 0$  and therefore  $\Delta_r S^\circ > 0$ , so the entropy term eventually dominates the  $\Delta_r H^\circ > 0$  on increasing temperature.

**Example.** The synthesis of ammonia:



is one of the most important industrial reactions today because ammonia is the key precursor for manufacturing fertilizer, which in turn is essential in order to maintain the world's food supply. The ammonia synthesis reaction is exothermic ( $\Delta_r H^\circ = -91.8 \text{ kJ/mol}$ ), so it is spontaneous at low temperature. However, there are more reactant than product gas molecules ( $\Delta\nu = 2 - 3 - 1 = -2 < 0$ ), so it stops being spontaneous at high temperature. In addition, the reaction at low temperature is slow because of the difficulty in breaking the N<sub>2</sub> triple bond, so high temperatures are required to obtain product at a reasonable rate. Therefore, there is a trade-off between the  $\Delta_r G^\circ$  of the reaction (which is more negative at low temperatures) and the rate of the reaction (faster at higher temperatures). A careful combination of reaction conditions, including temperature and pressure, as well as a catalyst is used in industrial practice, in what is known as the **Haber-Bosch process**. The catalyst, in general iron oxide manufactured in a very specific way for this reaction, increases the reaction rate but does not change the thermodynamic reaction properties  $\Delta_r G^\circ$  and  $\Delta_r H^\circ$ .

Occasionally, alternative versions of the standard pressure equilibrium constant  $K_p^\circ$  (Eq. 4.159) are used. The pressure equilibrium constant:

$$K_p = \prod_i (p_i^{\text{eq}})^{\nu_i} \quad (4.165)$$

is similar to  $K_p^\circ$  but it is not adimensional. It has units of pressure to the  $\Delta\nu = \sum_i \nu_i$  power and, like  $K_p^\circ$ , it depends on temperature only. Additionally, we can write the partial pressures as:

$$p_i = \frac{n_i RT}{V} = c_i RT \quad (4.166)$$

and the standard pressure equilibrium constant is:

$$K_p^\circ = \prod_i \left( \frac{p_i^{\text{eq}}}{p^\circ} \right)^{\nu_i} = \prod_i \left( \frac{c_i^{\text{eq}} RT c^\circ}{p^\circ c^\circ} \right)^{\nu_i} = \left( \frac{RT c^\circ}{p^\circ} \right)^{\Delta\nu} \prod_i \left( \frac{c_i^{\text{eq}}}{c^\circ} \right)^{\nu_i} = \left( \frac{RT c^\circ}{p^\circ} \right)^{\Delta\nu} K_c^\circ \quad (4.167)$$

where  $c^\circ = 1 \text{ M}$  and we defined the standard concentration equilibrium constant as:

$$K_c^\circ = \prod_i \left( \frac{c_i^{\text{eq}}}{c^\circ} \right)^{\nu_i} \quad (4.168)$$

The  $K_c^\circ$  is adimensional and, since  $(RTc^\circ/p^\circ)$  is a function of temperature,  $K_c^\circ$  is a function of temperature only. Nevertheless, because the standard state of gases is  $p = p^\circ$ , the only equilibrium constant that is directly related to  $\Delta_r G^\circ$  in a gas mixture is  $K_p^\circ$  (Eq. 4.158). Therefore, using  $K_p^\circ$  for gas mixtures in which a reaction is taking place at constant temperature and pressure is more natural than any of the alternatives.

#### 4.9.3 Temperature Dependence of the Equilibrium Constant

The standard equilibrium constant is (Eq. 4.158):

$$\ln K_p^\circ = -\frac{\Delta_r G^\circ}{RT} \quad (4.169)$$

and its temperature dependence is given by:

$$\frac{d \ln K_p^\circ}{dT} = -\frac{1}{R} \frac{d(\Delta_r G^\circ/T)}{dT} = \frac{\Delta_r H^\circ}{RT^2} \quad (4.170)$$

where we used the Gibbs-Helmholtz equation (Eq. 4.91). This is known as the **van't Hoff equation**. If the temperature change is small and we assume  $\Delta_r H^\circ$  is approximately constant, we can integrate this equation to find:

$$\ln \left( \frac{K_p^\circ(T_2)}{K_p^\circ(T_1)} \right) \approx \frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4.171)$$

In a reacting ideal gas mixture, if we apply a temperature change at constant pressure, the van't Hoff equation (Eq. 4.170) says that the change in standard equilibrium constant is:

$$\frac{dK_p^\circ}{dT} = K_p^\circ \frac{d \ln K_p^\circ}{dT} = \frac{K_p^\circ \Delta_r H^\circ}{RT^2} \quad (4.172)$$

But the  $K_p^\circ/RT^2$  factor on the right hand side is always positive. If the reaction is endothermic ( $\Delta_r H^\circ > 0$ ), the equilibrium constant increases with increasing temperature ( $dK_p^\circ/dT > 0$ ), and the equilibrium shifts towards the products. Conversely, if the reaction is exothermic ( $\Delta_r H^\circ < 0$ ), the equilibrium constant decreases with increasing temperature ( $dK_p^\circ/dT < 0$ ), and the equilibrium shifts towards the reactants. Therefore, in a closed system, a change in temperature at constant pressure shifts the equilibrium in the direction that tends to “counteract” the temperature shift. An increase in temperature shifts the equilibrium towards the products if the reaction is endothermic and towards the reactants if it is exothermic.

#### 4.9.4 Le Chatelier's Principle

We have just shown that a reacting ideal gas mixture in a closed system subjected to an isobaric temperature change shifts its  $K_p^\circ$  in the direction that counteracts the temperature change. A similar effect happens for changes in pressure ( $p$ ) and concentration ( $x_i$ ). However, since  $K_p^\circ$  depends only on temperature, changes in  $p$  and  $x_i$  do not modify the equilibrium constant, only the equilibrium partial pressures. To quantify this shift in partial pressures, we define the **standard (pressure) reaction quotient** as:

$$Q_p^\circ = \prod_i \left( \frac{p_i}{p^\circ} \right)^{\nu_i} \quad (4.173)$$

The definition of the quotient is the same as  $K_p^\circ$  (Eq. 4.159) except the partial pressures and not the equilibrium partial pressures. If  $Q_p^\circ = K_p^\circ$ , the system is at equilibrium. If  $Q_p^\circ < K_p^\circ$ , the numerator (products) in the reaction quotient is too small compared to the denominator (reactants) and the reaction proceeds to the right and generates more product to reach equilibrium. Conversely, if  $Q_p^\circ > K_p^\circ$ , the numerator (products) is too large compared to the denominator (reactants) and the reaction must progress towards the reactants to reach equilibrium. Similar reaction quotients can be defined for the other equilibrium constants ( $Q_p$ ,  $Q_c^\circ, \dots$ ).

Let us consider an isothermal change in pressure in a system at equilibrium, from pressure  $p^{\text{eq}}$  to  $p' = \alpha p^{\text{eq}}$  where  $\alpha > 1$  for a compression and  $\alpha < 1$  for an expansion. We can bring about this change in an ideal gas mixture, for instance, by changing the volume of the container where the reaction is taking place. Note that the pressure change is done in such a way that the mole fractions ( $x_i$ ) are not affected. Because  $K_p^\circ$  is a function of temperature only, it is not modified by the change in pressure. The new reaction quotient is:

$$Q_p' = \prod_i \left( \frac{p'_i}{p^\circ} \right)^{\nu_i} = \prod_i \left( \frac{x_i p'}{p^\circ} \right)^{\nu_i} = \prod_i \left( \frac{x_i p^{\text{eq}} \alpha}{p^\circ} \right)^{\nu_i} = \alpha^{\Delta\nu} \prod_i \left( \frac{p_i^{\text{eq}}}{p^\circ} \right)^{\nu_i} = \alpha^{\Delta\nu} K_p^\circ \quad (4.174)$$

where  $\Delta\nu = \sum_i \nu_i$ . In the case of a compression ( $\alpha > 1$ ),

- If there are more product than reactant molecules ( $\Delta\nu > 0$ ), the reaction quotient increases, and the reaction moves to the left (generates reactants).
- If there are more reactant than product molecules ( $\Delta\nu < 0$ ), the reaction quotient decreases, and the reaction moves to the right (generates products).
- If the number of reactant and product molecules are equal ( $\Delta\nu = 0$ ), the reaction quotient is unchanged.

In summary, an isothermal change in pressure makes the reaction shift in the direction that decreases the number of gas molecules (i.e. the system's volume), if the pressure increases, or increases the number of gas molecule (i.e. the system's volume) if the pressure decreases.

Lastly, let us consider the case in which we introduce more gas into the mixture at equilibrium at constant temperature and volume. As before, this does not alter the equilibrium constant  $K_p^\circ$  because it is a function of temperature only. If the added gas is inert, the partial pressures in the ideal gas mixture, which are the pressure the components would have in isolation, do not change and, therefore, the equilibrium is not affected. If, on the other hand, we add one of the reactants or products, the reaction quotient changes and the reaction shifts in the direction that consumes the species we introduced in order to restore equilibrium. (This is only the case if the gas is introduced at constant temperature and volume. Otherwise, if the volume changes, the partial pressure of all the other components change as well.)

The preceding results can be summarized as:

- If temperature changes at constant pressure, equilibrium shifts in the direction in which the system absorbs or releases heat to counteract the temperature change.
- If pressure changes at constant temperature, the reaction moves in the direction that decreases (compression) or increases (expansion) the number of gas molecules (the system's volume).
- If a reactant is added at constant temperature and volume, the reaction generates products to restore equilibrium. If product is added, the reaction shifts to generate reactants. If inert gas is added, no further reaction happens.

The combination of these results is **Le Chatelier's principle**, which states that in a chemical reaction between gases at equilibrium the change in one of the variables makes the system evolve in the direction that counteracts that change.

# Chapter 5

## Phase Diagrams

### 5.1 Phase Diagram of a Pure Substance

#### 5.1.1 Definition and Features

For a system to be in material equilibrium, reaction and phase equilibria must happen concurrently. We now study phase equilibria for the particularly simple case of a pure substance. A pure substance may exist in one or more phases, depending on the values of the chemical potentials for each phase. Specifically, the thermodynamically stable phase of a pure substance is the phase with lowest chemical potential (Eq. 4.126). If the pure substance comprises more than one phase at equilibrium, then all phases in the system must have the same chemical potential (Eq. 4.131).

The **phase diagram** is a graphical representation that gives the thermodynamically stable phase of a system as a function of its state variables. A very common example is the pressure-temperature ( $p$ - $T$ ) phase diagram, where the stable phase is represented as a function of temperature and pressure. However, any two other state variables can be used to construct the phase diagram. In systems with more than one component, the composition may also be a variable in the phase diagram.

The  $p$ - $T$  phase diagram of carbon dioxide is shown in Figure 5.1. If, for instance, we set the pressure and temperature of pure CO<sub>2</sub> to those of point A ( $-120^{\circ}\text{C}$  and 10 kPa) then the thermodynamically stable form of CO<sub>2</sub> is a solid. On isobaric heating (dotted line), the point in the diagram representing the system moves to the right until it reaches the line that separates the solid and gas phases, known as the **phase boundary**. Both phases at a phase boundary have equal chemical potential and can coexist in equilibrium, and the energy that flows in or out of the system, either as heat or work, is used to effect the transition. In this case, the heat absorbed by the system at the solid/gas phase boundary results in the transformation of solid into gas at constant temperature. The process in which one phase is converted into a different phase is known as a **phase transition** and, in a pure substance at a fixed pressure, it occurs at a single temperature, known as the **transition temperature** ( $T_{\text{trs}}$ ). Once all the solid has been converted into gas, further heat absorption by the system results in an increase in temperature until point B is reached.

Some transitions in a one-component phase diagram receive specific names. The transition from solid to liquid is known as **melting** or **fusion**. The temperature at which melting occurs at 1 atm is the **normal melting point** and the melting temperature at 1 bar is the **standard melting point**. The reverse transformation (from liquid to solid) is known as **freezing**, and the normal melting point is sometimes known as the normal freezing point. The phase transition from liquid to gas is known as **boiling** and the reverse (gas to liquid) is

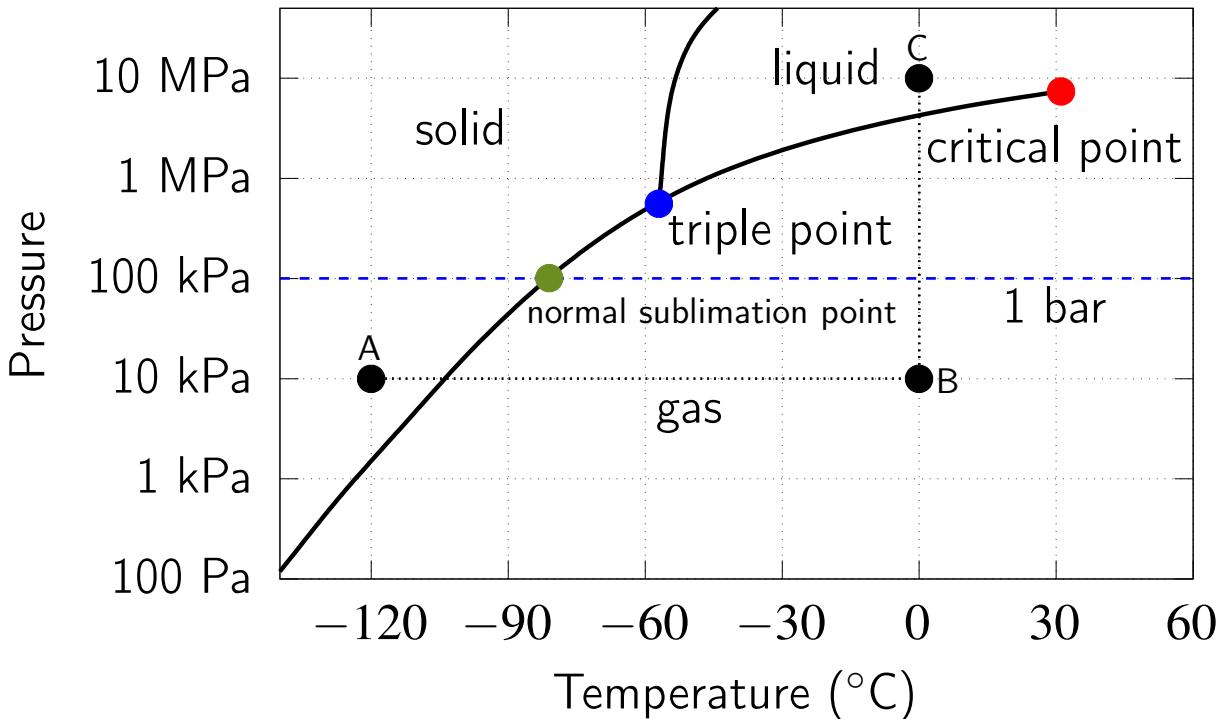


Figure 5.1: The phase diagram of carbon dioxide. Note the pressure scale is logarithmic. The normal sublimation point (green) is at  $-78.5^{\circ}\text{C}$  and 1 atm. The triple point (blue) is at  $-56.6^{\circ}\text{C}$  and 5.11 atm. The critical point (red) is at  $31.0^{\circ}\text{C}$  and 72.8 atm.

**condensation.** The transition from solid to gas is known as **sublimation** and the reverse transition (gas to solid) is a **deposition**. Normal and standard transition temperatures can be defined for all these transformations, corresponding to the transition temperatures at 1 atm and 1 bar, respectively. For instance, the **normal boiling point** of water is  $99.97^{\circ}\text{C}$  and its standard boiling point is  $99.61^{\circ}\text{C}$ . The normal sublimation point of  $\text{CO}_2$  is shown in green in Figure 5.1. The changes in thermodynamic properties for these transitions (transition enthalpy, entropy, etc.) have specific subscripts, shown in Table 2.2. In the case of solid-solid phase transitions, which are fairly common under high pressure, the generic “trs” (transition) subscript is used instead.

At point C in the phase diagram (Figure 5.1), carbon dioxide is stable as a liquid. Assume we place  $\text{CO}_2$  under the conditions of point C in a closed container with empty space above the liquid filled with inert gas, which we may use to control the pressure exerted on the liquid. Because the chemical potential of  $\text{CO}_2$  in the gas phase is lower the smaller the  $\text{CO}_2$  partial pressure (Eq. 4.97), some of the  $\text{CO}_2$  evaporates from the liquid into the gas phase until the  $\text{CO}_2$  chemical potential in both phases equalize. At equilibrium, we have:

$$\mu_l = \mu_g = \mu_g^\circ + RT \ln \left( \frac{p_v}{p^\circ} \right)$$

where we assume ideal behavior of the gas and used Eq. 4.153 for the chemical potential of a gas in an ideal gas mixture. The partial pressure exerted by the  $\text{CO}_2$  in contact with the liquid is its **vapor pressure**.

At point C, the total pressure exerted on the system equals the vapor pressure of  $\text{CO}_2$  plus the partial pressure of the inserted inert gas. Now we slowly release the pressure on the system by removing some of the inert gas and the system moves down the dotted line in the phase diagram. Once all inert gas has been removed, the pressure exerted on the liquid equals the vapor pressure and, therefore, molecules from the bulk of the liquid can escape freely and move

into the gas phase. Consequently, bubbles start forming throughout the liquid, and the liquid boils. Because at the liquid-gas phase boundary the system's pressure equals the vapor pressure, the liquid-gas phase boundary can be read both as a) **the vapor pressure of a liquid as a function of temperature** (in absence of additional external pressure), and b) **the boiling temperature of the liquid as a function of pressure**. Using the same arguments, the solid-gas line gives the **sublimation vapor pressure**, the pressure of the gas in equilibrium with the solid as a function of temperature in absence of additional external pressure.

There are some significant points with fixed temperature and pressure in the phase diagram of a pure substance. The **critical point** is the end point of the liquid-gas phase boundary, and marks the point at which the distinction between liquid and gas disappears (see Section 1.5.1). The critical point has fixed temperature (the critical temperature,  $T_c$ ) and pressure (the critical pressure,  $p_c$ ), and it is marked in red in Figure 5.1 for CO<sub>2</sub>. Above the critical temperature, the gas cannot be liquefied by compression and above the critical pressure, the liquid does not boil upon heating. Note that it is possible to transform a liquid into a gas, and vice versa, without a phase transition by having the system go around the critical point.

At temperatures and pressures above that of the critical point, the system behaves differently from a gas or a liquid. This aggregation state is known as a **supercritical fluid**. A supercritical fluid behaves, in general, as a liquid in which molecules have additional room for flowing. As a result, the properties of a supercritical fluid are different from either a gas or a liquid. In particular, it diffuses faster and has lower viscosity than the liquid, which has led to the use of supercritical fluids as solvents. For instance, supercritical CO<sub>2</sub> has been used to extract caffeine from coffee to make decaf and in the preparation of aerogels. The properties of a supercritical fluid close to the critical point are also tunable because they are very sensitive to temperature and pressure.

Solid, liquid, and gas coexist at a single point in the phase diagram known as the **triple point**, with fixed temperature  $T_3$  and pressure  $p_3$ . The triple point for CO<sub>2</sub> is shown as a blue dot in Figure 5.1. The triple point temperature is the lowest temperature at which the liquid phase can exist. If the slope of the solid-liquid line is positive, as is the case in most substances, the triple point pressure is also the lowest pressure at which the liquid phase can exist. In the particular case of carbon dioxide, the triple point is at a pressure higher than 1 atm, which means that the solid sublimes into gas without forming the liquid (hence the term “dry ice” for solid CO<sub>2</sub>). Compressed bottles contain liquid CO<sub>2</sub> which upon expansion to atmospheric pressure cool and form solid CO<sub>2</sub>, which is a common way of making dry ice.

The phase diagram of water is shown in Figure 5.2. In this case, the pressure range is extended to cover multiple high-pressure polymorphs of ice. A **polymorph** is each one among the several possible solid forms a pure substance can take. Polymorphism is very common and, for instance, many minerals show many different polymorphs that are stable at ambient conditions. Examples include the calcite and aragonite polymorphs of CaCO<sub>3</sub> and the multiple polymorphs of silica:  $\alpha$ -quartz,  $\beta$ -quartz, tridymite, cristobalite, coesite,... Many elements show polymorphism as well. The different forms (solid, liquid, or gas) of an element are known as **allotropes**. For instance, O<sub>2</sub> and O<sub>3</sub>, both gases, are allotropes of oxygen, and the polymorphs diamond and graphite, both solids, are allotropes of carbon.

In the case of water (Figure 5.2), the stable solid form at low temperature and ambient pressure commonly encountered is ice Ih, where the “h” refers to its hexagonal crystal structure. However, there are up to 20 different known ice phases, most of them occurring under extremely high pressure. Note that the existence of multiple solid forms in the phase diagram implies that the diagram has multiple triple points, not just the one corresponding to the solid-liquid-gas coexistence conditions.

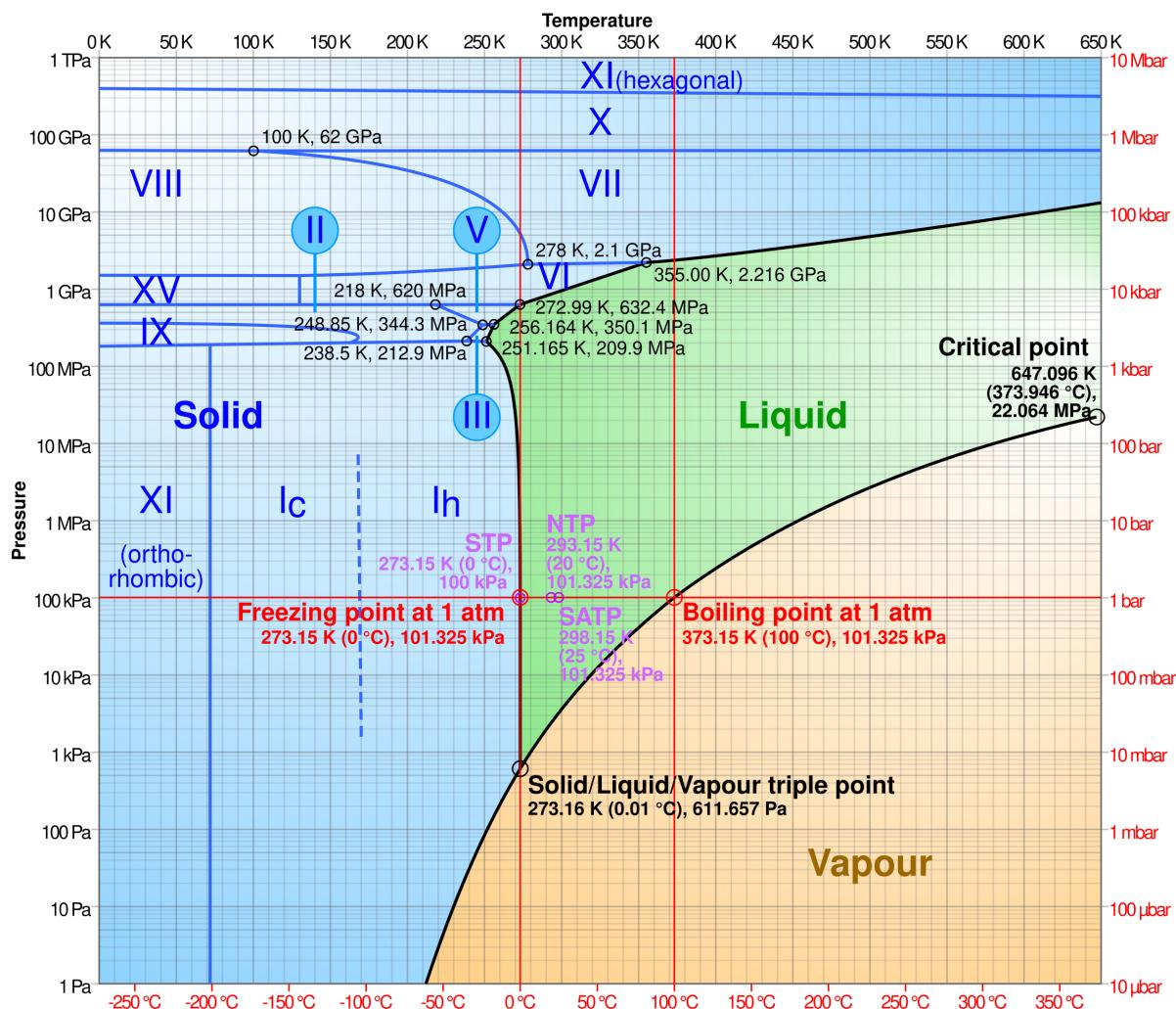


Figure 5.2: The phase diagram of water. Note the pressure scale is logarithmic. (Copyright Wikimedia Commons, User:Cmglee, CC-BY-SA-3.0.)

As mentioned before, a phase diagram shows only the thermodynamically stable phase, but other phases may coexist if the transformation to the stable phase is sufficiently slow. A phase is **metastable** if there is a different phase with lower  $G$  but the phase transition is so slow that the metastable phase does not transform. Metastable phases are very common in solid-solid phase transitions, where the transformation between different solid structures has a significant kinetic barrier and is often very slow. For instance, diamond is metastable at ambient conditions with respect to graphite because the transformation from one to the other is extremely slow.

Another example of metastability is supercooling and superheating of liquids. A liquid is **supercooled** if its temperature is below its freezing point and it is **superheated** if it is above its boiling point. The phenomenon of supercooling is important, for instance, in meteorology because clouds in the upper troposphere (7 to 12 km) often contain supercooled water droplets. Gases can also exist in metastable form; in this case, they are known as **supersaturated** vapors. The microscopic explanation for why supercooled liquids exist is that crystallization occurs by nucleation and growth. During the nucleation process, small thermodynamically stable nuclei are formed, which then undergo growth to form the macroscopic solid. In absence of a seed around which crystallization can occur, nuclei large enough to be stable may not form. This is why crystallization can be helped by adding a small seed, usually of the same solid, to the system.

### 5.1.2 Phase Boundaries

The phase boundaries in a phase diagram are determined by the condition that the chemical potentials of the two phases in equilibrium are equal:

$$\mu^\alpha(p, T) = \mu^\beta(p, T) \quad (5.1)$$

If we move reversibly along the phase boundary by an infinitesimal amount, the chemical potentials change by  $d\mu^\alpha$  and  $d\mu^\beta$ , and since we are still on the phase boundary:

$$\mu^\alpha + d\mu^\alpha = \mu^\beta + d\mu^\beta \quad (5.2)$$

Combining the last two equations:

$$d\mu^\alpha = d\mu^\beta \quad (5.3)$$

For a pure substance,  $\mu = G_m$ , and we can apply the fundamental relation (Eq. 4.44) to each of the phases:

$$V_m^\alpha dp - S_m^\alpha dT = V_m^\beta dp - S_m^\beta dT \quad (5.4)$$

Rearranging:

$$(S_m^\beta - S_m^\alpha)dT = (V_m^\beta - V_m^\alpha)dp \quad (5.5)$$

where the quantities in parentheses are the entropy and volume change for the transition:

$$\Delta_{trs}SdT = \Delta_{trs}Vdp \quad (5.6)$$

Solving this equation gives the slope of the boundary in the  $p$ - $T$  phase diagram is:

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} \quad (5.7)$$

which is known as the **Clapeyron equation**. The entropy change is related to the enthalpy of the transition,  $\Delta_{trs}H$  by Eq. 3.63. Therefore, this equation can also be written as:

$$\frac{dp}{dT} = \frac{\Delta_{trs}H}{T_{trs}\Delta_{trs}V} \quad (5.8)$$

The Clapeyron equation is exact and applies to the phase boundary of any transition in the  $p$ - $T$  phase diagram of a pure substance. It can be used to predict the dependence of transition temperatures with pressure as well as the vapor pressure of a liquid or solid as a function of temperature.

**Solid-liquid boundary.** The slope of the melting line is given by:

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}\Delta_{\text{fus}}V} \quad (5.9)$$

The enthalpy of fusion,  $\Delta_{\text{fus}}H$ , is almost always positive—fusion is endothermic, except for solid  ${}^3\text{He}$ , a stable but rare isotope of helium, under certain conditions. The change in volume during fusion,  $\Delta_{\text{fus}}V$ , is usually positive with the notable exception of water and a few other substances like Bi and Ge, in which the liquid is denser than the solid. In addition, since the change in volume between liquid and solid is relatively small and  $\Delta_{\text{fus}}V$  appears in the denominator, the solid-liquid line is quite steep (has a large slope). Note how the melting line is almost vertical and has a negative slope in the water phase diagram (Figure 5.2) but a positive slope in the  $\text{CO}_2$  diagram (Figure 5.1). The change in the melting point with pressure,  $dT/dp$ , is the inverse of Eq. 5.9. Since the transition line is approximately vertical,  $dT/dp$  for the solid-liquid transition is very low and the melting point is mostly unaffected by pressure.

**Liquid-gas boundary.** The slope of the liquid-gas line is given by:

$$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V} \quad (5.10)$$

The  $\Delta_{\text{vap}}H$  is always positive and  $\Delta_{\text{vap}}V$  is always positive and large because molar volumes of gases are much greater than molar volumes of liquids. Therefore, the slope of the liquid-gas boundary is positive but less steep than in the case of the melting line, and the boiling point is affected by the external pressure a lot more than the melting point. Compare the two in the phase diagrams of water (Figure 5.2) and  $\text{CO}_2$  (Figure 5.1).

In general, the molar volume of the gas is so much larger than the liquid that we can neglect  $V_m(\text{l})$  compared to  $V_m(\text{g})$ :

$$\Delta_{\text{vap}}V = V_m(\text{g}) - V_m(\text{l}) \approx V_m(\text{g}) \quad (5.11)$$

and, assuming ideal gas behavior of the gas phase:

$$\Delta_{\text{vap}}V \approx V_m(\text{g}) \approx \frac{RT}{p} \quad (5.12)$$

Substituting in Eq. 5.10,

$$\frac{dp}{dT} = \frac{p\Delta_{\text{vap}}H}{RT^2} \quad (5.13)$$

and rearranging:

$$\frac{d\ln p}{dT} = \frac{\Delta_{\text{vap}}H}{RT^2} \quad (5.14)$$

which is the **Clausius-Clapeyron equation**, which gives the variation of the vapor pressure of a liquid or a solid with temperature. (Remember that the  $p-T$  phase boundary for the liquid-gas transition gives the vapor pressure of the gas as a function of temperature.) Unlike the Clapeyron equation (Eq. 5.8), this equation is an approximation and valid only for the liquid-gas and solid-gas boundaries. In addition, the Clausius-Clapeyron does not apply close to the critical point, because in that case the assumption that the gas phase behaves ideally is not justified. The Clausius-Clapeyron equation is often written in the alternative form:

$$\frac{d\ln p}{d(1/T)} = -\frac{\Delta_{\text{vap}}H}{R} \quad (5.15)$$

Application of the chain rule to the left hand side of this equation shows that it is equivalent to Eq. 5.14:

$$\frac{d\ln p}{d(1/T)} = \frac{d\ln p}{dT} \frac{dT}{d(1/T)} = \frac{\frac{d\ln p}{dT}}{\frac{d(1/T)}{dT}} = \frac{\frac{d\ln p}{dT}}{\frac{-1}{T^2}} = -T^2 \frac{d\ln p}{dT} \quad (5.16)$$

Assuming the vaporization enthalpy does not change significantly with temperature, we can integrate the Clausius-Clapeyron equation to give:

$$\ln\left(\frac{p}{p^*}\right) = -\frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right) \quad (5.17)$$

where  $p^*$  and  $T^*$  is some point on the liquid-gas phase boundary (for instance, 1 atm and the normal boiling point). Solving for  $p$  gives the explicit temperature dependence of the vapor pressure with temperature:

$$p = p^* \exp\left[-\frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \quad (5.18)$$

for reasonably small temperature ranges, where the transition enthalpy can be assumed to be approximately constant.

**Solid-gas boundary.** In this case, the phase boundary slope is:

$$\frac{dp}{dT} = \frac{\Delta_{\text{sub}}H}{T\Delta_{\text{sub}}V} \quad (5.19)$$

The sublimation enthalpy is positive and higher than the vaporization enthalpy because:

$$\Delta_{\text{sub}}H = \Delta_{\text{vap}}H + \Delta_{\text{fus}}H \quad (5.20)$$

and, as mentioned above,  $\Delta_{\text{vap}}H$  is positive and  $\Delta_{\text{fus}}H > 0$  almost always. As in the liquid-gas case, the  $\Delta_{\text{sub}}V$  is approximately equal to  $V_m(g)$ . The numerator on the right hand side of the Clapeyron equation is higher in the solid-gas than in the liquid gas transition because  $\Delta_{\text{sub}}H > \Delta_{\text{vap}}H$ , so the solid-gas boundary has a steeper slope than the liquid-gas boundary, but not as steep as the solid-liquid line. See the phase diagrams of water (Figure 5.2) and CO<sub>2</sub> (Figure 5.1). The Clausius-Clapeyron equation can be derived in the same way as in the case of the liquid-gas boundary to give:

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{sub}}H}{RT^2} \quad (5.21)$$

and its integrated form is:

$$p = p^* \exp\left[-\frac{\Delta_{\text{sub}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \quad (5.22)$$

where  $p^*$  and  $T^*$  is some point in the sublimation line. This last equation gives the vapor pressure of the solid as a function of temperature. Using statistical thermodynamics, it is possible to show that this line goes to  $p \rightarrow 0$  at  $T \rightarrow 0$ , if the solid is stable at those conditions.

### 5.1.3 Phase Transition Classification

Phase transitions can be classified based on the change in thermodynamic properties at the transition and, in particular, based on the derivatives of the chemical potential in what is known as the **Ehrenfest classification of phase transitions**. Consider the evolution of the chemical potential in a liquid-gas phase transition shown in Figure 5.3. The temperature derivative of the chemical potential is (Eq. 4.52):

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m \quad (5.23)$$

so the chemical potential decreases with increasing temperature because  $S_m$  is positive. Since the molar entropy of the gas is greater than the liquid, its slope is steeper, and the chemical

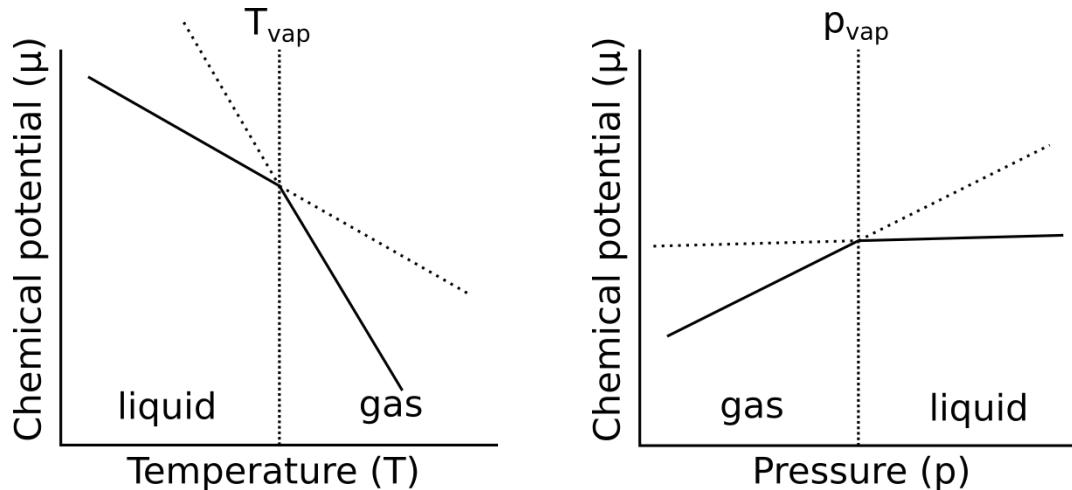


Figure 5.3: Evolution of the chemical potential as a function of temperature (left) and pressure (right) in a liquid-gas phase transition.

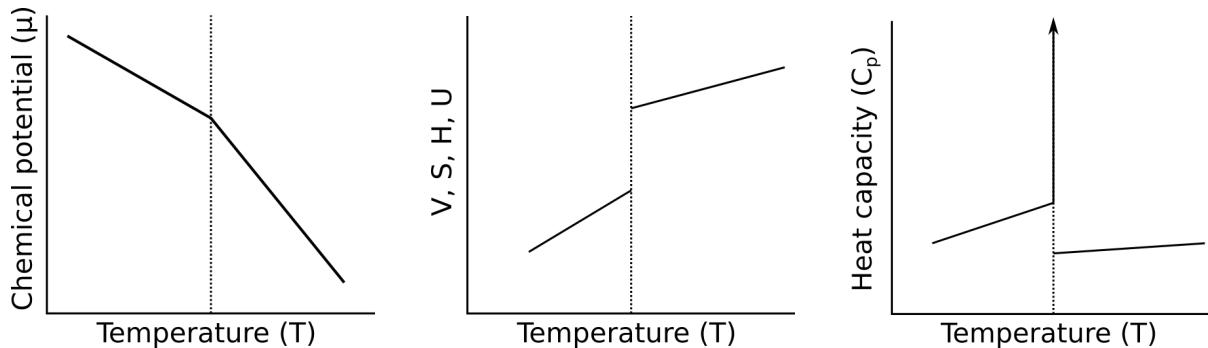


Figure 5.4: Evolution of the chemical potential (left), first derivatives of  $\mu$  such as volume, enthalpy, entropy, or internal energy (middle), and second derivatives of  $\mu$  such as the constant-pressure heat capacity (right) across a first-order phase transition.

potential curves for the liquid and the gas meet at the transition temperature, as shown in Figure 5.3. The dependence of the chemical potential with pressure is (Eq. 4.52):

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m \quad (5.24)$$

so, because the molar volume is positive,  $\mu$  increases during an isothermal compression. Because the molar volume of the gas is greater than that of the liquid, its slope is steeper, and the  $\mu(p)$  curves of liquid and gas meet at the transition pressure (right plot in Figure 5.3).

The characteristic feature of the pressure- or temperature-induced liquid-gas transition is that the chemical potential is continuous across the transition, but changes in slope. Therefore, the first derivatives of the chemical potential with respect to pressure ( $V_m$ , Eq. 5.24) and temperature ( $S_m$ , Eq. 5.23) are discontinuous at the transition, and  $\Delta_{\text{trs}}V \neq 0$  and  $\Delta_{\text{trs}}S \neq 0$ . This discontinuity also affects other properties that can be calculated by combining first derivatives of the chemical potential such as, for instance, the enthalpy (Eq. 3.63) so  $\Delta_{\text{trs}}H \neq 0$  as well. A phase transition where the first derivatives of the chemical potential are discontinuous is known as **first order** or **discontinuous** phase transition. A first-order phase transition has a non-zero change in volume and a latent heat (enthalpy change) associated with it. The two phases involved in a first-order phase transition coexist while the transition is happening. The familiar solid-liquid, solid-gas, and liquid-gas phase transitions are always first order.

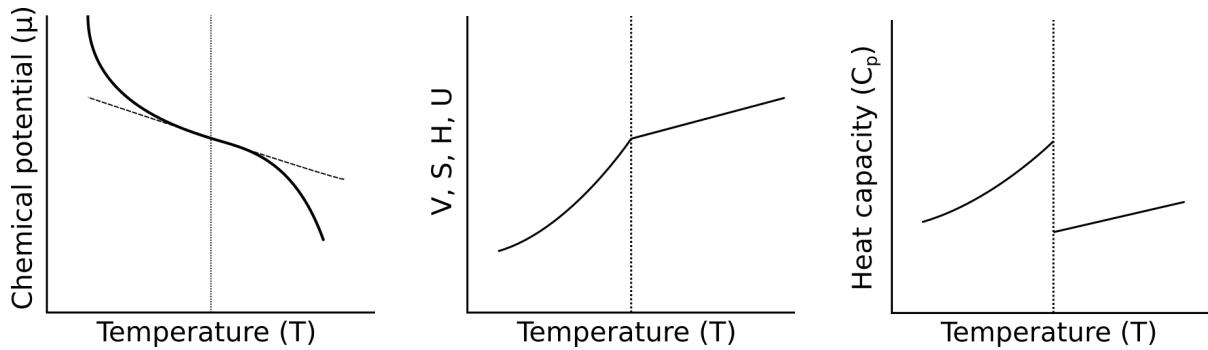


Figure 5.5: Evolution of the chemical potential (left), first derivatives of  $\mu$  such as volume, enthalpy, entropy, or internal energy (middle), and second derivatives of  $\mu$  such as the constant-pressure heat capacity (right) across a second-order phase transition.

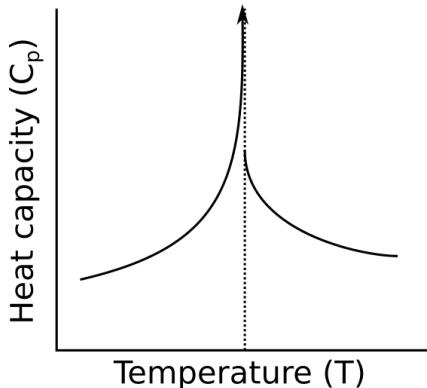


Figure 5.6: Heat capacity as a function of temperature across a lambda transition.

There are thermodynamic properties that are second derivatives of the chemical potential. For instance, the constant-pressure heat capacity ( $C_p$ ), is the temperature derivative of the entropy (Eq. 4.71), and is therefore a second derivative of  $\mu$  since  $S_m$  is a first temperature derivative already. The entropy is already discontinuous at the transition and, consequently, since the heat capacity is its derivative,  $C_p$  has a singularity. This can be understood by noting that a first-order phase transition has an associated enthalpy change. While the transition is happening, heat is absorbed or released by the system but its temperature does not change. Therefore, the heat capacity at the transition is infinite (see Figure 5.4).

Phase transitions that have no associated latent heat or volume change ( $\Delta H = \Delta V = 0$ ) are known as **higher-order** or **continuous**. In these transitions, the chemical potential has an inflection point, as shown in Figure 5.5, which causes a change in slope, but not a discontinuity, in the first derivatives (enthalpy, entropy, volume,...). The heat capacity, which is a second derivative of the chemical potential, shows a discontinuity at the transition, but not a singularity. Because the enthalpy and volume changes are both zero, the Clapeyron equation (Eq. 5.8) does not apply to higher-order phase transitions. Higher-order phase transitions can be further classified into **second-order**, where the heat capacity has a finite discontinuity at the transition, and **lambda transitions**, where the heat capacity diverges at the transition, showing a characteristic curve like the Greek letter lambda (Figure 5.6). Examples of higher-order transitions include:

- The ferromagnetic to paramagnetic transition in iron and other ferromagnetic materials. At low temperature, ferromagnetic materials have magnetic domains where the atomic magnetic moments are aligned and pointing in the same direction. This ferromagnetic order is energetically favorable but has lower entropy than the paramagnetic state, where

the atomic moments are disordered. When the temperature is increased, the entropy contribution to the free energy ( $T\Delta S$ ) increases in importance and at a certain temperature, known as the **Curie temperature**, the order of the magnetic moments is lost and the material stops being ferromagnetic.

- Conductor-superconductor transitions at low temperature. Many metals undergo a transition to a superconducting state at low temperature, in which their electrical resistance drops to exactly zero.
- Order-disorder transitions. For instance, brass is an alloy of copper and zinc. In the structure of  $\beta$ -brass at low temperature, each Zn is surrounded by eight Cu atoms and each Cu is surrounded by eight Zn atoms, in an ordered crystalline arrangement. As temperature increases, the entropy term in the free energy favors the onset of atomic disorder, where Cu and Zn exchange positions in the crystal at random. At the transition temperature (739 K), the system becomes completely disordered. Another example is the ammonium chloride crystal ( $\text{NH}_4\text{Cl}$ ), where at low temperature the four protons in  $\text{NH}_4^+$  point towards the neighboring  $\text{Cl}^-$  anions. At the order-disorder transition temperature, the protons break away from those directions and the  $\text{NH}_4^+$  rotates freely.

Sometimes higher-order transitions are referred to as second-order transitions in the literature, i.e. no distinction is made with lambda transitions.

## 5.2 The Phase Rule

We now calculate how many variables determine the thermodynamic state of a system as a function of the number of phases and components in it. Instead of considering the thermodynamic state of the system itself, which depends on the size of the system, we consider its **intensive state**, the set of all intensive thermodynamic properties in the system. The intensive state completely specifies the thermodynamic state, except for the total amount of matter ( $n$ ) in the system. The reason for using the intensive state is that the amount of substance in each phase is irrelevant regarding its position in a  $p$ – $T$  phase diagram, since both pressure and temperature are intensive properties.

In a system with  $P$  phases and  $C$  components at equilibrium, the intensive state is determined by at least two variables: temperature ( $T$ ) and pressure ( $p$ ). These variables are the same throughout the system because all phases are in equilibrium. In addition, the mole fraction of each component  $i$  in each phase  $\alpha$  ( $x_i^\alpha$ ) is required to determine the composition. However, we only need the mole fractions of all components minus one since the mole fraction of the last component equals one minus the sum of all other mole fractions:

$$x_1^\alpha + \dots + x_C^\alpha = 1, \text{ for every phase } \alpha \quad (5.25)$$

Therefore, for a system with  $P$  phases and  $C$  components, we need  $P(C - 1) + 2$  intensive variables to determine the intensive state: temperature, pressure, and  $C - 1$  mole fractions for each of the  $P$  phases.

Since the system has  $P$  phases and is at equilibrium, the chemical potentials for all components in those phases must be equal (Eq. 4.131):

$$\begin{aligned} \mu_1^\alpha &= \mu_1^\beta & \mu_1^\alpha &= \mu_1^\gamma & \dots & \mu_1^\alpha &= \mu_1^\zeta \\ \mu_2^\alpha &= \mu_2^\beta & \mu_2^\alpha &= \mu_2^\gamma & \dots & \mu_2^\alpha &= \mu_2^\zeta \\ &\dots&&\dots&&\dots&\dots\\ \mu_C^\alpha &= \mu_C^\beta & \mu_C^\alpha &= \mu_C^\gamma & \dots & \mu_C^\alpha &= \mu_C^\zeta \end{aligned} \quad (5.26)$$

There are  $(P - 1)C$  equations relating the chemical potentials of the different phases. These equations act as constraints and reduce the number of **degrees of freedom** ( $F$ ), the independent intensive variables required to determine the intensive state of the system. We can find the number of degrees of freedom by subtracting the number of constraints from the number of intensive variables:

$$\begin{aligned} F &= P(C - 1) + 2 - (P - 1)C = PC - P + 2 - PC + C \\ F &= C - P + 2 \end{aligned} \quad (5.27)$$

This is the **phase rule**, valid for a closed system at equilibrium with only  $p$ - $V$  work, and in which there are no walls physically separating the phases. The phase rule states that the number of independent intensive variables that determine the intensive state ( $F$ ) equals the number of components minus the number of phases plus two.

Let us apply the phase rule to the phase diagram of carbon dioxide (Figure 5.1), which is a one-component system ( $C = 1$ ). If there is a single phase in the system ( $P = 1$ ), then the number of degrees of freedom is:

$$F = 1 - 1 + 2 = 2 \quad (5.28)$$

so two variables determine the intensive state of the system, in this case, temperature and pressure. We can change  $T$  and  $p$  and change the thermodynamic state of the system but remain within the stability range of the same phase.

If we have two phases in equilibrium (for instance, solid and gas),  $P = 2$  and:

$$F = 1 - 2 + 2 = 1 \quad (5.29)$$

so only one intensive variable determines the intensive state. We can either change the temperature or the pressure but the other variable is determined by the solid-gas line in the phase diagram. Lastly, if three phases (solid, liquid, and gas) are at equilibrium, then:

$$F = 1 - 3 + 2 = 0 \quad (5.30)$$

There are no degrees of freedom, meaning that the temperature and pressure at the triple point have fixed values. Any change in temperature or pressure in the system will make it move away from the triple point and lose at least one of the phases in equilibrium. The phase rule says that it is not possible that four or more phases coexist in equilibrium in this phase diagram because  $F$  cannot be negative. Also, since there is at least one phase  $P > 0$ , at most two variables are required to determine the intensive state of a pure substance.

The application of the phase rule is slightly more complicated if there are reactions present. For every independent reaction in the system, we have one additional constraint of the type (Eq. 4.145):

$$\sum_i \nu_i \mu_i = 0 \quad (5.31)$$

(A set of chemical reactions is independent if none of them can be written as linear combination of the others.) In addition, some reactions often impose additional balance of mass and electroneutrality constraints. For instance, if we dissolve HCN in water, the dissociation reaction is:



and the self-ionization of water reaction is:



These two reactions impose two constraints based on the chemical potentials:

$$\mu(\text{CN}^-) + \mu(\text{H}^+) = \mu(\text{HCN}) \quad (5.34)$$

and:

$$\mu(\text{H}^+) + \mu(\text{OH}^-) = \mu(\text{H}_2\text{O}) \quad (5.35)$$

and the solution must be neutral so the amount of positive and negative charges must be equal:

$$n(\text{H}^+) = n(\text{OH}^-) + n(\text{CN}^-) \quad (5.36)$$

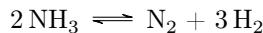
or, dividing by the total amount:

$$x(\text{H}^+) = x(\text{OH}^-) + x(\text{CN}^-) \quad (5.37)$$

which is an additional constraint on the intensive variables.

The simplest way to take into account these additional constraints is to count the number of **independent components**. In this example, out of the five possible components in the system ( $\text{HCN}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ , and  $\text{CN}^-$ ) only two are independent ( $\text{HCN}$  and  $\text{H}_2\text{O}$ ) because the other three are generated by reactions happening within the system and, as we have seen, there are three additional constraints that determine the amount of each of the three dependent components. To apply the phase rule in the presence of reactions, use the number of independent components as  $C$  in the phase rule equation (Eq. 5.27).

**Example.** In the ammonia decomposition reaction:



we have three components ( $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$ ) but there are two additional constraints, namely, the relation between the chemical potentials:

$$\mu(\text{N}_2) + 3\mu(\text{H}_2) = 2\mu(\text{NH}_3)$$

and, if the system started only with an initial amount of ammonia, there is also a balance of mass condition:

$$n(\text{N}_2) = 3n(\text{H}_2)$$

or, dividing by the total amount,

$$x(\text{N}_2) = 3x(\text{H}_2)$$

so there is only one independent component ( $\text{NH}_3$ ).

## 5.3 Binary Phase Diagrams

A **binary system** is a system with two components (A and B). Using the phase rule, we have  $C = 2$  and  $F = 4 - P$ , so we can have at most 3 degrees of freedom, when the system contains a single phase. To make a bi-dimensional representation of the phase diagram we choose two of the three degrees of freedom (for instance,  $T$  and  $x_A$  or  $p$  and  $x_A$ ) and fix the remaining one. The temperature-composition at atmospheric pressure and the pressure-composition at room temperature binary phase diagrams are commonly represented.

### 5.3.1 Liquid-Vapor Phase Diagrams

Figure 5.7 shows model temperature-mole fraction ( $T$ - $x$ ) and pressure-mole fraction ( $p$ - $x$ ) phase diagrams for two miscible liquids as well as the equivalent experimental diagrams for the acetone-ethanol system. In these diagrams the  $x$  axis represents the overall mole fraction of one of the components (A). The left edge of the diagram corresponds to pure B ( $x_A = 0$ ) and the

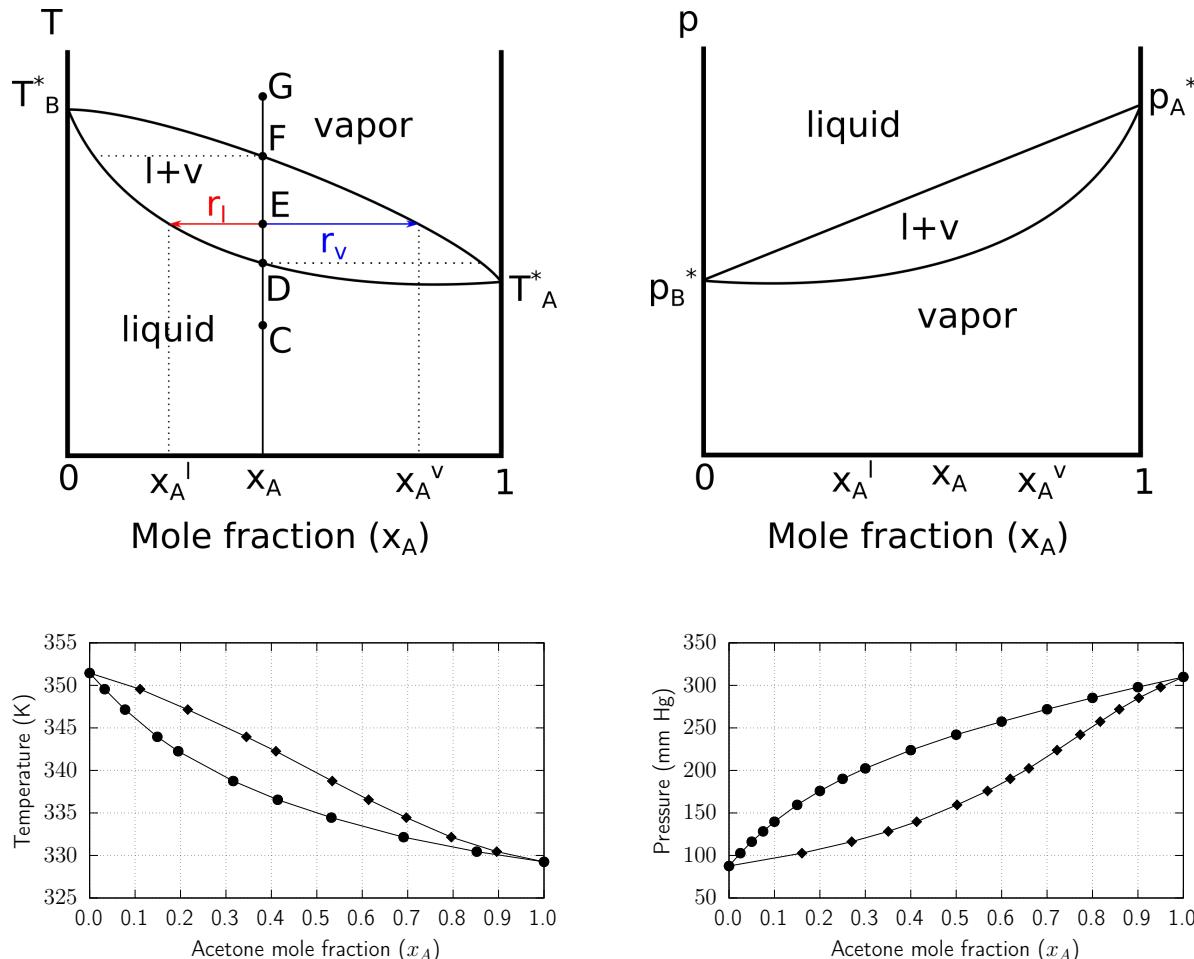


Figure 5.7: Idealized temperature-composition (top left) and pressure-composition (top right) binary diagrams for two completely miscible liquids. Bottom left: experimental temperature-composition phase diagram for the acetone/ethanol mixture from Amer et al. “Methanol-ethanol-acetone vapor-liquid equilibria”, *Ind. Eng. Chem.* **48** 142 (1956) (retrieved via the [Dortmund Data Bank](#)). Bottom right: experimental pressure-composition phase diagram for the acetone/ethanol mixture from Gordon and Hines “Liquid-vapour equilibrium for the system ethanol-acetone”, *Can. J. Res.* **24** 254 (1946).

right edge to pure A ( $x_B = 0$ ). The liquid-vapor transitions indicated at those edges correspond to the single boiling temperature ( $T$ - $x$  diagram) or the vapor pressure ( $p$ - $x$  diagram) of the pure components, B on the left and A on the right of the diagram. In these diagrams, A is the more volatile compound because  $T_A^* < T_B^*$  and its vapor pressure at room temperature is higher ( $p_A^* > p_B^*$ ). For any mixture with composition intermediate between pure A and pure B, there is a temperature range over which the transition is effected, and the extent of this temperature range depends on the particular composition of the mixture.

We focus for now on the  $T$ - $x$  diagram; the following discussion is applicable to the  $p$ - $x$  diagram as well. At any point in the diagram, the system composition is determined by four amounts:  $n_A^l$ ,  $n_B^l$ ,  $n_A^v$ , and  $n_B^v$ , which correspond to the number of moles of A and B in the liquid and vapor phases. In the one-phase regions of the phase diagram, either  $n_A^l = n_B^l = 0$ , if the system is a gas, or  $n_A^v = n_B^v = 0$ , if it is a liquid.

The total amounts of A and B are:

$$n_A = n_A^l + n_A^v \quad ; \quad n_B = n_B^l + n_B^v \quad (5.38)$$

The total amounts of liquid and vapor are:

$$n^l = n_A^l + n_B^l \quad ; \quad n^v = n_A^v + n_B^v \quad (5.39)$$

And the total number of moles in the system is:

$$n = n^l + n^v = n_A + n_B = n_A^l + n_B^l + n_A^v + n_B^v \quad (5.40)$$

The mole fractions of the components in the liquid and vapor phases are:

$$x_A^l = \frac{n_A^l}{n^l} = \frac{n_A^l}{n_A^l + n_B^l} \quad ; \quad x_B^l = \frac{n_B^l}{n^l} = \frac{n_B^l}{n_A^l + n_B^l} \quad (5.41)$$

$$x_A^v = \frac{n_A^v}{n^v} = \frac{n_A^v}{n_A^v + n_B^v} \quad ; \quad x_B^v = \frac{n_B^v}{n^v} = \frac{n_B^v}{n_A^v + n_B^v} \quad (5.42)$$

And, finally, the overall mole fraction is:

$$x_A = \frac{n_A}{n_A + n_B} = \frac{n_A^l + n_A^v}{n_A^l + n_A^v + n_B^l + n_B^v} \quad (5.43)$$

The bottom curve in the  $T$ - $x$  diagram of Figure 5.7 that separates the two-phase (liquid+vapor) region from the one-phase liquid region gives the boiling point of the solution as a function of overall composition  $x_A$ , so it is known as the **boiling-point curve**. At point D on this curve, there is only liquid and a very small amount of vapor, both in equilibrium.

Therefore, this curve also gives the temperature at which a liquid of composition  $x_A^l = x_A$  is in equilibrium with its vapor. Similarly, the top curve (the **condensation-point curve**) in the diagram represents the temperature at which a vapor with overall mole fraction  $x_A$  starts condensing or, equivalently, the temperature at which a vapor with mole fraction  $x_A^v = x_A$  is in equilibrium with the liquid.

Assume the system is at point C. At this temperature, the system is a liquid with overall composition  $x_A^l = x_A$ . Now we isobarically increase the temperature at constant composition, following the CDEFG line (a constant-composition line is called an **isopleth**). At point D, the vapor pressure of the solution equals the system's pressure and therefore the liquid starts boiling. Contrary to what happens in a pure liquid, the boiling does not happen at constant temperature and, as the temperature is increased further, the liquid is converted into vapor and the composition of both liquid and vapor change. At point F, all liquid disappears and the

system transforms into a gaseous single phase at the same mole fraction as the starting point ( $x_A = x_A^v$ ).

Consider an arbitrary point E inside the two-phase liquid+vapor region (Figure 5.7, top left). At this point, we have a liquid with mole fraction  $x_A^l$  in equilibrium with vapor with mole fraction  $x_A^v$ , and the system has overall mole fraction  $x_A$ . The concentration of the liquid in equilibrium with its vapor at this temperature is given by the boiling-point curve, so to find  $x_A^l$  at point E we need to trace a horizontal line left to the boiling-point curve, as done in the diagram. Similarly, the concentration of the vapor in equilibrium with the liquid at temperature  $T$  is given by the condensation-point curve, so to find  $x_A^v$  for this system we extend the horizontal line to the right until it intersects the condensation-point curve. This horizontal line is called a **tie line**. By the discussion above, the end points of the tie line give the mole fractions of the liquid and vapor phases at any point inside the two-phase liquid+vapor region.

The tie line can also be used to calculate the amounts of vapor and liquid in contact. To do this, we write:

$$x_A = \frac{n_A^l + n_A^v}{n_A^l + n_A^v + n_B^l + n_B^v} = \frac{n_A}{n^l + n^v} \quad (5.44)$$

Solving for  $n_A$ :

$$n_A = x_A n^l + x_A n^v \quad (5.45)$$

but  $n_A$  is also:

$$n_A = n_A^l + n_A^v = x_A^l n^l + x_A^v n^v \quad (5.46)$$

Equating the two, we find:

$$x_A n^l + x_A n^v = x_A^l n^l + x_A^v n^v \quad (5.47)$$

and rearranging:

$$n^l r_l = n^v r_v \quad (5.48)$$

where we defined:

$$r_l = x_A - x_A^l \quad ; \quad r_v = x_A^v - x_A \quad (5.49)$$

Note that  $r_l$  and  $r_v$  are the distances from the isopleth (the vertical line) along the tie line to the boiling-point and condensation-point curves, respectively (see Figure 5.7). Equation 5.48 is known as the **lever rule**, by analogy to the lever equation in physics. At any point in the two-phase liquid+vapor region **the mole fractions of liquid and vapor are given by the tie line endpoints and the amounts of liquid and vapor are inversely proportional to the distance to the corresponding phase boundary**. As the system progresses from point C to E to F in Figure 5.7, the amount of liquid ( $n^l$ ) decreases and, at the same time, the amount of vapor ( $n^v$ ) increases, as shown in the diagram.

Temperature-composition binary diagrams are important for understanding distillation, the main process used to separate two liquids with different boilings points. Consider a liquid within the  $T$ - $x$  phase diagram shown in Figure 5.8 with an initial mole fraction  $x_A$  and we are interested in separating the minority component (A) from the solution. The liquid is brought to boil and the vapor is removed from the system and condensed. The topmost tie line (in red) indicates that this vapor is enriched in the more volatile component (A) and its composition is given by  $x_1$  in the diagram. This process is known as a **simple distillation**.

If the vapor resulting from a simple distillation is cooled and condensed, following the vertical line at  $x_1$ , the distillation process can be repeated. This gives a second vapor phase with an even higher fraction of volatile component ( $x_2$ ). Subsequent distillation steps can be carried out to obtain fractions with composition  $x_3$ ,  $x_4$ , ... and ever increasing concentration of the volatile component A. This process is known as a **fractional distillation** and the number of steps in the process is known as the number of **theoretical plates**. Fractional distillation is

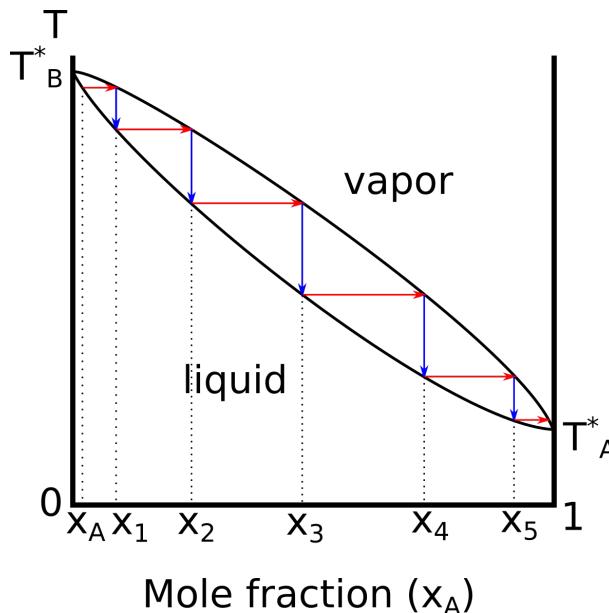


Figure 5.8: A temperature-composition phase diagram showing the fractional distillation of a binary mixture. The initial mole fraction is enriched in B ( $x_A$ ) and successive distillation steps are used to separate the more volatile component (A).

important in many industrial applications. For instance, in the petroleum industry, the fractional distillation (also known as refinement) of crude oil produces fuels and other products with different compositions and purposes. In increasing order of average molecular weight and decreasing order of volatility, the petroleum fractions are: gasoline, kerosene, diesel, fuel oil, and bitumen. Often, the “plates” involved in a fractional distillation are truly theoretical, and the consecutive boiling and condensation steps are effected by the packing material inside the distillation column.

Mixtures where there are sufficiently strong interactions between the component molecules of the two liquids may show a maximum or a minimum in their boiling-point curve, as depicted in Figure 5.9. In these diagrams there is a particular composition ( $x_A^{aze}$ ) for which the mixture boils at a single temperature generating vapor with the same composition as the liquid. This point is known as an **azeotrope**. If the intermolecular interactions between the liquids are more favorable than in the pure compounds, the liquid phase of the mixture is stabilized relative to the vapor and we have a “high-boiling” azeotrope at the maximum of the boiling-point curve, shown on the right of Figure 5.9. Conversely, if the interactions are unfavorable, the liquid mixture is destabilized compared to the gas and we have a minimum in the boiling-point curve, known as a “low-boiling” azeotrope (Figure 5.9 left). Note that, despite the fact that an azeotrope boils at a single temperature to a vapor that has the same composition as the liquid, it is still a binary mixture, not a pure compound. Azeotropes are important for fractional distillation because it is not possible to carry out the sequence of distillation steps (Figure 5.8) past an azeotrope. Therefore, the presence of an azeotrope marks the maximum concentration one can achieve from the distillation of a binary mixture. A well-known example of an azeotrope happens in the water/ethanol system at 96% in weight of ethanol. This is why ethanol available in drug stores always has this concentration.

### 5.3.2 Liquid-Liquid Phase Diagrams

In the previous section we assumed that the two liquids form a single phase at all compositions and temperatures, i.e. they are **completely miscible**. Depending on the nature and strength of the intermolecular interactions between the two compounds, this needs not be the case. Two

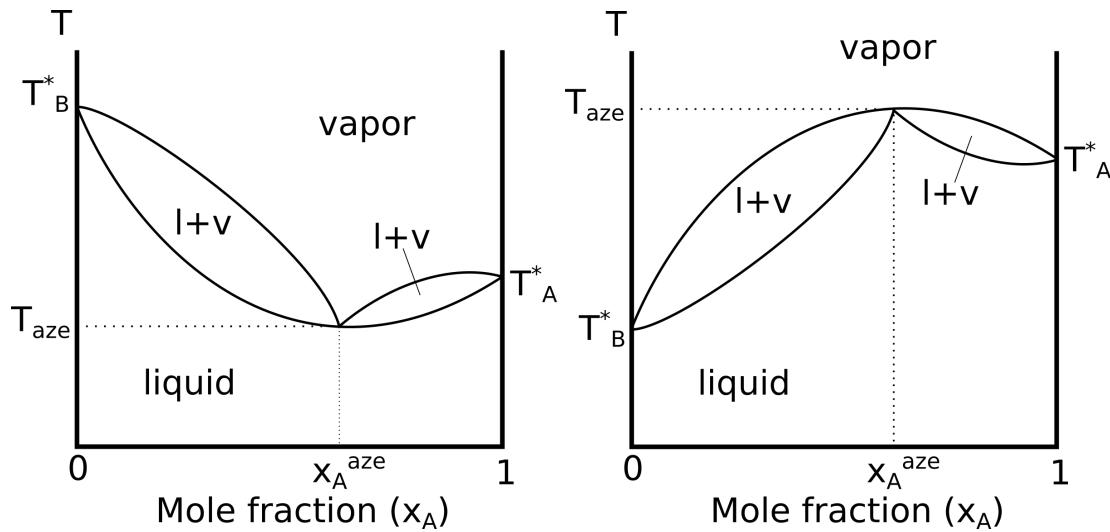


Figure 5.9: Temperature-composition diagrams with low-boiling (left) and high-boiling (right) azeotropes.

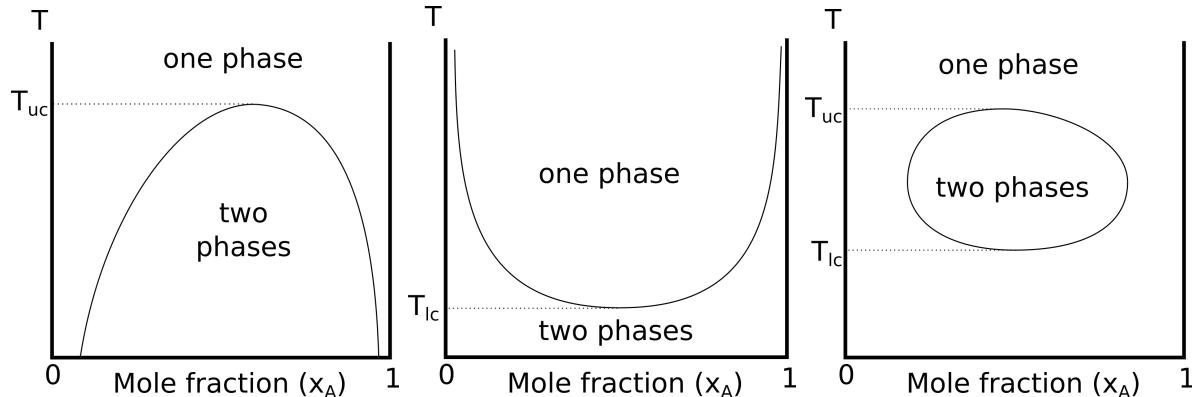


Figure 5.10: Three kinds of miscibility gaps in a temperature-composition phase diagram of two partially miscible liquids.

Liquids A and B are **partially miscible** if there is a composition range for which they form two distinct phases: a phase that is mostly A with a little B and another phase with mostly B and a little A. Liquids A and B are **inmiscible** if they remain in separate phases regardless of the overall composition of the mixture.

For partially miscible compounds, whether one or two phases are formed depends on temperature as well as composition. The regions in the  $T$ - $x$  phase diagram in which two partially miscible compounds separate into two liquid phases are known as the **miscibility gaps**. Typical shapes for the miscibility gaps are shown in Figure 5.10. The most usual case is shown on the left, where the two liquids are partially miscible at low temperature and become fully miscible past the **(upper) critical solution temperature** ( $T_{uc}$ ). The butanol/water system is an example of this behavior. It is also possible to have mixtures, as in the water/triethylamine system, where the miscibility decreases with temperature and the phase diagram shows a lower critical solution temperature  $T_{lc}$  (Figure 5.10 middle). Lastly, there are systems like water/nicotine, where the liquids are partially miscible only in a certain temperature range and present both an upper and a lower critical temperature (Figure 5.10 right). For a point within the two-phase region in any of these diagrams, the phase compositions and amounts are given by the horizontal tie lines and the lever rule, same as in Section 5.3.1.

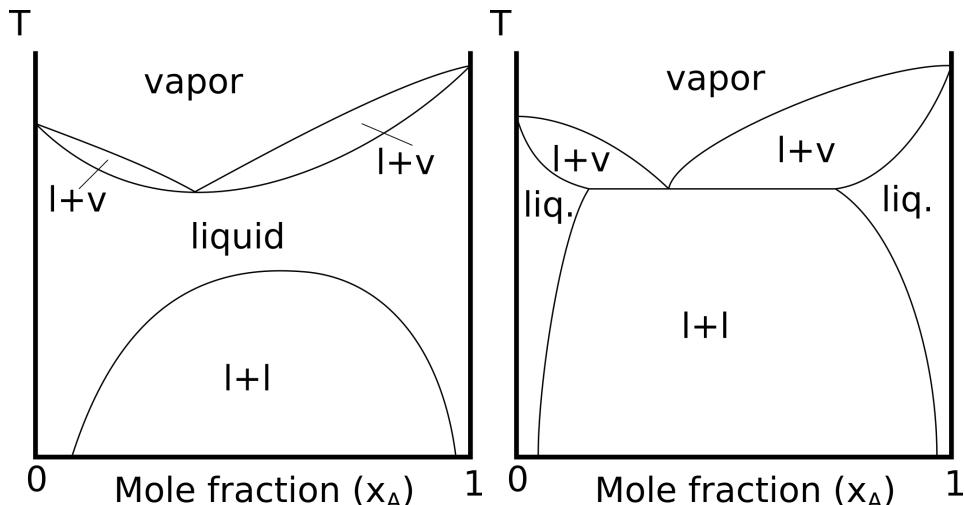


Figure 5.11: Model phase diagrams of two partially miscible liquids.

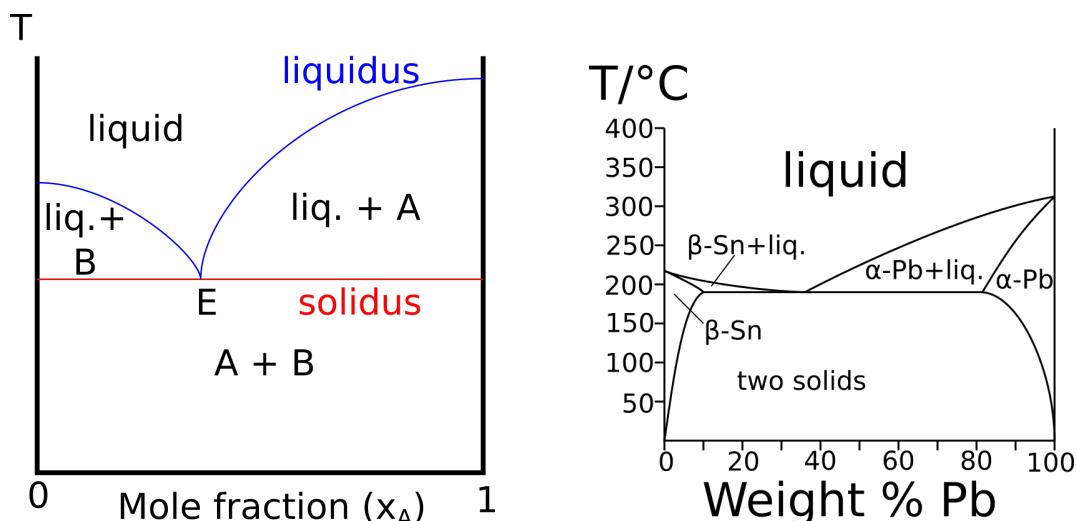


Figure 5.12: Left: Temperature-composition phase diagram for two non-reacting immiscible solids. Right: the experimental tin-lead phase diagram.

Partial miscibility of liquids can also affect the phase diagram close to the boiling point, as shown in Figure 5.11. If the miscibility gap is separated from the boiling-point curve, then the phase diagram is a simple combination of the two types of diagrams seen before (Figure 5.11, left). However, if the miscibility gap intersects the boiling-point curve, then a diagram like the one shown in Figure 5.11 (right) may be observed. In this system, the two-phase liquid solution boils directly, with the presence of an azeotrope at an intermediate composition.

### 5.3.3 Binary Phase Diagrams of Solids

We consider first the simple case of two immiscible solids that do not react with each other. A sketch of the temperature-composition phase diagram for this system is shown in Figure 5.12. This diagram has two-phase solid+liquid regions at either side of point E. When the liquid is cooled and the system enters one of these regions, a solid phase of pure A or B is formed and the system freezes over a temperature range. The phase boundary at which the first drop of liquid forms any of the solid phases is known as the **solidus line**. The phase boundary at which the first amount of solid forms from the liquid phase is known as the **liquidus line**.

Point E is a composition at the mixture of solids A and B melts at a single temperature into a

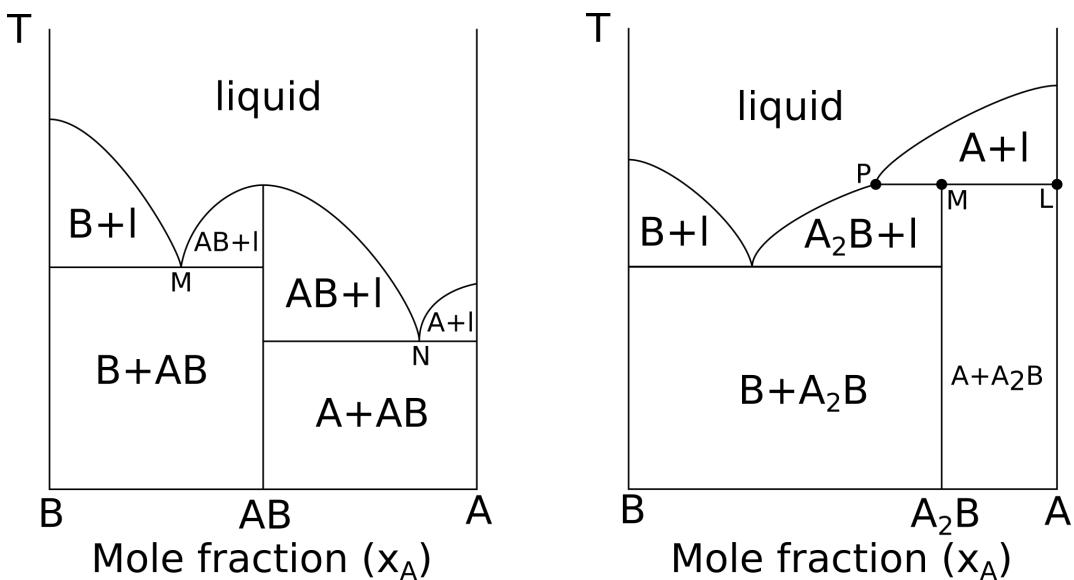


Figure 5.13: Left: a phase diagram for two insoluble solids A and B that react to form compound AB with congruent melting. Right: a similar diagram with formation of compound  $A_2B$  which then undergoes incongruent melting.

liquid with the same overall composition. This point is known as an **eutectic**. The eutectic temperature is lower than the melting point of either of the two solids and, similar to an azeotrope, the composition of the melt at the eutectic is the same as in the solid phase. Some examples of eutectics include:

- The water/NaCl system has an eutectic at  $-21.1\text{ }^\circ\text{C}$ , which is lower than the melting points of either ice ( $0\text{ }^\circ\text{C}$ ) or NaCl ( $801\text{ }^\circ\text{C}$ ). A water/salt mixture is used in winter to remove ice from roads and other surfaces.
- A mixture of tin and lead that is 63-37% in weight is an eutectic with melting temperature  $183\text{ }^\circ\text{C}$  used for soldering in electronic circuits.

This last eutectic is shown in the experimental Sn/Pb phase diagram in Figure 5.12. The Sn/Pb phase diagram has composition ranges in which Sn and Pb are partially soluble. If the amount of lead is not too high, tin can incorporate some lead into its  $\beta$ -Sn crystal structure. In the same way, if the amount of tin is not too high, lead can accept some tin into its  $\alpha$ -Pb structure. The one-phase regions in the Sn/Pb phase diagram are examples of **solid solutions** in which the crystal structure of a solid incorporates extraneous atoms. Solid solutions can be of different kinds depending on how the foreign atoms are brought into the crystal structure of the host. In an **interstitial** solid solution, the foreign atoms occupy the voids in host. For instance, steel under certain conditions is an interstitial solid solution where carbon atoms occupy the interstitial voids of iron. In **substitutional** solid solutions, the foreign atoms are similar in size and chemistry to those from the host, and therefore can replace them in the crystal structure. Examples of substitutional solid solutions include the Au/Ag and Al/Ga alloys.

It is possible that the two solids in a system react with each other to form compounds with mixed stoichiometries. In the simplest case, the phase diagram in this case may look like two adjacent phase diagrams, one for each pair of compositions, as shown in Figure 5.13 (left). In this case, the two solids A and B react with each other to form a compound with stoichiometry AB. The overall phase diagram is equivalent to two phase diagrams placed side by side, one for solids A plus AB and another for AB plus B, and each with its own eutectic. Note that pure AB melts at a single temperature to form a liquid with the same composition. This is known as

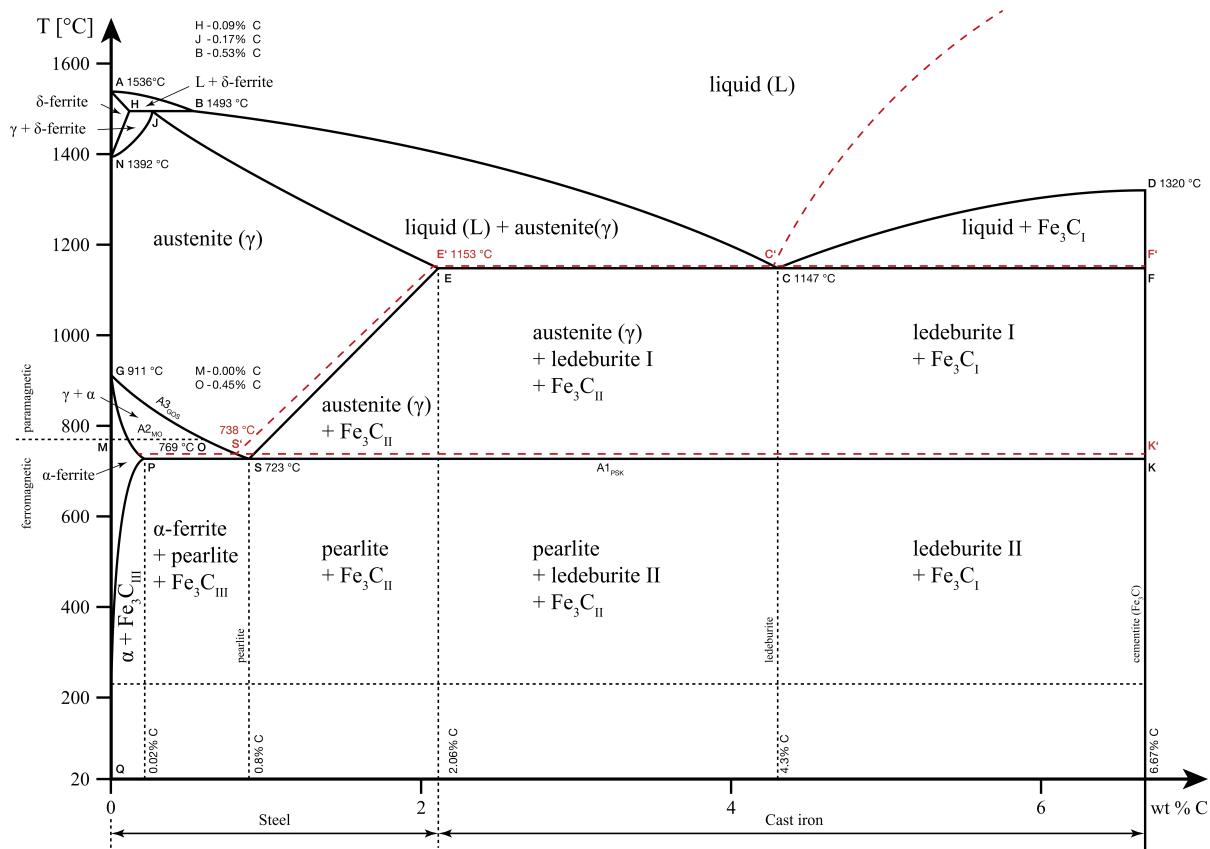


Figure 5.14: Phase diagram of Fe/C with low carbon content (steel). (Copyright Wikimedia Commons, User:AG Caesar, CC-BY-SA-3.0.)

### congruent melting.

Figure 5.13 (right) shows another possible binary phase diagram for reacting solids. In this case, a compound with stoichiometry  $A_2B$  is formed. If pure  $A_2B$  is heated, it melts at point M into a solid and a liquid, both with composition different from  $A_2B$ . When a solid melts into a liquid with a different composition, the phenomenon is known as **incongruent melting**. A phase transition in which a solid transforms into a liquid and a different solid is known as a **peritectic transition**, and P is known as a **peritectic point**. The melting of  $A_2B$  into A and a liquid at point M in the phase diagram (Figure 5.13, right) is an example of a peritectic transition. In general, for a peritectic transition:



Note the difference with an **eutectic transition**, such as the two transitions at the eutectic points M and N in the left diagram of Figure 5.13, at which two solids react with each other to form a single liquid:



In the right diagram of the figure, line PML corresponds to a situation in which three phases (liquid,  $A_2B$ , and A) are in equilibrium, and is known as a **peritectic line**.

More than one compound with intermediate stoichiometry can be found in the same phase diagram, so more complex phase diagrams have multiple eutectic and peritectic points. Figure 5.14 shows the phase diagram for the Fe/C system in the low-carbon region, relevant to the manufacturing of steel and cast iron, and industrially very important. In this diagram we see several interstitial solid solutions in which carbon is dissolved into iron:  $\alpha$ -ferrite (body-centered cubic iron), austenite (face-centered cubic), and  $\delta$ -ferrite (body-centered cubic

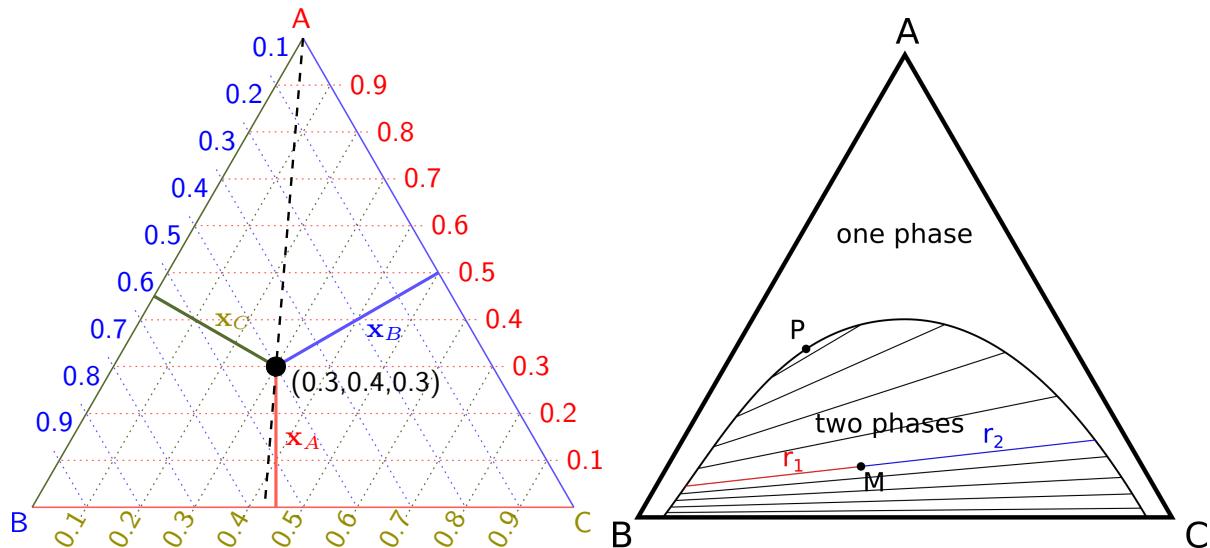


Figure 5.15: Left: Coordinates in a triangular composition diagram used for a ternary mixture. Right: a typical triangular diagram showing one-phase and two-phase regions with the tie lines.

again, but at much higher temperature). The right edge of the diagram corresponds to the Fe<sub>3</sub>C solid, known as cementite. Point C is an eutectic (austenite + cementite → liquid) and point J is a peritectic (austenite → δ-ferrite + liquid). By analogy with an eutectic, a point in which two solids react with each other to form a third solid:



is known as an **eutectoid** (compare to Eq. 5.51 for an eutectic point). Point S in the Fe/C phase diagram is an eutectoid (Figure 5.14). Similarly, a point at which a single solid decomposes to form two other solids:



is known as a **peritectoid**.

## 5.4 Ternary Phase Diagrams

A ternary system has three components ( $C = 3$ ). Applying the phase rule, we have  $F = 5 - P$  degrees of freedom. To make a bidimensional representation, we fix the two degrees of freedom corresponding to temperature and pressure, and therefore there are at most two degrees of freedom left when  $P = 1$ .

A common representation for a ternary phase diagram is an equilateral triangle, such as the one shown in Figure 5.15 (left). In a ternary system, we have:

$$x_A + x_B + x_C = 1 \quad (5.54)$$

The diagram in Figure 5.15 is an equilateral triangle with height equal to one. For a given point inside the triangle, it is possible to show that the sum of the distances from the point to the edges of the triangle also sum to one. Therefore, these distances, shown as red, green, and blue lines, can be identified with  $x_A$ ,  $x_B$ , and  $x_C$ , respectively. A point in the diagram has higher mole fraction of A when it is closer to the A vertex of the triangle and, conversely,  $x_A = 0$  if the system is on the side of the triangle connecting B to C. In addition, the line that intersect both the A vertex a point M inside the diagram is a line that has the same ratio of B

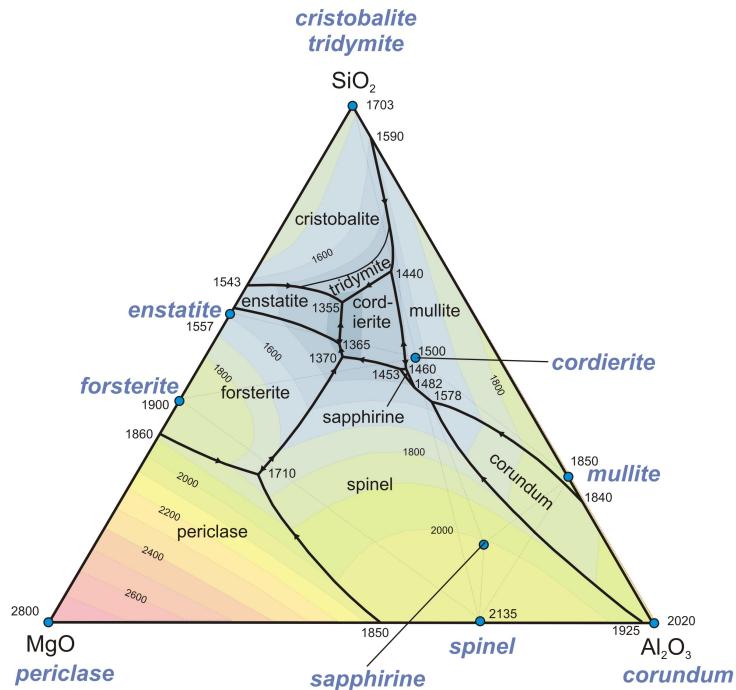


Figure 5.16: Solid-state ternary phase diagram for the  $\text{SiO}_2/\text{MgO}/\text{Al}_2\text{O}_3$  system. The colors and the numbers denote the melting temperatures. (Copyright D. Perkins and J. Brady, “[Ternary Phase Diagrams](#)”, Science Education Resource Center at Carleton College, CC-NC-SA-3.0. Data from Levin et al. “Phase diagrams for ceramicists”, American Ceramic Society, 1969.)

and C concentrations (same  $x_B/x_C$ ) as point M. Note that the sides of this triangle correspond to the binary systems formed by the AB, AC, and BC pairs.

The stability regions are shown in a ternary diagram in the same way as for the binary diagrams. For instance, Figure 5.15 shows a sketch of the miscibility diagram for three liquids A, B, and C. In this diagram, the A/B and A/C pairs are completely miscible because only one phase is present at the AB and AC edges of the triangle. In contrast, the B and C liquids are only partially miscible, and this creates a miscibility gap (two-phase region) in the diagram.

The miscibility gap in Figure 5.15 shows the tie lines for this system. Contrary to what happens in a binary diagram, the tie lines are not horizontal in general, but otherwise they function in exactly the same way. Namely, for a given point M inside the diagram, we follow the tie line on which the point is located. The endpoints of the tie line give the composition of the two phases in equilibrium, and application of the lever rule with the distances to the phase boundary along the tie line (in red and blue in Figure 5.15) give the amounts of each of the two phases. The point P at which the tie lines converge is known as the **plait point**. At this point, two liquids with the same composition merge to form a single phase.

Solid-state ternary diagrams are also common. For instance, Figure 5.16 shows the phase diagram of the  $\text{SiO}_2/\text{MgO}/\text{Al}_2\text{O}_3$  used in petrology, since these solids are common materials in the Earth’s interior. The diagram shows the stability range of each mineral as well as their melting temperatures.

# Chapter 6

## Solutions

### 6.1 Introduction

A **solution** is a homogeneous system with more than one component. Usual solutions are liquid but solid solutions, in which atoms move around freely inside a crystal structure, are also common. Often, one component in the solution, known as the **solvent**, is much more abundant than the others. The components other than the solvent are the **solutes**. In the following, we denote the solvent with the letter A and the solutes with B, C,... Many reactions of interest in chemistry and all biochemical reactions happen in solution, so the thermodynamic description of these systems is very important.

The concentration of each component in a solution can be given in different ways. The mole fraction ( $x_i$ , Section 1.4) and the molar concentration or molarity ( $c_i$ , Section 1.2.2) are commonly used. The **standard molar concentration** is  $c^\circ = 1 \text{ mol}/\text{dm}^3$ . The mole fraction is often awkward to use if the solution is very dilute and, because the molar concentration depends on the volume of the solution, it changes with temperature and pressure, which is often undesirable. An alternative concentration measure that circumvents this problem is the **molality** ( $b_i$ ), defined as the number of moles of component  $i$  divided by the mass of the solvent:

$$b_i = \frac{n_i}{m_A} = \frac{n_i}{n_A M_A} \quad (6.1)$$

where  $M_A$  is the molar mass of the solvent. The SI units of molality are mol/kg, and the **standard molality** is  $b^\circ = 1 \text{ mol}/\text{kg}$ .

### 6.2 Partial Molar Quantities

#### 6.2.1 Partial Molar Volumes

Water and ethanol are completely miscible liquids, they form a solution when they are mixed in any proportions. Assume we mix  $n_w$  moles of water and  $n_e$  moles of ethanol. The volume of the components before mixing is:

$$V^* = n_w V_{m,w}^* + n_e V_{m,e}^* \quad (6.2)$$

where the asterisk (\*) represents thermodynamic properties (molar volume, in this case) for the pure components before mixing. When water and ethanol are mixed, the volume of the solution does not equal the sum of the volumes of the pure components:

$$V(T, p, n_w, n_e) \neq V^*(T, p, n_w, n_e)$$

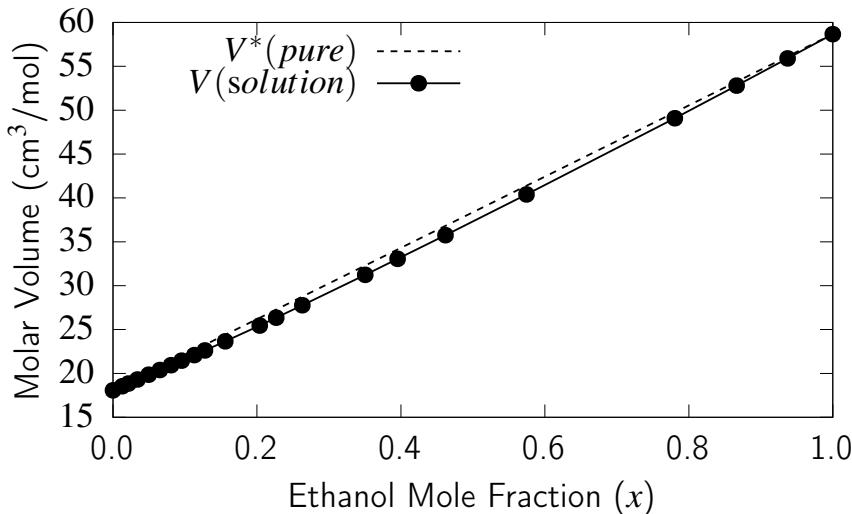


Figure 6.1: Molar volume of a water/ethanol solution as a function of ethanol mole fraction. The dashed line represents the sum of the molar volumes of the pure components before mixing. Data from Ott et al. “Excess volumes for (ethanol+water) at the temperatures (298.15 and 348.15) K and pressures (0.4, 5, and 15) MPa and at the temperature 323.15 K and pressures (5 and 15) MPa”, *J. Chem. Thermodyn.* **25** 307 (1993) via the Dortmund Data Bank.

For instance, if we mix 10 mL of water and 10 mL of ethanol, the result is not 20 mL of solution. This happens because, when pure, water molecules interact only with other water molecules and ethanol interacts only with ethanol. In solution, however, there are also interactions between water and ethanol molecules and, since these interactions are different from water-water and ethanol-ethanol, the end result is that the volume is not simply the sum of the corresponding volumes for the pure components. In general, **the extensive thermodynamic properties of a solution are different from the sum of the properties for the pure components**.

For convenience, we define the **mean molar volume** of the solution as:

$$V_m = \frac{V}{n} \quad (6.3)$$

where  $n$  equals the total number of moles. By analogy, the mean molar volume of the pure components is:

$$V_m^* = \frac{V^*}{n} = \frac{\sum_i n_i V_{m,i}^*}{n} = \sum_i x_i V_{m,i}^* \quad (6.4)$$

In the water/ethanol example, the experimental mean molar volume of the solution as a function of the ethanol mole fraction is shown in Figure 6.1. The mean molar volume of the pure components (Eq. 6.4) in this case is:

$$V_m^* = x_e V_{m,e}^* + (1 - x_e) V_{m,w}^* \quad (6.5)$$

because  $x_w = 1 - x_e$ . This is a straight line involving the molar volumes of pure water ( $V_{m,w}^* = 18.07 \text{ cm}^3/\text{mol}$ ) and ethanol ( $V_{m,e}^* = 58.67 \text{ cm}^3/\text{mol}$ ), shown as a dotted line in the figure. Note how the experimental mean molar volume of the solution ( $V_m$ ), shown as points and a continuous line in the figure, is similar but not exactly equal to  $V_m^*$ .

The volume of the solution depends on temperature, pressure, and the number of moles of each component,  $V(T, p, n_1, \dots)$ . To describe how the volume of the solution changes with the addition of a component, we define the **partial molar volume** as:

$$\bar{V}_i = \left( \frac{\partial V}{\partial n_i} \right)_{T,p,n_j \neq i} \quad (6.6)$$

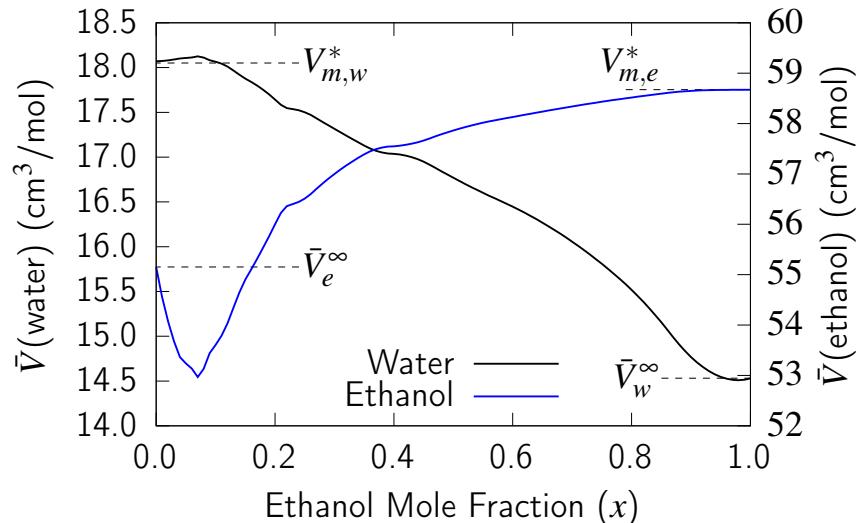


Figure 6.2: Partial molar volumes of water (black) and ethanol (blue) in solution as a function of the ethanol mole fraction. Data obtained from the [Dortmund Data Bank](#), in the public domain.

The partial molar volume of component  $i$  gives the infinitesimal change in the volume of a solution when the number of moles of component  $i$  changes at constant  $T$ ,  $p$ , and number of moles of all the other components. Because it is the ratio of two extensive properties,  $\bar{V}_i$  is intensive, and can be written as a function of the intensive state,  $\bar{V}_i(T, p, x_1, \dots)$ . Partial molar volumes have SI units of  $\text{m}^3/\text{mol}$ , although  $\text{cm}^3/\text{mol}$  are commonly used for solutions. For a pure substance,

$$V^*(T, p, n) = nV_m^*(T, p) \quad (6.7)$$

and the partial molar volume is:

$$\bar{V}^* = \left( \frac{\partial V^*}{\partial n} \right)_{T,p} = V_m^* = \frac{V^*}{n} \quad (6.8)$$

Therefore, **the partial molar volume of a pure substance equals its molar volume and its mean molar volume**.

Figure 6.2 shows the partial molar volumes for water and ethanol in a water/ethanol solution. Because the partial molar volume equals the molar volume for a pure component,

$\bar{V}_{\text{water}} = V_{m,\text{water}}^*$  at  $x_{\text{ethanol}} = 0$  and  $\bar{V}_{\text{ethanol}} = V_{m,\text{ethanol}}^*$  at  $x_{\text{ethanol}} = 1$ . The

**infinite-dilution partial molar volume** of component  $i$  ( $\bar{V}_i^\infty$ ) is its partial molar volume at  $x_i = 0$ , that is, the change in volume with addition of a small amount of  $i$  to pure solvent (i.e. at infinite dilution). In Figure 6.2, the infinite-dilution partial molar volumes are on the other end of the plot, with  $\bar{V}_{\text{water}} = \bar{V}_{\text{water}}^\infty$  at  $x_{\text{ethanol}} = 1$  and  $\bar{V}_{\text{ethanol}} = \bar{V}_{\text{ethanol}}^\infty$  at  $x_{\text{ethanol}} = 0$ .

Some examples of  $\bar{V}_i^\infty$  for various solutes in water at ambient conditions are  $16.6 \text{ cm}^3/\text{mol}$  ( $\text{NaCl}$ ),  $14.1 \text{ cm}^3/\text{mol}$  ( $\text{H}_2\text{SO}_4$ ), and  $-7.0 \text{ cm}^3/\text{mol}$  ( $\text{MgSO}_4$ ). The infinite-dilution partial molar volume of  $\text{MgSO}_4$  is negative, indicating that the volume of the solution decreases when  $\text{MgSO}_4$  is added to pure water. This is likely due to the very strong interactions between the ions in solution and the water molecules.

### 6.2.2 Solution Volume in Terms of Partial Molar Volumes

The volume of the solution can be written in terms of the partial volumes of all components. The volume differential is:

$$\begin{aligned} dV &= \left( \frac{\partial V}{\partial T} \right)_{p,n_i} dT + \left( \frac{\partial V}{\partial p} \right)_{T,n_i} dp + \sum_i \left( \frac{\partial V}{\partial n_i} \right)_{T,p,n_j \neq i} dn_i \\ &= \left( \frac{\partial V}{\partial T} \right)_{p,n_i} dT + \left( \frac{\partial V}{\partial p} \right)_{T,n_i} dp + \sum_i \bar{V}_i dn_i \end{aligned} \quad (6.9)$$

Consider a process in which we change the total number of moles ( $dn$ ) at constant temperature ( $dT = 0$ ), pressure ( $dp = 0$ ), and mole fractions:

$$dV = \sum_i \bar{V}_i dn_i = \left( \sum_i x_i \bar{V}_i \right) dn \quad (6.10)$$

where we have used  $n_i = x_i n$  so  $dn_i = x_i dn$  because  $x_i$  are constant in this process. On the other hand, the solution volume is an extensive property, so it can be written as  $n$  times a function of the intensive variables:

$$V = nf(T, p, x_1, \dots) \quad (6.11)$$

Therefore, for a process at constant  $T$ ,  $p$ , and mole fractions it is also true that:

$$dV = f(T, p, x_1, \dots) dn \quad (6.12)$$

Comparing this equation with Eq. 6.10, we have:

$$f(T, p, x_1, \dots) = \sum_i x_i \bar{V}_i \quad (6.13)$$

and substituting the  $f$  function in Eq. 6.11 gives:

$$V = n \sum_i x_i \bar{V}_i = \sum_i n_i \bar{V}_i \quad (6.14)$$

so the volume of the solution equals the sum of the partial molar volumes times the number of moles of each component. Dividing this last equation by  $n$  we find that the mean molar volume of the solution can be written in terms of the partial molar volumes and the mole fractions:

$$V_m = \frac{V}{n} = \frac{\sum_i n_i \bar{V}_i}{n} = \sum_i x_i \bar{V}_i \quad (6.15)$$

The result in Eq. 6.14 can also be obtained by applying **Euler's homogeneous function theorem**. A function  $f(\mathbf{x})$  is homogeneous of degree  $n$  if  $f(\alpha \mathbf{x}) = \alpha^n f(\mathbf{x})$  for any scalar  $\alpha$ . Euler's theorem says that, for a homogeneous function of degree  $n$ :

$$\sum_i x_i \frac{\partial f}{\partial x_i} = nf(\mathbf{x})$$

In our case, at constant temperature and pressure,  $V(\alpha n_1, \dots, \alpha n_k) = \alpha V(n_1, \dots, n_k)$ , so the volume is a homogeneous function of the first degree. Application of the theorem gives Eq. 6.14 directly.

### 6.2.3 Other Extensive Properties

In addition to the volume, partial molar variants of all other extensive thermodynamic properties can be defined. For instance, the partial molar enthalpy of component  $i$  is:

$$\overline{H}_i = \left( \frac{\partial H}{\partial n_i} \right)_{T,p,n_j \neq i} \quad (6.16)$$

and the partial molar Gibbs free energy of component  $i$  is identical to its chemical potential:

$$\overline{G}_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq i} = \mu_i \quad (6.17)$$

In general, for any extensive property  $Y$ , we define the corresponding partial molar quantity as:

$$\overline{Y}_i = \left( \frac{\partial Y}{\partial n_i} \right)_{T,p,n_j \neq i} \quad (6.18)$$

Following the same steps as for the volume above,

- $\overline{Y}_i = Y_{m,i}^*$  for the pure component.
- The infinite-dilution partial molar property ( $\overline{Y}_i^\infty$ ) is defined as  $\overline{Y}_i$  at  $x_i = 0$ .
- The  $Y$  and  $Y_m$  of the solution can be written in terms of partial molar quantities:

$$Y = \sum_i n_i \overline{Y}_i \quad (6.19)$$

$$Y_m = \sum_i x_i \overline{Y}_i \quad (6.20)$$

- The total differential can be written as:

$$dY = \left( \frac{\partial Y}{\partial T} \right)_{p,n_i} dT + \left( \frac{\partial Y}{\partial p} \right)_{T,n_i} dp + \sum_i \overline{Y}_i dn_i \quad (6.21)$$

In particular, the Gibbs free energy of the solution can be expressed in terms of the chemical potentials:

$$G = \sum_i n_i \mu_i \quad (6.22)$$

Lastly, note that the usual thermodynamic relations hold also for partial molar quantities. For instance,  $G = H - TS$  and, taking the derivative with respect to  $n_i$  at constant  $T$ ,  $p$ , and  $n_{j \neq i}$ , we have:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq i} = \left( \frac{\partial (H - TS)}{\partial n_i} \right)_{T,p,n_j \neq i} = \overline{H}_i - T \overline{S}_i \quad (6.23)$$

Likewise, it is easy to show in the same manner that:

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{p,n_j \neq i} = -\overline{S}_i \quad ; \quad \left( \frac{\partial \mu_i}{\partial p} \right)_{T,n_j \neq i} = \overline{V}_i \quad (6.24)$$

Since  $G$ ,  $S$ ,  $V$ , etc. can be written in terms of the corresponding partial molar quantities, and those can be obtained from  $\mu_i$ , **knowledge of all the  $\mu_i$  as a function of  $T$ ,  $p$ , and the mole fractions of all components completely determines the thermodynamic properties of a solution**. This is also valid for any homogeneous mixture like, for instance, a gas mixture and, in fact, for any multicomponent system.

### 6.2.4 The Gibbs-Duhem Equation

The Gibbs free energy of a solution can be written in terms of the chemical potentials (the partial molar Gibbs free energies) as (Eq. 6.19):

$$G = \sum_i n_i \mu_i \quad (6.25)$$

Taking the differential:

$$dG = \sum_i \mu_i dn_i + n_i d\mu_i \quad (6.26)$$

On the other hand, the differential of  $G$  at constant  $T$  and  $p$  is (Eq. 6.21):

$$dG = \sum_i \mu_i dn_i \quad (6.27)$$

Combining these two equations, we find:

$$\sum_i n_i d\mu_i = 0 \quad (6.28)$$

This is the **Gibbs-Duhem equation**, valid for a process at constant  $T$  and  $p$ . It states that the chemical potentials of the components in a solution are not all independent and gives the relation between their changes. For instance, in a binary solution:

$$n_A d\mu_A = -n_B d\mu_B \quad (6.29)$$

so the changes in the chemical potentials of  $A$  and  $B$  must have opposite signs and be related by the  $n_A/n_B$  ratio. The Gibbs-Duhem equation applies to any extensive property, not just the Gibbs free energy. For instance, the changes in partial molar volumes of a binary solution are related by:

$$n_A d\bar{V}_A = -n_B d\bar{V}_B \quad (6.30)$$

For instance, in the water/ethanol example (Figure 6.2), the partial molar volume of water increases when the  $\bar{V}$  of ethanol decreases and vice versa. The Gibbs-Duhem equation is useful because it allows the experimental determination of partial molar quantities of components that are difficult to measure by instead measuring the same quantities for all the other components.

## 6.3 Mixing Properties

### 6.3.1 Definition

The volume of a solution is similar but not quite the same as the sum of the volumes of the pure components (Figure 6.1). To measure the deviation between the two, it is convenient to define the **volume change on mixing** or **mixing volume** ( $\Delta_{\text{mix}}V$ ) as the volume of the solution minus that of the pure components:

$$\Delta_{\text{mix}}V = V - V^* = V - \sum_i n_i V_{m,i}^* \quad (6.31)$$

Therefore, the mixing volume is the change in volume when the pure components are mixed and the solution is formed. In the water/ethanol example, the  $\Delta_{\text{mix}}V$  per mole of solution is the difference between the full and dashed lines in Figure 6.1, and it is shown in Figure 6.3.

In general, for any extensive property  $Y$ , we define the corresponding mixing quantity as the property for the solution minus the same property for the pure components:

$$\Delta_{\text{mix}}V = V - V^* \quad \Delta_{\text{mix}}S = S - S^* \quad (6.32)$$

$$\Delta_{\text{mix}}H = H - H^* \quad \Delta_{\text{mix}}G = G - G^* \quad (6.33)$$

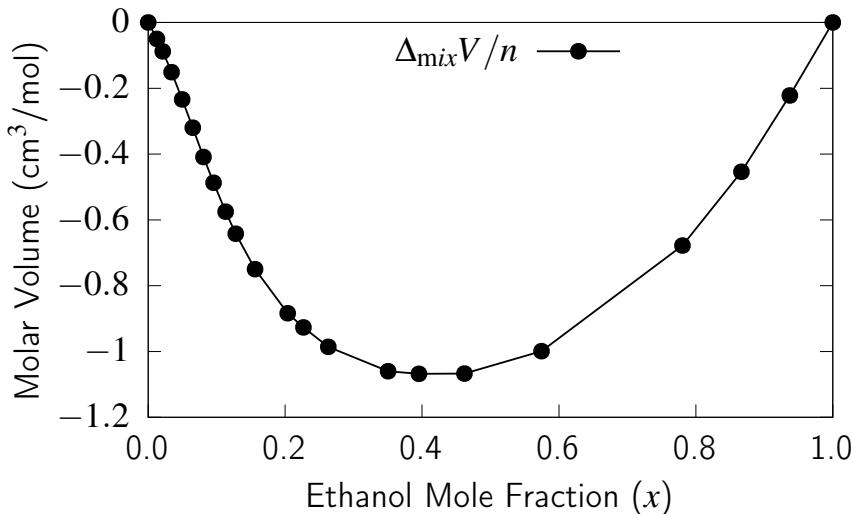


Figure 6.3: Molar volume change per mole ( $\Delta_{\text{mix}}V/n$ ) on mixing water and ethanol as a function of composition, calculated as the difference between the two curves in Figure 6.1.

This definition is consistent with the entropy of mixing defined in Section 3.3.2 and corresponds to the mixing process in Table 2.2, in which  $n$  moles of pure components are mixed to form the solution in a closed system at constant  $T$  and  $p$ . Specifically, the  $\Delta_{\text{mix}}G$  indicates whether the mixing of the solution components is spontaneous at a given temperature and pressure. Two liquids whose  $\Delta_{\text{mix}}G < 0$  at all concentrations are completely miscible whereas  $\Delta_{\text{mix}}G > 0$  indicates they are immiscible. The  $\Delta_{\text{mix}}H$  gives the heat released by the formation of the solution at constant pressure.

The mixing quantities can be written in terms of the partial molar quantities. For instance, for the volume, we substitute the volume in terms of partial molar volumes (Eq. 6.14) into Eq. 6.31:

$$\Delta_{\text{mix}}V = V - V^* = \sum_i n_i \bar{V}_i - \sum_i n_i V_{m,i}^* = \sum_i n_i (\bar{V}_i - V_{m,i}^*) \quad (6.34)$$

and likewise for the mixing Gibbs free energy we have:

$$\Delta_{\text{mix}}G = G - G^* = \sum_i n_i \mu_i - \sum_i n_i \mu_i^* = \sum_i n_i (\mu_i - \mu_i^*) \quad (6.35)$$

The usual thermodynamic relations also hold for the mixing properties. For instance:

$$\Delta_{\text{mix}}G = G - G^* = H - TS - (H^* - TS^*) = (H - H^*) - T(S - S^*) = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S \quad (6.36)$$

and it is easy to show that:

$$\left( \frac{\partial \Delta_{\text{mix}}G}{\partial T} \right)_{p,n_i} = -\Delta_{\text{mix}}S \quad ; \quad \left( \frac{\partial \Delta_{\text{mix}}G}{\partial p} \right)_{T,n_i} = \Delta_{\text{mix}}V \quad (6.37)$$

As an example, let us consider for a moment the formation of an ideal gas mixture, which can be considered a solution, since it is a homogeneous system with more than one component, from the corresponding ideal gases. Because the mixing happens at constant  $T$  and  $p$  and the gas molecules do not interact with each other,  $\Delta_{\text{mix}}V = 0$ . In addition,  $U$  and  $H$  depend only on temperature in an ideal gas, so  $\Delta_{\text{mix}}U = \Delta_{\text{mix}}H = 0$  because the mixing is an isothermal process. However, the entropy of mixing  $\Delta_{\text{mix}}S$  for ideal gases is not zero. We showed in Section 3.3.2 that when two ideal gases are mixed (Eq. 3.49):

$$\Delta_{\text{mix}}S = -n_a R \ln x_a - n_b R \ln x_b \quad (6.38)$$

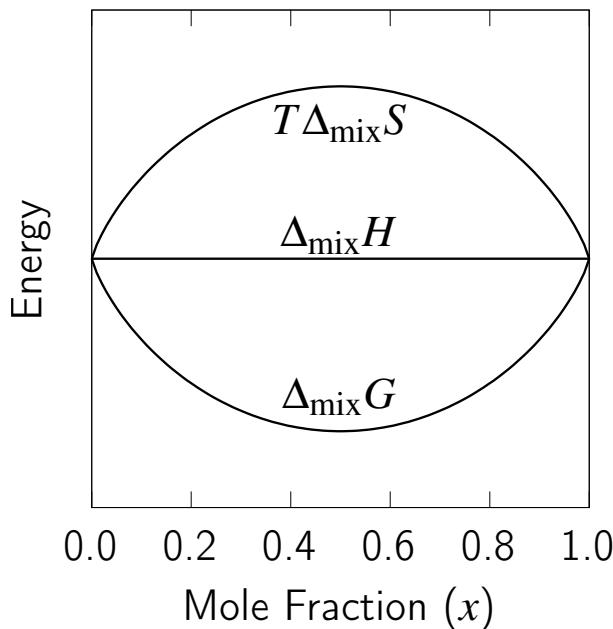


Figure 6.4: Mixing quantities for a two-component ideal gas mixture.

and therefore the mixing Helmholtz and Gibbs free energies are:

$$\Delta_{\text{mix}}A = \Delta_{\text{mix}}H - T\Delta_{\text{mix}}S = -T\Delta_{\text{mix}}S = n_aRT \ln x_a + n_bRT \ln x_b \quad (6.39)$$

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}A + p\Delta_{\text{mix}}V = \Delta_{\text{mix}}A = n_aRT \ln x_a + n_bRT \ln x_b \quad (6.40)$$

The mixing free energy, enthalpy and entropy for a binary ideal gas mixture are shown in Figure 6.4. Because  $\Delta_{\text{mix}}G < 0$  at all compositions, the formation of an ideal gas mixture at constant  $T$  and  $p$  is always spontaneous and happens without absorbing or releasing any heat ( $\Delta_{\text{mix}}H = 0$ ) and without change in the volume of the system ( $\Delta_{\text{mix}}V = 0$ ).

As we shall see, the expression for the mixing quantities in ideal gas mixtures is the same as in ideal solutions. Because there are no intermolecular interactions in an ideal gas mixture, a consequence of the above is that in a real gas mixture (and in a real solution) the values of  $\Delta_{\text{mix}}V$ ,  $\Delta_{\text{mix}}U$ , and  $\Delta_{\text{mix}}H$  arise strictly from the intermolecular interactions between components in the mixture, whereas  $\Delta_{\text{mix}}S$ ,  $\Delta_{\text{mix}}G$ , and  $\Delta_{\text{mix}}A$  have an additional term that comes from the increase in entropy caused by the mixing process (Eq. 6.38). This is why mixing entropies of solutions are often positive except in a few cases when the structuring in the solution caused by the mixing overcomes the contribution in Eq. 6.38.

## 6.4 Ideal Solutions

### 6.4.1 Definition

There are two ideal models used for solutions: **ideal solutions** and **ideal-dilute solutions**. These models are approached when the solution has certain limiting properties, and therefore their use is appropriate for different kinds of solutions.

In an **ideal solution**, the molecules of all components are so similar that the intermolecular interactions between different component molecules are the same as in the corresponding pure phases. For instance, if we have a binary ideal solution with components A and B, the A-B intermolecular interactions are equivalent in strength and properties to the A-A and B-B interactions such that the chemical environment of, for instance, an A molecule in the ideal solution is the same as in pure A. Real solutions that are close to being ideal comprise very

similar component molecules that enter the solution in any proportion. Examples include benzene/toluene, chloroethane/bromoethane, neopentane/tetramethylsilane, and mixtures of isotopologues (the same molecule with different isotopic compositions).

Vapor pressure experiments show that solutions close to the ideal solution behavior have a mixing free energy that is approximately the same as in an ideal gas mixture (Eq. 6.40):

$$\Delta_{\text{mix}}G = RT \sum_k n_k \ln x_k = RT \left( \sum_k n_k \ln n_k - \sum_k n_k \ln n \right) = RT \left( \sum_k n_k \ln n_k - n \ln n \right) \quad (6.41)$$

where we used  $x_k = n_k/n$ . Since  $\Delta_{\text{mix}}G = G - G^*$ , the derivative of the mixing free energy with respect to  $n_i$  is:

$$\left( \frac{\partial \Delta_{\text{mix}}G}{\partial n_i} \right)_{T,p,n_j \neq i} = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq i} - \left( \frac{\partial G^*}{\partial n_i} \right)_{T,p,n_j \neq i} = \mu_i - \mu_i^* \quad (6.42)$$

but, from Eq. 6.41:

$$\left( \frac{\partial \Delta_{\text{mix}}G}{\partial n_i} \right)_{T,p,n_j \neq i} = RT \left( \ln n_i + n_i \times \frac{1}{n_i} - \ln n - n \times \frac{1}{n} \right) = RT \ln \left( \frac{n_i}{n} \right) = RT \ln x_i \quad (6.43)$$

Combining the last two equations,

$$\mu_i = \mu_i^* + RT \ln x_i \quad (6.44)$$

An ideal solution is defined as a solution in which every component has a chemical potential given by Eq. 6.44 at all compositions. This definition sets the chemical potential of all the components under any condition and therefore, as mentioned previously, completely determines all thermodynamic properties of an ideal solution—we study those next. Note that the chemical potential of component  $i$  goes to the chemical potential of the pure component ( $\mu_i^*$ ) in the  $x_i \rightarrow 1$  limit and to  $-\infty$  in the  $x_i \rightarrow 0$  limit.

### 6.4.2 Thermodynamic Properties

**Standard states.** The standard state of a component  $i$  in an ideal liquid solution is defined as pure liquid  $i$  at the same temperature and pressure as the solution:

$$\mu_i^\circ = \mu_i^*(T, p) \quad (6.45)$$

In an ideal solid solution, pure solid  $i$  is used. With this choice of standard state, the chemical potential (Eq. 6.44) becomes:

$$\mu_i = \mu_i^\circ + RT \ln x_i \quad (6.46)$$

**Mixing quantities.** The mixing Gibbs free is:

$$\Delta_{\text{mix}}G = \sum_i n_i(\mu_i - \mu_i^*) = RT \sum_i n_i \ln x_i = nRT \sum_i x_i \ln x_i \quad (6.47)$$

Because  $0 < x_i < 1$ , the mixing of the components in an ideal solution is spontaneous ( $\Delta_{\text{mix}}G < 0$ ) at any temperature, pressure, and composition. The mixing entropy is:

$$\Delta_{\text{mix}}S = - \left( \frac{\Delta_{\text{mix}}G}{\partial T} \right)_{p,n_i} = -nR \sum_i x_i \ln x_i \quad (6.48)$$

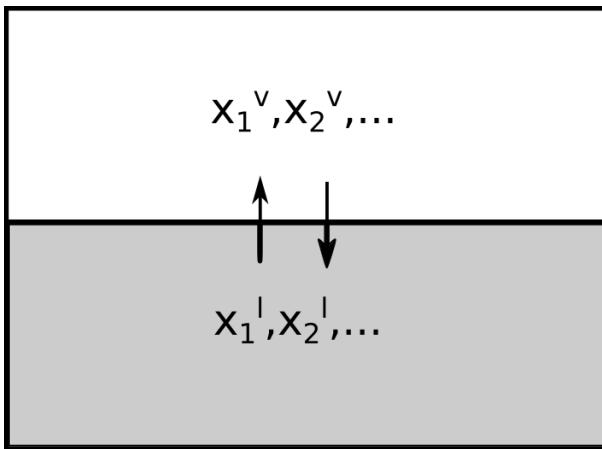


Figure 6.5: A solution in equilibrium with its vapor. The mole fractions in the liquid ( $x_1^l, x_2^l, \dots$ ) and vapor ( $x_1^v, x_2^v, \dots$ ) phases are different.

The other mixing quantities are:

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T\Delta_{\text{mix}}S = 0 \quad (6.49)$$

$$\Delta_{\text{mix}}V = \left( \frac{\partial \Delta_{\text{mix}}G}{\partial p} \right)_{T,n_i} = 0 \quad (6.50)$$

$$\Delta_{\text{mix}}U = \Delta_{\text{mix}}H - p\Delta_{\text{mix}}V = 0 \quad (6.51)$$

The mixing properties of ideal solutions are entirely equivalent to those of ideal mixtures, see Figure 6.4 and Section 6.3.1.

**Vapor pressure.** Consider an ideal solution in equilibrium with its vapor, as shown in Figure 6.5. The mole fractions in the liquid ( $x_1^l, x_2^l, \dots$ ) are different from those in the vapor ( $x_1^v, x_2^v, \dots$ ) and their values are determined by the equilibrium conditions (Eq. 4.131):

$$\mu_i^l = \mu_i^v \quad (6.52)$$

for every component  $i$ . The chemical potential in the liquid is (Eq. 6.44):

$$\mu_i^l = \mu_i^{*,l} + RT \ln x_i^l \quad (6.53)$$

and, assuming the vapor behaves like an ideal gas mixture, the chemical potential in the gas is (Eq. 4.153):

$$\mu_i^v = \mu_i^{\circ,v} + RT \ln \left( \frac{p_i}{p^\circ} \right) \quad (6.54)$$

Therefore, the equilibrium condition (Eq. 6.52) is:

$$\mu_i^{*,l} + RT \ln x_i^l = \mu_i^{\circ,v} + RT \ln \left( \frac{p_i}{p^\circ} \right) \quad (6.55)$$

The pure liquid is in equilibrium with its gas phase at temperature  $T$  when the external pressure equals its vapor pressure:

$$\mu_i^{*,l}(T, p_i^*) = \mu_i^{*,v}(T, p_i^*) = \mu_i^{\circ,v} + RT \ln \left( \frac{p_i^*}{p^\circ} \right) \quad (6.56)$$

where  $p_i^*$  is the vapor pressure of pure liquid  $i$  at temperature  $T$ . Subtracting the last two equations gives:

$$\mu_i^{*,l}(T, p) - \mu_i^{*,l}(T, p_i^*) + RT \ln x_i^l = RT \ln \left( \frac{p_i}{p_i^*} \right) \quad (6.57)$$

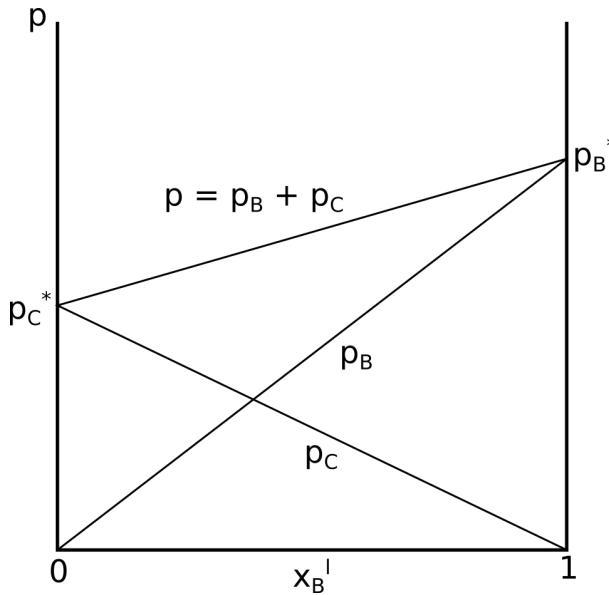


Figure 6.6: Pressure as a function of mole fraction in a binary ideal solution. The partial pressures ( $p_B$  and  $p_C$ ) and total pressure ( $p = p_B + p_C$ ) of the ideal gas mixture in equilibrium with the solutions are given by Raoult's law (Eq. 6.58).

Since the chemical potential of a liquid is mostly insensitive to pressure, the first two terms in this equation cancel out. After simplifying, we have:

$$p_i = x_i^l p_i^* \quad (6.58)$$

which is known as **Raoult's law**, valid for ideal solutions in equilibrium with an ideal gas mixture.

In a binary ideal solution with components B and C, the total pressure of the vapor is:

$$p = p_B + p_C = x_B^l p_B^* + x_C^l p_C^* = p_C^* + x_B^l (p_B^* - p_C^*) \quad (6.59)$$

where we used that  $x_C^l = 1 - x_B^l$ . The partial pressures as a function of mole fraction in the liquid are straight lines between zero and the vapor pressure of the pure component, and the total pressure is a straight line between  $p_B^*$  and  $p_C^*$  (Figure 6.6).

#### 6.4.3 Excess Functions

The thermodynamic properties of real solutions are often expressed as deviations from those of ideal solutions. In general, for extensive property  $Y$  we define the excess  $Y$  property as:

$$Y^E = Y - Y^{\text{id}} \quad (6.60)$$

where  $Y^{\text{id}}$  is the value of  $Y$  for an ideal solution at the same temperature, pressure, and composition as the real solution. For instance, the excess Gibbs free energy is:

$$G^E = G - G^{\text{id}} \quad (6.61)$$

Excess functions can also be written in terms of mixing quantities:

$$Y^E = Y - Y^{\text{id}} = (Y - Y^*) - (Y^{\text{id}} - Y^*) = \Delta_{\text{mix}} Y - \Delta_{\text{mix}} Y^{\text{id}} \quad (6.62)$$

so the excess functions also measure the deviation of mixing quantities from the ideal behavior in Figure 6.4. Specifically, note that:

$$G^E = \Delta_{\text{mix}}G - \Delta_{\text{mix}}G^{\text{id}} = \Delta_{\text{mix}}G - nRT \sum_i x_i \ln x_i \quad (6.63)$$

$$S^E = \Delta_{\text{mix}}S + \Delta_{\text{mix}}S^{\text{id}} = \Delta_{\text{mix}}S - nR \sum_i x_i \ln x_i \quad (6.64)$$

where we substituted Eqs. 6.47 and 6.48. On the other hand, since  $\Delta_{\text{mix}}H^{\text{id}} = \Delta_{\text{mix}}V^{\text{id}} = 0$ , we have:

$$H^E = \Delta_{\text{mix}}H - \Delta_{\text{mix}}H^{\text{id}} = \Delta_{\text{mix}}H \quad (6.65)$$

$$V^E = \Delta_{\text{mix}}V - \Delta_{\text{mix}}V^{\text{id}} = \Delta_{\text{mix}}V \quad (6.66)$$

The usual thermodynamic relations apply to excess functions:

$$G^E = H^E - TS^E \quad (6.67)$$

$$\left( \frac{\partial G^E}{\partial T} \right)_{p,n_j \neq i} = -S^E \quad ; \quad \left( \frac{\partial G^E}{\partial p} \right)_{T,n_j \neq i} = V^E \quad (6.68)$$

which can be shown by differentiation of Eq. 6.61.

By rearranging Equation 6.63 and substituting Eq. 6.67, the mixing Gibbs free energy can be written as:

$$\Delta_{\text{mix}}G = H^E - TS^E + nRT \sum_i x_i \ln x_i \quad (6.69)$$

The solution forms spontaneously when the pure components are mixed if  $\Delta_{\text{mix}}G < 0$  and this determines, for instance, whether two liquids are miscible, immiscible, or partially miscible under certain conditions. There are three contributing factors to the mixing Gibbs free energy: i) the strength of the intermolecular interactions between the component molecules determines whether the mixing is endothermic or exothermic ( $H^E = \Delta_{\text{mix}}H$ ), and exothermic mixing favors solubility, ii) the entropic contribution arising from the interactions between component molecules  $S^E$ , which measures whether their chemical environments are more or less structured than in the pure components, and iii) an additional third term that is always negative (because  $0 < x_i < 1$  and  $\ln x_i < 0$ ) that comes from the entropy gain due to the component mixing, even in absence of intermolecular interactions, and always favors the spontaneity of the solution formation.

## 6.5 Ideal-Dilute Solutions

### 6.5.1 Definition

The ideal-dilute solution model is the second of the models used to approximate the behavior of real solutions. In an **ideal-dilute solution**, the solute concentration is so low that we can assume that each solute molecule interacts with solvent molecules only and that solute-solute interactions do not occur. Ideal-dilute solutions are approximated by real solutions of non-electrolytes when the mole fraction of all solutes tends to zero. (In electrolyte solutions, the solute dissociates into charged species. The charged molecules interact via long-range Coulomb forces with each other, so the assumption that solute-solute interactions are absent is no longer valid, except at extremely low concentrations.) Based on experimental measurements of dilution free energies and statistical mechanical arguments, we define an ideal-dilute solution as one where the chemical potentials of the components are:

$$\mu_A = \mu_A^* + RT \ln x_A \quad (6.70)$$

$$\mu_i = f_i(T, p) + RT \ln x_i \quad (6.71)$$

for the solvent (A) and the solutes (*i*). The chemical potential of the solvent is the same as in the ideal solution. For the solutes,  $\mu_i$  involves a function  $f_i(T, p)$  that depends on temperature, pressure and the nature of both solvent and solute *i* but not on the solution concentration. By definition,  $f_i(T, p)$  is equal to  $\mu_i$  in the  $x_i \rightarrow 1$  limit. Since  $x_i \propto c_i \propto b_i$  when  $x_i \rightarrow 0$  (see Eqs. 6.98 and 6.100 below), sometimes molarities or molalities are used to define the chemical potential in ideal-dilute solutions, as we shall see next. Real non-electrolyte solutions approach ideal-dilute behavior in the limit  $x_A \rightarrow 1$ .

### 6.5.2 Thermodynamic Properties

**Standard states.** In an ideal-dilute solution, the standard state of the solvent is pure liquid solvent at the same temperature and pressure as the solution:

$$\mu_A^\circ = \mu_A^*(T, p) \quad (6.72)$$

from where:

$$\mu_A = \mu_A^\circ + RT \ln x_A \quad (6.73)$$

For the solute, the standard state is:

$$\mu_i^\circ = f_i(T, p) \quad (6.74)$$

Based on Eq. 6.71, the standard state of the solute corresponds to a fictitious state at the same temperature and pressure as the solution in which the solute is pure but experiences interactions only with solvent molecules. This state is not realizable experimentally but  $f_i(T, p)$  can be obtained by extrapolation of  $\mu_i$  vs.  $x_i$  data measured at low  $x_i$  to the  $x_i \rightarrow 1$  limit. It is also reasonably easy to model this fictitious state computationally and theoretically. Since  $f_i(T, p)$  depends on the nature of A, so does the  $\mu_i^\circ$  in an ideal-dilute solution. With these definitions, the chemical potential of the solute is:

$$\mu_i = \mu_i^\circ + RT \ln x_i \quad (6.75)$$

Note that the equations for the chemical potentials are the same as in an ideal solution, but the standard states of the solutes are different.

**Vapor pressure.** Consider an ideal-dilute solution in contact with its vapor (Figure 6.5). The solvent has the same chemical potential as in an ideal solution, so the vapor pressure of the solvent follows Raoult's law (Eq. 6.58). For the solute, the chemical potential in the liquid is (Eq. 6.75):

$$\mu_i^l = \mu_i^{\circ,l} + RT \ln x_i \quad (6.76)$$

and for the vapor, assuming ideal gas mixture behavior:

$$\mu_i^v = \mu_i^{\circ,v} + RT \ln \left( \frac{p_i}{p^\circ} \right) \quad (6.77)$$

At equilibrium  $\mu_i^l = \mu_i^v$ , so:

$$\mu_i^{\circ,l} + RT \ln x_i = \mu_i^{\circ,v} + RT \ln \left( \frac{p_i}{p^\circ} \right) \quad (6.78)$$

$$\frac{\mu_i^{\circ,l} - \mu_i^{\circ,v}}{RT} = \ln \left( \frac{p_i}{x_i^l p^\circ} \right) \quad (6.79)$$

Solving for the partial pressure:

$$p_i = p^\circ \exp \left( \frac{\mu_i^{\circ,l} - \mu_i^{\circ,v}}{RT} \right) x_i^l = K_i(T, p) x_i^l \quad (6.80)$$

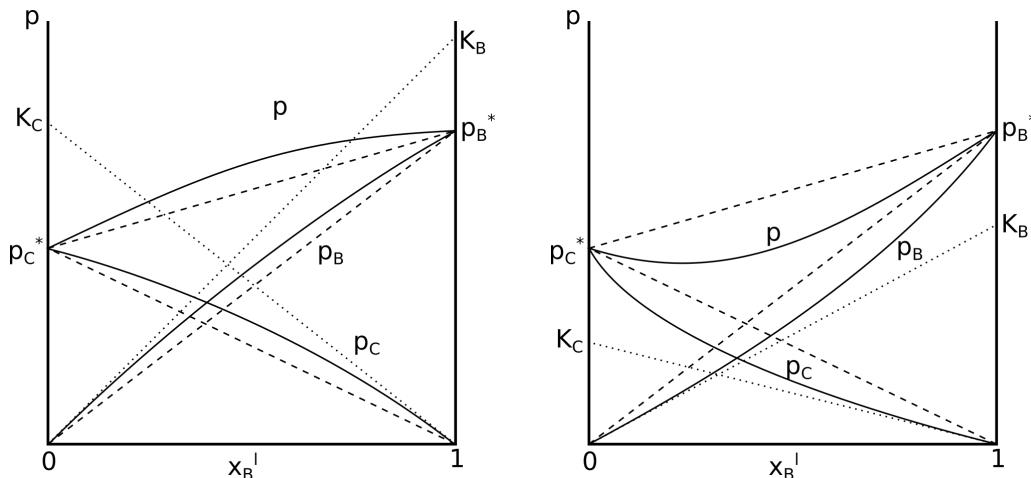


Figure 6.7: Vapor pressure as a function of liquid mole fraction in a solution that shows positive (left) and negative (right) deviations from Raoult's law (Eq. 6.58). The dashed lines indicate the partial pressures for an ideal solution (Raoult's law). The dotted lines indicate the partial pressures predicted by Henry's law (Eq. 6.80).

This is **Henry's law** and  $K_i(T, p)$  is **Henry's law constant**:

$$K_i(T, p) = p^\circ \exp\left(\frac{\mu_i^{\circ,l} - \mu_i^{\circ,v}}{RT}\right) \quad (6.81)$$

which has units of pressure and depends on the nature of solute and solvent, temperature, and pressure but not on the solution composition (the mole fractions). Because only  $\mu_i^{\circ,l}$  depends on pressure and this dependence is very mild, effectively  $K_i$  can be considered a function of temperature only.

Raoult's law (Eq. 6.58) and Henry's law (Eq. 6.80) are very similar. In the former,  $p_i$  is proportional to  $x_i^l$  and the proportionality constant is the vapor pressure of pure liquid  $i$  ( $p_i^*$ ). In the latter, the proportionality constant is the slope of the  $p_i$  versus  $x_i^l$  plot for a real solution at  $x_i^l = 0$  because at this point the real solution tends to the ideal-dilute limit. An **ideal-dilute solution in equilibrium with an ideal gas mixture follows Raoult's law for the solvent and Henry's law for the solute. An ideal solution follows Raoult's law for all components.**

Two examples of vapor pressure as a function of solution composition for binary real solutions of completely miscible non-electrolytes are given in Figure 6.7. If the solution behaves like an ideal solution, the partial pressures are given by Raoult's law (dashed lines, same as Figure 6.6). In the limit  $x_B^l \rightarrow 0$ , the system resembles an ideal-dilute solution of B in C, and the partial pressure of B is given by Henry's law with constant  $K_B$  (dotted lines). Likewise,  $x_B^l \rightarrow 1$  is approximated by an ideal-dilute solution of C in B, and  $p_C$  is also given by Henry's law but this time with constant  $K_C$ .

Solutions whose pressure is lower than the Raoult's law prediction are said to show a **negative deviation** from Raoult's law (Figure 6.7, right). Because Raoult's law is exact for an ideal solution, where intermolecular interactions are identical to those in the pure liquids, a negative deviation from Raoult's law indicates that the intermolecular interactions in the mixture are stronger than the average interactions in the pure liquids, resulting in a lower tendency of the molecules to escape to the vapor and a corresponding decrease in vapor pressure. Solutions that show negative deviations from Raoult's law include chloroform/acetone (because a weak hydrogen bond is formed), acetone/aniline, and chloroform/benzene. If the vapor pressure of the solution is above the Raoult's law prediction, it shows a **positive deviation** (Figure 6.7,

left). This indicates that the intermolecular interactions in solution are weaker than in the pure liquids on average, resulting in a greater escaping tendency to the vapor and an increase in vapor pressure. Examples include benzene/methanol, chloroform/ethanol, and acetone/CS<sub>2</sub>.

## 6.6 Nonideal Solutions

### 6.6.1 Activities

The thermodynamic properties of a solution are completely determined if the chemical potentials of all of its components are known. For an ideal or ideal-dilute solution, the chemical potential of any component is:

$$\mu_i^{\text{id/dil-id}} = \mu_i^\circ + RT \ln x_i \quad (6.82)$$

where  $\mu_i^\circ$  is the chemical potential of a suitably chosen standard state. In a real (nonideal) solution, this equation is no longer valid. We define the **activity** of component  $i$  as:

$$a_i = \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right) \quad (6.83)$$

The activity is an adimensional positive quantity that replaces  $x_i$  in the chemical potential equation:

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (6.84)$$

Since  $a_i = x_i$  for an ideal (or ideal-dilute) solution, the activity tends to the mole fraction if the real solution tends to ideality. For this reason, we define the **activity coefficient** as:

$$\gamma_i = \frac{a_i}{x_i} \quad (6.85)$$

and use it to measure the deviation from ideality of a given real solution. The activity coefficient is an adimensional and positive quantity and, by definition:

$$\mu_i - \mu_i^{\text{id/dil-id}} = RT \ln a_i - RT \ln x_i = RT \ln \gamma_i \quad (6.86)$$

so:

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i \quad (6.87)$$

where  $\gamma_i$  measures the departure of the chemical potential  $\mu_i$  from its ideal value.

The activity and activity coefficients are intensive properties because  $\mu_i$  is intensive, and therefore they can be written as a function of the intensive state:  $a_i(T, p, x_1, \dots)$  and  $\gamma_i(T, p, x_1, \dots)$ . For a given choice of standard state, knowledge of these activity or activity coefficient functions is equivalent to knowing the chemical potentials and, therefore, allow the calculation of any thermodynamic property of the solution. In addition, activities are monotonically increasing functions of the chemical potential and therefore they increase with increasing concentration.

Like the chemical potential, activities measure the escaping tendency of a component from the solution. Activities are often used as an alternative to chemical potentials because they are the equivalent of mole fractions (i.e. an “effective” mole fraction that takes into account the interactions with other solute molecules) in nonideal solutions. Therefore their values are easier to understand than the raw chemical potentials. Activities replace mole fractions in equations in which nonideal solutions are involved. In addition, they do not have a singularity at  $x_i = 0$  like the chemical potential ( $\mu_i \rightarrow -\infty$ ) and, unlike the chemical potential, absolute values of  $a_i$  can be determined experimentally. (For  $\mu_i$ , only differences relative to some arbitrary state can be obtained.)

### 6.6.2 Choice of Standard State

To complete the definition of the activity of a real solution (Eq. 6.83), a standard state must be chosen. This choice is made according to the nature of the solution. The most natural standard state for a nonideal solution is the model out of the two models we defined (ideal and ideal-dilute) that it most resembles, although ultimately this choice is a matter of convenience.

If the solution comprises several liquid components that can have mole fractions ranging all the way from 0 to 1, then we choose the same standard state as in an ideal solution. Because an ideal solution follows Raoult's law exactly (assuming ideal gas mixture for the vapor), this is known as the **Raoult's law standard state** or the **symmetrical convention**, since all components are treated equally. The Raoult's law standard state of each component  $i$  is the pure component at the same temperature and pressure as the solution:

$$\mu_{i,R}^\circ = \mu_i^*(T, p) \quad (6.88)$$

and the **Raoult's law activities** and **Raoult's law activity coefficients** are:

$$a_{i,R} = \exp\left(\frac{\mu_i - \mu_{i,R}^\circ}{RT}\right) \quad (6.89)$$

$$\gamma_{i,R} = \frac{a_{i,R}}{x_i} \quad (6.90)$$

and:

$$\mu_i = \mu_{i,R}^\circ + RT \ln a_{i,R} \quad (6.91)$$

Since the standard state of component  $i$  is pure  $i$ ,  $\gamma_{i,R} \rightarrow 1$  in the limit  $x_i \rightarrow 1$ . In addition, for an ideal solution,  $a_{i,R} = x_i$  and  $\gamma_{i,R} = 1$  under all conditions.

If the nonideal solution is composed mostly of solvent with a few solutes at low concentration, then the appropriate standard state is the same as in an ideal-dilute solution. Because an ideal-dilute solution follows Henry's law exactly for the solutes (assuming ideal gas mixture for the vapor), then this convention is known as the **Henry's law standard state** or **unsymmetrical convention**, since we are singling out one of the components as the solvent. The Henry's law standard state for the solvent is the pure solvent at the same temperature and pressure as the solution:

$$\mu_{A,H}^\circ = \mu_A^*(T, p) \quad (6.92)$$

For the solutes, the standard state is a fictitious state in which molecules of solute  $i$  experience interactions only with solvent molecules, but nonetheless the mole fraction is  $x_i = 1$ . The activities and activity coefficients are:

$$a_{i,H} = \exp\left(\frac{\mu_i - \mu_{i,H}^\circ}{RT}\right) \quad (6.93)$$

$$\gamma_{i,H} = \frac{a_{i,H}}{x_i} \quad (6.94)$$

and:

$$\mu_i = \mu_{i,H}^\circ + RT \ln a_{i,H} \quad (6.95)$$

In the infinite-dilution limit:

$$\gamma_{i,H}^\infty = \lim_{x_A \rightarrow 1} \gamma_{i,H} = 1 \quad (6.96)$$

$$\gamma_{A,H}^\infty = \lim_{x_A \rightarrow 1} \gamma_{A,H} = 1 \quad (6.97)$$

and the activities tend to the corresponding mole fractions ( $a_{A,H} \rightarrow x_A$  and  $a_{i,H} \rightarrow x_i$ ) in that limit. For an ideal-dilute solution,  $\gamma_{A,H} = \gamma_{i,H} = 1$ ,  $a_{A,H} = x_A$ , and  $a_{i,H} = x_i$  under all conditions.

The concentrations of dilute solutions involving solid or gas solutes are often more conveniently given in terms of molality ( $b_i$ ) or molar concentration ( $c_i$ ). If we use the molality,

$$b_i = \frac{n_i}{m_A} = \frac{n_i}{n_A M_A} = \frac{x_i}{x_A M_A} \quad (6.98)$$

and substituting  $x_i$  in Eq. 6.84 with the Henry's law standard state:

$$\begin{aligned} \mu_i &= \mu_{i,H}^\circ + RT \ln \gamma_{i,H} x_i = \mu_{i,H}^\circ + RT \ln \left( \frac{\gamma_{i,H} b_i x_A M_A b^\circ}{b^\circ} \right) \\ &= \underbrace{\mu_{i,H}^\circ + RT \ln (M_A b^\circ)}_{\mu_{i,b}^\circ} + RT \ln \left( \underbrace{\gamma_{i,H} x_A}_{\gamma_{i,b}} \times \frac{b_i}{b^\circ} \right) = \mu_{i,b}^\circ + RT \ln \left( \underbrace{\gamma_{i,b} \times \frac{b_i}{b^\circ}}_{a_{i,b}} \right) \\ &= \mu_{i,b}^\circ + RT \ln a_{i,b} \end{aligned} \quad (6.99)$$

The chemical potential in terms of the molality is said to be in the **molality scale**, and  $a_{i,b}$  and  $\gamma_{i,b}$  are the molality-scale activities and activity coefficients. The molality scale standard state, with chemical potential  $\mu_{i,b}^\circ$ , corresponds to a fictitious state in which the solution behaves like an ideal-dilute solution (solute molecules experience interactions only with solvent molecules) but the molality is  $b_i = b^\circ = 1 \text{ mol/kg}$ . Same as in the mole fraction scale,  $\gamma_{i,b} \rightarrow 1$  as  $x_A \rightarrow 1$ , and  $\gamma_{i,b} = 1$  and  $a_{i,b} = b_i/b^\circ$  for an ideal-dilute solution under all conditions.

Activities in the molality scale play in nonideal solutions the same role that molalities play in ideal-dilute solutions.

If we use molar concentrations instead of molalities, we have:

$$c_i = \frac{n_i}{V} \approx \frac{n_i \rho}{m_A} = \frac{n_i \rho}{n_A M_A} = \frac{x_i \rho}{x_A M_A} \quad (6.100)$$

where  $\rho$  is the solution density and we used than in a dilute solution the mass of the solution is approximately equal to the mass of the solvent ( $m \approx m_A$ ). Since  $x_i$  is proportional to  $c_i$ , following the same steps as above, we define the **concentration scale** activity ( $a_{i,c}$ ), activity coefficients ( $\gamma_{i,c}$ ), and standard state ( $\mu_{i,c}^\circ$ ), as:

$$\mu_i = \mu_{i,c}^\circ + RT \ln a_{i,c} \quad (6.101)$$

$$a_{i,c} = \gamma_{i,c} \times \frac{c_i}{c^\circ} \quad (6.102)$$

where the standard state (with chemical potential  $\mu_{i,c}^\circ$ ) is a hypothetical state with ideal-dilute behavior and solute concentration  $c_i = c^\circ = 1 \text{ mol/dm}^3$ . As in the other cases,  $\gamma_{i,c} \rightarrow 1$  as  $x_A \rightarrow 1$ , and  $\gamma_{i,c} = 1$  and  $a_{i,c} = c_i/c^\circ$  for an ideal-dilute solution. Activities in the concentration scale play in nonideal solutions the same role that concentrations play in ideal-dilute solutions.

The standard states used for the different components in solution, and the corresponding activity and chemical potential expressions, are summarized in Appendix A.

### 6.6.3 Vapor Pressure

Knowledge of the activity coefficients ( $\gamma_i$ ) determines the chemical potentials of all species, and therefore it also determines all thermodynamic properties of a solution. A common way of determining activity coefficients is to measure the vapor pressure of the solution, since the partial pressure of a component in the vapor is a reflection of its escaping tendency from the solution. In the following, we assume the vapor behaves as an ideal gas mixture.

In the case of the Raoult's law activity coefficients, we have (Eq. 6.91):

$$\mu_i = \mu_{i,R}^\circ + RT \ln a_{i,R} \quad (6.103)$$

and, following the same procedure as in Eq. 6.4.2, it is possible to show that:

$$p_i = a_{i,R} p_i^* \quad (6.104)$$

For the ideal solution (Eq. 6.44), Raoult's law (Eq. 6.58) applies:

$$p_i^{\text{id}} = x_i p_i^* \quad (6.105)$$

Dividing the last two equations:

$$\frac{p_i}{p_i^{\text{id}}} = \frac{a_{i,R} p_i^*}{x_i p_i^*} = \gamma_{i,R} \quad (6.106)$$

so the deviation between the actual vapor pressure and Raoult's law is a direct measure of  $\gamma_{i,R}$ . Solutions that show a negative deviation from Raoult's law (Figure 6.7, right) have  $p_i < p_i^{\text{id}}$  and  $\gamma_{i,R} < 1$ , indicating that the solution is more stable than the ideal solution or, equivalently, that favorable intermolecular interactions stabilize the solution and lower the chemical potentials of the components. Conversely, if the solution shows a positive deviation from Raoult's law (Figure 6.7, left),  $p_i > p_i^{\text{id}}$  and  $\gamma_{i,R} > 1$ . In this case, intermolecular interactions are unfavorable and increase the activity and the chemical potential in the solution, making more molecules escape to the vapor than in an ideal solution.

In the case of Henry's law activity coefficients, we differentiate between solute and solvent. For the solvent, the standard state is the same as in Raoult's law activity coefficients, so the discussion above applies. For the solutes, we have (Eq. 6.95):

$$\mu_i = \mu_{i,H}^\circ + RT \ln a_{i,H} \quad (6.107)$$

and following the same steps as in Section 6.5.2, we find:

$$p_i = K_i a_{i,H} \quad (6.108)$$

whereas for an ideal-dilute solution, Henry's law (Eq. 6.80) applies:

$$p_i^{\text{id-dil}} = K_i x_i^l \quad (6.109)$$

Dividing the two:

$$\frac{p_i}{p_i^{\text{id-dil}}} = \frac{K_i a_{i,H}}{K_i x_i^l} = \gamma_{i,H} \quad (6.110)$$

so the Henry's law coefficients are determined as the ratio between the observed partial pressure of solute  $i$  and the value predicted by Henry's law (dotted lines in Figure 6.7).

#### 6.6.4 Nonideal Gas Mixtures

Due to their similarities with solutions, we now briefly consider nonideal (real) mixtures of gases. The standard state of a gas in a real gas mixture is the same as in an ideal gas mixture and in a pure gas: the pure ideal gas at the same temperature as in the mixture and at a pressure of  $p^\circ = 1 \text{ bar}$ . We can define the activity for a gas mixture in the same way as for a solution (Eq. 6.83):

$$a_i = \exp \left( \frac{\mu_i - \mu_i^\circ}{RT} \right) \quad (6.111)$$

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (6.112)$$

We define the **fugacity** ( $f_i$ ) of component  $i$  as the activity times the standard pressure:

$$f_i = a_i p^\circ \quad (6.113)$$

The fugacity has units of pressure. It is intensive because  $a_i$  is intensive, so it can be written as a function of the intensive state ( $f_i(T, p, x_1, \dots)$ ). In addition, the chemical potential in terms of fugacity is:

$$\mu_i = \mu_i^\circ + RT \ln \left( \frac{f_i}{p^\circ} \right) \quad (6.114)$$

to be compared to the chemical potential of an ideal gas mixture (Eq. 4.153):

$$\mu_i = \mu_i^\circ + RT \ln \left( \frac{p_i}{p^\circ} \right) \quad (6.115)$$

Therefore, the fugacity plays the same role in a nonideal gas mixture as the partial pressure does in an ideal gas mixture. Since the partial pressure is  $p_i = x_i p$ , we can define the **fugacity coefficient** ( $\phi_i$ ) as:

$$\phi_i = \frac{f_i}{p_i} = \frac{f_i}{x_i p} \quad (6.116)$$

In the  $p \rightarrow 0$  limit, all real gases tend to the ideal gas behavior, so  $f_i \rightarrow p_i$  and  $\phi_i \rightarrow 1$ . In addition,  $f_i = p_i$  and  $\phi_i = 1$  for an ideal gas mixture under all conditions. When  $\phi_i < 1$ , the gas is more stable in the mixture than if it were an ideal gas mixture, indicating favorable intermolecular attractions. Conversely, if  $\phi_i > 1$ , the gas is less stable in the mixture due to intermolecular repulsions.

If the fugacities or the fugacity coefficients are known, then the chemical potentials and consequently all thermodynamic properties of the mixture can be calculated. Gas fugacities can be used to lift the assumption that the gas mixture in the vapor is ideal in the derivation of Raoult's law (Eq. 6.58) and Henry's law (Eq. 6.80). For instance, Raoult's law for a nonideal solution in contact with nonideal vapor is (compare to Eq. 6.106):

$$f_i = a_{i,R} f_i^* = \gamma_{i,R} x_i^l f_i^* \quad (6.117)$$

where  $f_i$  is the fugacity of  $i$  in the mixture and  $f_i^*$  is the fugacity in the pure gas.

Fugacities can be determined experimentally from isothermal compressibility data for real gases. The partial molar volume of component  $i$  in a mixture is:

$$\bar{V}_i = \left( \frac{\partial V}{\partial n_i} \right)_{p,T,n_j \neq i} = \left[ \frac{\partial}{\partial n_i} \left( \frac{\partial G}{\partial p} \right)_{T,n_j} \right]_{p,T,n_j \neq i} = \left[ \frac{\partial}{\partial p} \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_j \neq i} \right]_{T,n_j} = \left( \frac{\partial \mu_i}{\partial p} \right)_{T,n_j} \quad (6.118)$$

Substituting Eq. 6.114 and noting that  $\mu_i^\circ$  is a function of  $T$  only if  $i$  is a gas,

$$\bar{V}_i = RT \left( \frac{\partial (\ln f_i)}{\partial p} \right)_{T,n_j} \quad (6.119)$$

But the logarithm of the fugacity can be written as (Eq. 6.116):

$$\ln f_i = \ln(\phi_i x_i p) = \ln \phi_i + \ln x_i + \ln p \quad (6.120)$$

and of the three terms,  $\ln x_i$  does not change with pressure, so:

$$\bar{V}_i = RT \left( \frac{\partial (\ln \phi_i)}{\partial p} \right)_{T,n_j} + \frac{RT}{p} \quad (6.121)$$

This equation can be re-written as:

$$d(\ln \phi_i) = \left( \frac{\bar{V}_i}{RT} - \frac{1}{p} \right) dp \quad (6.122)$$

Integrating this expression between  $p = 0$ , for which  $\phi_i = 1$ , and pressure  $p$ , we have:

$$\ln \phi_i = \ln \phi_i - \ln 1 = \int_0^p \left( \frac{\bar{V}_i}{RT} - \frac{1}{p} \right) dp \quad (6.123)$$

where the integration is carried out at constant temperature and composition.

This equation also applies to pure real gases as well as mixtures. In a pure gas  $\bar{V}_i = V_{m,i}^*$  and:

$$\ln \phi_i^* = \int_0^p \left( \frac{V_{m,i}^*}{RT} - \frac{1}{p} \right) dp \quad (6.124)$$

Using the virial equation of state (Eq. 1.30), we can write the fugacity coefficients in terms of the virial coefficients. The virial equation of state says:

$$pV_m = RT \left( 1 + B^\dagger(T)p + C^\dagger(T)p^2 + \dots \right) \quad (6.125)$$

$$\frac{V_m}{RT} = \frac{1}{p} + B^\dagger(T) + C^\dagger(T)p + \dots \quad (6.126)$$

$$\frac{V_m}{RT} - \frac{1}{p} = B^\dagger(T) + C^\dagger(T)p + \dots \quad (6.127)$$

Carrying out the integration we find:

$$\ln \phi_i^* = B^\dagger(T)p + \frac{1}{2}C^\dagger(T)p^2 + \dots \quad (6.128)$$

Note that  $\ln \phi_i^*$  measures the deviation of a real gas from ideality in a manner similar to, but not exactly the same as, the compression factor  $Z$ :

$$Z = \frac{pV_m}{RT} = 1 + B^\dagger(T)p + C^\dagger(T)p^2 + \dots \quad (6.129)$$

Also, unlike  $Z$ ,  $\ln \phi_i$  can be defined for any component in a gas mixture. A common approximation for  $\ln \phi$  is to use the second virial coefficient ( $B^\dagger$ ) only. In accordance with the law of corresponding states, different gases at the same reduced temperature and reduced pressure have approximately the same fugacity coefficient. This allows the representation of graphs of fugacity against reduced pressure and reduced temperature for pure simple gases, similar to the compressibility factor chart in Figure 1.9.

Determining the fugacity of the components of a gas mixture using Eq. 6.123 is a lot of work, since it requires determining the partial volume for all components under all conditions. A common approximation is the **Lewis-Randall rule** in which the fugacity of component  $i$  in the mixture is assumed to be the same as in pure  $i$  at the same temperature and pressure as in the mixture:

$$\phi_i \approx \phi_i^*(T, p) \quad (6.130)$$

The Lewis-Randall rule implicitly assumes that the intermolecular interactions in the mixture have approximately the same nature and strength as in the pure gas. This is only a good approximation if the component molecules of the mixture are all similar to each other.

Alternatively one can use experimental equations of state for the mixture to determine the fugacities.

## 6.7 Electrolyte Solutions

### 6.7.1 Activities, Mean Ionic Activity Coefficients, and Chemical Potentials

An electrolyte is a substance that dissociates into cations and anions in solution and, as a result, conducts electricity. Electrolytes are classified into **strong**, if they are mostly dissociated into ions and are good electricity conductors, and **weak**, if they are dissociated only slightly and are poor conductors. For instance, HCl is a strong electrolyte:



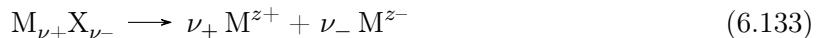
whereas acetic acid (HAc) is weak:



**True electrolytes** are those in which the pure substance is ionic whereas **potential electrolytes** generate ions only when in solution, but the pure substance is neutral. Sodium chloride (NaCl) is an ionic solid, so it is a true electrolyte. Hydrogen chloride (HCl) is a gas composed of neutral molecules, so it is a potential electrolyte.

When an electrolyte dissociates in solution, the resulting ions are surrounded by solvent molecules, a process known as **solvation**. In addition, because the ions are charged and the Coulomb interaction between them decays only as the first power of the distance, assuming that ions in solution are not interacting with each other (as in an ideal-dilute solution) is a poor approximation except at extremely low concentrations.

Let us consider a strong electrolyte that dissociates into  $\nu_+$  cations with charge  $z_+$  and  $\nu_-$  anions with charge  $z_-$ :



For instance, Ba(NO<sub>3</sub>)<sub>2</sub> has  $\nu_+ = 1$ ,  $\nu_- = 2$ ,  $z_+ = 2$ , and  $z_- = -1$ . If  $n_i$  moles of the electrolyte dissolve, the amount of cations is  $n_+ = \nu_+ n_i$  and the amount of anions is  $n_- = \nu_- n_i$ . The chemical potential of the ions:

$$\mu_+ = \left( \frac{\partial G}{\partial n_+} \right)_{T,p,n_j \neq +} \quad \mu_- = \left( \frac{\partial G}{\partial n_-} \right)_{T,p,n_j \neq -} \quad (6.134)$$

are difficult to determine individually because it is not possible to increase the number of one type of ion keeping the counterion amount fixed. Instead, we consider the chemical potential of the electrolyte as a whole:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p,n_j \neq i} \quad (6.135)$$

In solution, there are cations, anions, and solvent, so the differential of  $G$  is:

$$dG = -SdT + Vdp + \mu_A dn_A + \mu_+ dn_+ + \mu_- dn_- \quad (6.136)$$

and since  $dn_+ = \nu_+ dn_i$  and  $dn_- = \nu_- dn_i$ :

$$dG = -SdT + Vdp + \mu_A dn_A + (\nu_+ \mu_+ + \nu_- \mu_-) dn_i = -SdT + Vdp + \mu_A dn_A + \mu_i dn_i \quad (6.137)$$

so the chemical potential of the electrolyte as a whole is related to the cation and anion chemical potentials by:

$$\mu_i = \nu_+ \mu_+ + \nu_- \mu_- \quad (6.138)$$

The molality scale is often used for ionic concentrations and potentials:

$$\mu_+ = \mu_+^\circ + RT \ln \left( \gamma_+ \frac{b_+}{b^\circ} \right) \quad (6.139)$$

$$\mu_- = \mu_-^\circ + RT \ln \left( \gamma_- \frac{b_-}{b^\circ} \right) \quad (6.140)$$

Substituting in Eq. 6.138, we find:

$$\begin{aligned} \mu_i &= \nu_+ \left[ \mu_+^\circ + RT \ln \left( \gamma_+ \frac{b_+}{b^\circ} \right) \right] + \nu_- \left[ \mu_-^\circ + RT \ln \left( \gamma_- \frac{b_-}{b^\circ} \right) \right] \\ &= \underbrace{\nu_+ \mu_+^\circ + \nu_- \mu_-^\circ}_{\mu_i^\circ} + RT \left[ \nu_+ \ln \left( \gamma_+ \frac{b_+}{b^\circ} \right) + \nu_- \ln \left( \gamma_- \frac{b_-}{b^\circ} \right) \right] \\ &= \mu_i^\circ + RT \ln \left[ \gamma_+^{\nu_+} \gamma_-^{\nu_-} \left( \frac{b_+}{b^\circ} \right)^{\nu_+} \left( \frac{b_-}{b^\circ} \right)^{\nu_-} \right] \end{aligned} \quad (6.141)$$

where we defined the standard chemical potential of the electrolyte as:

$$\mu_i^\circ = \nu_+ \mu_+^\circ + \nu_- \mu_-^\circ \quad (6.142)$$

In addition, we define the **(molality-scale) mean ionic activity coefficient** as:

$$\gamma_\pm^\nu = \gamma_\pm^{\nu_+ + \nu_-} = (\gamma_+)^{\nu_+} (\gamma_-)^{\nu_-} \quad (6.143)$$

where  $\nu = \nu_+ + \nu_-$ . In a strong electrolyte, the ionic concentrations can be written in terms of the stoichiometric molality ( $b_i$ ) as  $b_+ = \nu_+ b_i$  and  $b_- = \nu_- b_i$ , so we can re-write Eq. 6.141 as:

$$\mu_i = \mu_i^\circ + RT \ln \left[ \gamma_\pm^\nu \underbrace{\nu_+^{\nu_+} \nu_-^{\nu_-}}_{\nu_\pm^\nu} \left( \frac{b_i}{b^\circ} \right)^\nu \right] = \mu_i^\circ + \nu RT \ln \left[ \nu_\pm \gamma_\pm \left( \frac{b_i}{b^\circ} \right) \right] \quad (6.144)$$

where we defined  $\nu_\pm^\nu = \nu_+^{\nu_+} \nu_-^{\nu_-}$  by analogy with the mean ionic activity coefficient (Eq. 6.143).

The chemical potential of the electrolyte as a whole given by Eq. 6.144 is similar to the chemical potential of other species in solution, except for the inclusion of the ionic stoichiometric coefficients. In order to make it fully consistent, we define the electrolyte activity as:

$$a_i = \left( \gamma_\pm \nu_\pm \frac{b_i}{b^\circ} \right)^\nu \quad (6.145)$$

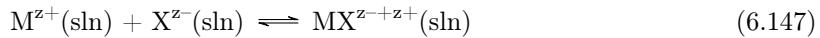
so that Eq. 6.144 reduces to the familiar expression:

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (6.146)$$

As a consequence of this definition of activity, the standard state of the electrolyte as a whole is a fictitious state where the ions do not interact with each other ( $\gamma_\pm = 1$ ) and the electrolyte concentration is  $\nu_\pm b_i = b^\circ = 1 \text{ mol/kg}$ .

In the infinite-dilution limit ( $x_A \rightarrow 1$  and  $b_i \rightarrow 0$ ),  $\gamma_\pm = \gamma_+^\infty = \gamma_-^\infty = 1$ . However, except at extremely low concentrations, the ionic and mean ionic activity coefficients deviate significantly from one. For instance, at 0.1 mol/kg concentration in water,  $\gamma_\pm$  is 0.797 (HCl), 0.517 (CaCl<sub>2</sub>), 0.446 (Na<sub>2</sub>SO<sub>4</sub>), to be compared with ethanol ( $\gamma_i = 0.988$ ). At the much lower concentration of 0.001 mol/kg,  $\gamma_\pm$  is 0.965 (HCl), 0.888 (CaCl<sub>2</sub>), 0.886 (Na<sub>2</sub>SO<sub>4</sub>), whereas the activity coefficient of ethanol is essentially one ( $\gamma_i = 0.9999$ ).

Even in strong electrolytes, the number of ions in solution is most often not given by the stoichiometric relations  $n_+ = \nu_+ n_i$  and  $n_- = \nu_- n_i$ . This is because ions of opposite charge in solution attract each other and, often, they associate into **ionic pairs**:



where the ionic pairs may also be charged. Ionic pairing is favored by high ionic charges ( $z_+$  and  $|z_-|$ ) and solvents with low dielectric constants, and it is negligible only in dilute 1:1 solutions using a high dielectric constant solvent (like water). It is possible to show that, in the presence of neutral ionic pair formation, the chemical potential of the electrolyte as a whole (Eq. 6.144) stays the same but the mean ionic activity coefficient becomes:

$$\gamma_{\pm}^{\dagger} = \alpha^{\nu_+/v} \left[ 1 - (1 - \alpha) \left( \frac{\nu_+}{\nu_-} \right) \right] \gamma_{\pm} \quad (6.148)$$

where  $\alpha$  measures the extent of electrolyte dissociation into individual pairs:

$$n_+ = \alpha \nu_+ n_i \quad n_- = \alpha \nu_- n_i \quad (6.149)$$

and  $\gamma_{\pm}$  is the mean ionic activity coefficient in absence of ionic pairing. Since ionic pairing is so prevalent, thermodynamic tables reporting  $\gamma_{\pm}$  and empirical models such as the Davies equation (see below) approximate  $\gamma_{\pm}^{\dagger}$  instead of  $\gamma_{\pm}$ .

### 6.7.2 The Debye-Hückel theory

Because isolated cations or anions cannot exist in solution, it is not possible to determine  $\gamma_+$  or  $\gamma_-$  experimentally. However, it is possible to derive theoretical expressions for these quantities using statistical mechanics. Debye and Hückel developed a simple but insightful theory for  $\gamma_+$  and  $\gamma_-$  in 1923. The Debye-Hückel theory is based on the assumptions that i) ions are uniformly charged hard spheres all with the same radius  $a$ , ii) the solvent is a continuum with dielectric constant  $\epsilon_{r,A}$ , and iii) the solution is very dilute. Under these assumptions, the ionic activity coefficients are:

$$\ln \gamma_+ = -\frac{z_+^2 A I_b^{1/2}}{1 + B a I_b^{1/2}} \quad \ln \gamma_- = -\frac{z_-^2 A I_b^{1/2}}{1 + B a I_b^{1/2}} \quad (6.150)$$

The  $A$  and  $B$  constants depend only on the nature of the solvent and the temperature:

$$A = (2\pi N_A \rho_A)^{1/2} \left( \frac{e^2}{4\pi \epsilon_0 \epsilon_{r,A} k_B T} \right) \quad (6.151)$$

$$B = e \left( \frac{2N_A \rho_A}{\epsilon_0 \epsilon_{r,A} k_B T} \right) \quad (6.152)$$

where  $N_A$  is Avogadro's constant,  $\rho_A$  is the solvent density,  $e$  is the charge of an electron,  $\epsilon_0$  is the vacuum permittivity, and  $k_B = R/N_A$  is Boltzmann's constant. The units of  $A$  and  $B$  are  $(\text{kg/mol})^{1/2}$  and  $(\text{kg/mol})^{1/2} \text{ m}^{-1}$ , respectively. The  $I_b$  in the Debye-Hückel activity coefficients (Eq. 6.150) is the **(molality-scale) ionic strength**, defined as:

$$I_b = \frac{1}{2} \sum_j z_j^2 b_j \quad (6.153)$$

where the sum runs over all ionic species in solution, not just the ions from the electrolyte we are interested in. The ionic strength has units of molality, and it increases with the amount and charge of the dissolved ions. The ionic strength measures the “chargedness” of the solution, and its ability to stabilize the charges of ions dissolved in it.

From the activity coefficients of the individual ions (Eq. 6.150), we can determine the mean ionic activity coefficient by substitution in Eq. 6.143:

$$\gamma_{\pm}^{\nu} = (\gamma_+)^{\nu+}(\gamma_-)^{\nu-} \quad (6.154)$$

$$\ln \gamma_{\pm} = \frac{\nu_+ \ln \gamma_+ + \nu_- \ln \gamma_-}{\nu_+ + \nu_-} = -\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-} \frac{AI_b^{1/2}}{1 + BaI_b^{1/2}} \quad (6.155)$$

The electrolyte is electrically neutral, so  $\nu_+ z_+ + \nu_- z_- = 0$ . From this,

$$\begin{aligned} \nu_+ z_+^2 &= -\nu_- z_+ z_- \\ \nu_- z_-^2 &= -\nu_+ z_+ z_- \\ \hline \nu_+ z_+^2 + \nu_- z_-^2 &= -(\nu_+ + \nu_-) z_+ z_- \end{aligned} \quad (6.156)$$

Substituting in Eq. 6.155, we find:

$$\ln \gamma_{\pm} = z_+ z_- \frac{AI_b^{1/2}}{1 + BaI_b^{1/2}} = -z_+ |z_-| \frac{AI_b^{1/2}}{1 + BaI_b^{1/2}} \quad (6.157)$$

where we used that  $z_+ > 0$  and  $z_- < 0$ . The mean ionic activity coefficient expression in the Debye-Hückel theory is very similar to the activity coefficients of the individual ions (Eq. 6.150). For very dilute solutions, the second term in the denominator of Eq. 6.157 is negligible compared to 1, and we have:

$$\ln \gamma_{\pm} = -z_+ |z_-| AI_b^{1/2} \quad (6.158)$$

which is known as the **Debye-Hückel limiting law**, because it is only valid in the limit of infinite dilution.

The Debye-Hückel activity coefficients (Eqs. 6.150 and 6.157) allow the calculation of the chemical potentials (Eqs. 6.139 and 6.140) and therefore determine completely the thermodynamic properties of an electrolytic solution. The Debye-Hückel activity coefficients are valid in 1:1 electrolyte solutions up to approximately  $I_b = 0.1 \text{ mol/kg}$ . The Debye-Hückel limiting law (Eq. 6.158), which is obtained by further approximating the Debye-Hückel law, is valid only up to approximately  $I_b = 0.01 \text{ mol/kg}$  for 1:1 electrolytes. For electrolytes with charges higher than one, the concentration range in which the Debye-Hückel theory is valid is more restricted, since the ions interact more strongly.

For electrolytic solutions with concentrations that exceed the Debye-Hückel's law range of validity, empirical relations have been derived for the mean ionic activity coefficients. For instance, the **Davies equation**:

$$\log_{10} \gamma_{\pm} = -0.51 z_+ |z_-| \left[ \frac{(I_b/b^\circ)^{1/2}}{1 + (I_b/b^\circ)^{1/2}} - 0.30 (I_b/b^\circ) \right] \quad (6.159)$$

is useful for aqueous electrolytic solutions at room temperature. Other empirical mean ionic activity coefficient relations for other solvents exist that are used in practice. Note that both in the Davies equation (Eq. 6.159) and in the Debye-Hückel equation (Eq. 6.157) the activity coefficients depend only on the ionic strength and the nature of the solvent and not on the interactions between specific ion pairs. There are more sophisticated models (like the Pitzer model) where specific ion-ion interactions are taken into account.

## 6.8 Chemical Reactions in Solution

### 6.8.1 General Results

Chemical reactions in solution equilibrium conditions similar to gas mixtures (Section 4.9.2). Consider the chemical reaction in solution:



When the reaction is at equilibrium, the sum of the chemical potentials of reactants and products must be zero (Eq. 4.145):

$$\sum_i \nu_i \mu_i = 0 \quad (6.161)$$

For any species involved in the reaction, the chemical potential is written as (Eq. 6.84):

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (6.162)$$

Substitution in the equation above gives:

$$\sum_i \nu_i \mu_i^\circ + RT \sum_i \nu_i \ln a_i = 0 \quad (6.163)$$

The first term is the standard reaction Gibbs free energy (Eq. 4.155) and the second term is rearranged to give:

$$\Delta_r G^\circ = -RT \ln K^\circ \quad (6.164)$$

where we defined the **(standard) equilibrium constant** as:

$$K^\circ = \prod_i a_i^{\nu_i} \quad (6.165)$$

Note the similarity between this constant and the  $K_p^\circ$  equilibrium constant (Eq. 4.159) for ideal gas mixtures.

The equilibrium constant ( $K^\circ$ , Eq. 6.165) determines the equilibrium composition for a chemical reaction in any nonideal homogeneous system. This includes solutions but also nonideal gas mixtures, in which it translates into:

$$K^\circ = \prod_i a_i^{\nu_i} = \prod_i \left( \frac{f_i}{p^\circ} \right)^{\nu_i} = \prod_i \left( \frac{\phi_i x_i p}{p^\circ} \right)^{\nu_i} \quad (6.166)$$

where  $f_i$  are the fugacities and  $\phi_i$  are the fugacity coefficients. Compare to Eq. 4.159 and note how the equilibrium partial pressures present in the equilibrium constant for an ideal gas mixture, have been replaced by fugacities in the case of real gas mixtures.

In order to use the equilibrium condition in Eq. 6.165, the activity must be defined, which requires establishing the standard state of all reactants and products. We will see a few important examples of how this is done next. Note that the standard state of components in solution is usually adopted to be a certain state at the same temperature and pressure as the solution. Therefore, unlike gases,  $\mu_i^\circ$  depends on pressure as well as on temperature, and therefore  $K^\circ$  also depends on pressure. However, because liquids and solids are relatively incompressible, this dependence is usually negligible unless gases are involved in the reaction.

### 6.8.2 Non-electrolyte Solutions

Let us now assume that the chemical reaction happens between the components of a relatively dilute solution. Because the solution resembles an ideal-dilute solution, we adopt Henry's law standard states. With this choice, the activities, standard chemical potentials, and equilibrium constants can be variously written in the concentration, molality, or mole fraction scales, depending on which is most convenient:

$$\Delta_r G_x^\circ = \sum_i \nu_i \mu_{i,H}^\circ = -RT \ln K_x^\circ \quad (6.167)$$

$$\Delta_r G_b^\circ = \sum_i \nu_i \mu_{i,b}^\circ = -RT \ln K_b^\circ \quad (6.168)$$

$$\Delta_r G_c^\circ = \sum_i \nu_i \mu_{i,c}^\circ = -RT \ln K_c^\circ \quad (6.169)$$

where the corresponding equilibrium constants are defined as:

$$K_x^\circ = \prod_i a_{i,H}^{\nu_i} = \prod_i (\gamma_{i,H} x_i)^{\nu_i} \quad (6.170)$$

$$K_b^\circ = a_{A,H}^{\nu_A} \prod_{i \neq A} a_{i,b}^{\nu_i} = (\gamma_{A,H} x_A)^{\nu_A} \prod_{i \neq A} \left( \gamma_{i,b} \frac{b_i}{b^\circ} \right)^{\nu_i} \quad (6.171)$$

$$K_c^\circ = a_{A,H}^{\nu_A} \prod_{i \neq A} a_{i,c}^{\nu_i} = (\gamma_{A,H} x_A)^{\nu_A} \prod_{i \neq A} \left( \gamma_{i,c} \frac{c_i}{c^\circ} \right)^{\nu_i} \quad (6.172)$$

Note that, in the case of the molality and molarity scales, the solvent is separated from the other components because its standard state is different from the solutes (pure solvent at the same temperature and pressure as the solution), and therefore its activity is always defined in terms of the mole fraction  $a_A = \gamma_A x_A$ . In reactions in which the solvent is not a reactant or a product,  $\nu_A = 0$  and this term disappears.

These equilibrium constants can all be used to determine the equilibrium composition of a reacting mixture, but they are all numerically different and, when reported, it is necessary to specify what standard state they are referred to. The molality scale is most commonly used in thermodynamic tables. Note that, in the limit  $x_A \rightarrow 1$ , the solution goes to the ideal-dilute limit so  $\gamma_i \rightarrow 1$  for all  $i$ , and the equations for the equilibrium constants reduce to the familiar expressions:

$$K_x^\circ \approx \prod_{i \neq A} (x_i)^{\nu_i} \quad (6.173)$$

$$K_b^\circ \approx \prod_{i \neq A} \left( \frac{b_i}{b^\circ} \right)^{\nu_i} \quad (6.174)$$

$$K_c^\circ \approx \prod_{i \neq A} \left( \frac{c_i}{c^\circ} \right)^{\nu_i} \quad (6.175)$$

This is a reasonable approximation for reactions happening in dilute non-electrolyte solutions. Note that the equilibrium constants depend on the nature of the solvent, because the standard states of the solutes do, even if the solvent concentration does not appear explicitly in the equilibrium constant equation.

### 6.8.3 Electrolyte Solutions

For chemical reactions in electrolytic solutions, the preceding equations are also valid although, in this case, the solution is often not dilute enough to assume that the activity coefficients are

one. The molality scale is often preferred when dealing with reactions between electrolytes, so we have:

$$\Delta_r G^\circ = \sum_i \nu_i \mu_{i,b}^\circ = -RT \ln K^\circ \quad (6.176)$$

$$K^\circ = a_{A,x}^{\nu_A} \prod_{i \neq A} a_{i,b}^{\nu_i} = (\gamma_{A,x} x_A)^{\nu_A} \prod_{i \neq A} \left( \gamma_{i,b} \frac{b_i}{b^\circ} \right)^{\nu_i} \quad (6.177)$$

Most often, the solvent is water and the solution is dilute. Since 1 L of dilute aqueous solution at ambient conditions weighs approximately 1 kg, the molality is approximately equal the molarity ( $b \approx c$ ).

For example, in the **self-ionization of water** reaction:



the equilibrium constant is the **(standard) water equilibrium constant**:

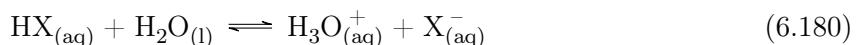
$$K_w^\circ = \frac{a(\text{H}_3\text{O}^+)a(\text{OH}^-)}{a(\text{H}_2\text{O})^2} \quad (6.179)$$

Under usual conditions, the extent of the self-ionization in water is very small, and so the mole fraction of the solvent (non-dissociated water) is approximately one  $x_A \approx 1$ . Since in the  $x_A \rightarrow 1$  limit  $\gamma_A \rightarrow 1$  and the solvent molecule is neutral (so it converges to this limit faster than a charged molecule), then  $a_A \approx x_A \approx 1$ , and so the equilibrium constant reduces to:

$$\begin{aligned} K_w^\circ &= a(\text{H}_3\text{O}^+)a(\text{OH}^-) = \left( \frac{\gamma(\text{H}_3\text{O}^+)b(\text{H}_3\text{O}^+)}{b^\circ} \right) \left( \frac{\gamma(\text{OH}^-)b(\text{OH}^-)}{b^\circ} \right) \\ &= \gamma_\pm^2 \frac{b(\text{H}_3\text{O}^+)b(\text{OH}^-)}{(b^\circ)^2} \end{aligned}$$

where  $\gamma_\pm^2 = \gamma(\text{H}_3\text{O}^+)\gamma(\text{OH}^-)$ . Experiments show that at room temperature and 1 bar,  $K_w^\circ = 1 \times 10^{-14}$ . If we assume  $\gamma_\pm \approx 1$ , this gives  $b(\text{H}_3\text{O}^+) = b(\text{OH}^-) = 1 \times 10^{-7} \text{ mol/kg}$ . Application of the Davies equation (Eq. 6.159) with these molalities indicates that  $\gamma_\pm = 0.9996$ , proving *a posteriori* the validity of our assumption that the solution is dilute enough to have  $\gamma_\pm \approx 1$ . In solutions with higher ionic strength, this may no longer be the case, and the molalities can deviate from  $1 \times 10^{-7} \text{ mol/kg}$ .

Another example is the ionization of a weak acid in water:



The equilibrium constant for this reaction is the **(standard) acid dissociation constant**:

$$K_a^\circ = \frac{a(\text{H}_3\text{O}^+)a(\text{X}^-)}{a(\text{HX})a(\text{H}_2\text{O})} \approx \frac{\left( \frac{\gamma(\text{H}_3\text{O}^+)b(\text{H}_3\text{O}^+)}{b^\circ} \right) \left( \frac{\gamma(\text{X}^-)b(\text{X}^-)}{b^\circ} \right)}{\left( \frac{\gamma(\text{HX})b(\text{HX})}{b^\circ} \right)} \quad (6.181)$$

where we have already assumed that the solution is dilute enough that  $a(\text{H}_2\text{O}) \approx 1$  and, since HX is uncharged, we can also assume that  $\gamma(\text{HX}) \approx 1$ . Using  $\gamma_\pm^2 = \gamma(\text{H}_3\text{O}^+)\gamma(\text{X}^-)$ , we have:

$$K_a^\circ = \gamma_\pm^2 \frac{b(\text{H}_3\text{O}^+)b(\text{X}^-)}{b(\text{HX})b^\circ} \quad (6.182)$$

Note that, in general,  $\gamma_{\pm}$  cannot be assumed to be one. Sometimes the acid dissociation constant is given with units of molality:

$$K_a = \gamma_{\pm}^2 \frac{b(\text{H}_3\text{O}^+)b(\text{X}^-)}{b(\text{HX})} \quad (6.183)$$

and often the  $pK_a$  are reported instead:

$$\text{p}K_a = -\log_{10} K_a^\circ \quad (6.184)$$

Examples of  $\text{p}K_a$  for a few weak acids are: 3.20 (HF), 4.76 (HAc), and 9.21 (HCN). The  $\text{p}K_a$  is defined in analogy with the pH, which is:

$$\text{pH} = -\log_{10} a(\text{H}^+) \quad (6.185)$$

The definition of pH involves activities, not concentrations or molalities. For instance, the pH of a 0.1 M HCl solution decreases (the solution becomes more acidic) when it is diluted with a 5 M solution of CaCl<sub>2</sub> because, even though  $c(\text{H}^+)$  decreases, the activity  $a(\text{H}^+)$  is increasing due to the change in the ionic strength (see McCarty et al. “pH paradoxes: demonstrating that it is not true that  $\text{pH} = -\log[\text{H}^+]$ ”, *J. Chem. Educ.* **83** 752 (2006)).

Equilibrium constants for other common reactions in solution receive specific names. For instance, the **base dissociation constant** is the constant associated with the protonation of a base. The **stability constant** is the constant associated with the formation of a complex in solution. The equilibrium corresponding to a solid in contact with a solution into which it dissolves is the **solubility constant**.

In laboratory practice, when studying reaction equilibria of dilute electrolyte solutions, it is common to “fix” the ionic strength by adding an excess amount of a strong electrolyte. Since the ionic activity coefficients are mostly determined by the ionic strength (Section 6.7.2), adding an excess of a strong electrolyte essentially makes the  $\gamma_i$  and  $\gamma_{\pm}$  of reactants and products constant. In turn, this makes the equilibrium constant equation (Eq. 6.165) reduce to:

$$K^\circ = \prod_i a_i^{\nu_i} = \prod_i \gamma_i^{\nu_i} \left( \frac{b_i}{b^\circ} \right)_i^{\nu_i} \quad (6.186)$$

$$K_{\text{eff}}^\circ = K^\circ \prod_i \gamma_i^{-\nu_i} = \prod_i \left( \frac{b_i}{b^\circ} \right)_i^{\nu_i} \quad (6.187)$$

As long as the ionic strength is the same in all experiments, the left hand side of this equation is approximately constant, and so  $K_{\text{eff}}^\circ$  is known as the **effective equilibrium constant** (or **apparent equilibrium constant**).

#### 6.8.4 Reactions Involving Pure Solids and Pure Liquids

The equilibrium conditions (Eqs. 6.161 and 6.165) apply even if some of the reactants or products are in a phase other than the solution. A particularly important case is reactions involving pure solids (for instance, a precipitation reaction) or pure liquids. For the pure solid or liquid, the usual expression for the chemical potential applies (Eq. 6.162) but, in this case, the standard state is the pure solid or liquid at the same temperature as the solution and  $p^\circ = 1$  bar. The chemical potential is:

$$RT \ln a_i = \mu_i - \mu_i^\circ = \mu_i^*(T, p) - \mu_i^*(T, p^\circ) = \int_{p^\circ}^p V_{m,i} dp \quad (6.188)$$

where we used that  $\mu_i = \mu_i^*$  because the solid or liquid is pure in its own phase. Since solids and liquids are relatively incompressible, we can assume  $V_{m,i}$  is constant for a moderate pressure range and write:

$$\ln a_i = \frac{(p - p^\circ) V_{m,i}}{RT} \quad (6.189)$$

Because  $V_{m,i}$  is small for solids and liquids, at moderate pressures the right hand side of this equation is approximately zero and  $a_i \approx 1$ .

**Example.** Water at room temperature and 1 bar has molar volume:

$$V_m = \frac{V}{n} = \frac{VM}{m} = \frac{M}{\rho} = \frac{18.015\,28\text{ g/mol}}{1\text{ g/cm}^3} = 18.015\,28\text{ cm}^3/\text{mol}$$

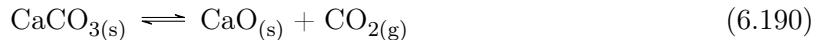
The activity at room temperature and 100 bar is:

$$a_i = \exp\left(\frac{(p - p^\circ) V_{m,i}}{RT}\right) = \exp\left(\frac{(100\text{ bar} - 1\text{ bar}) 18.015\,28\text{ cm}^3/\text{mol} \times \frac{1\text{ m}^3}{1 \times 10^6\text{ cm}^3}}{8.314\text{ J/K/mol} \times 298.15\text{ K}}\right) = 1.000\,000\,72$$

Therefore, the activity of water can be assumed to be equal to one except at very high pressure.

Because  $a_i \approx 1$  for a pure solid or liquid unless the pressure is exceptionally high, the corresponding activity disappears from the equilibrium expression. Note, however, that the  $\mu_i^\circ$  still enters the  $\Delta_r G^\circ$  because the standard chemical potential is not zero.

For example, the thermal decomposition of calcite releases CO<sub>2</sub> gas:



The equilibrium condition (Eq. 6.165) is:

$$K^\circ = \frac{a(\text{CaO}_{(s)}) a(\text{CO}_{2(g)})}{a(\text{CaCO}_{3(s)})} \approx a(\text{CO}_{2(g)}) \quad (6.191)$$

where we used  $a(\text{CaO}_{(s)}) \approx 1$  and  $a(\text{CaCO}_{3(s)}) \approx 1$ . Assuming ideal gas behavior ( $a_i = f_i/p^\circ \approx p_i/p^\circ$ , Eq. 6.113), we have that the equilibrium constant is numerically equal to the pressure of CO<sub>2</sub> in equilibrium with the solid phases at the decomposition temperature:

$$K^\circ \approx \frac{p(\text{CO}_{2(g)})}{p^\circ} \quad (6.192)$$

However, this equilibrium constant involving only the pressure of CO<sub>2</sub> is related to the standard reaction Gibbs free energy (Eq. 6.164):

$$\begin{aligned} \Delta_r G^\circ &= -RT \ln K^\circ = \mu^\circ(\text{CaO}_{(s)}) + \mu^\circ(\text{CO}_{2(g)}) - \mu^\circ(\text{CaCO}_{3(s)}) \\ &= G_m^\circ(\text{CaO}_{(s)}) + G_m^\circ(\text{CO}_{2(g)}) - G_m^\circ(\text{CaCO}_{3(s)}) \end{aligned} \quad (6.193)$$

where we used  $\mu^\circ = G_m^\circ$  because every species in this reaction are alone and pure in their own phase. Like all reactions, the decomposition of calcite may be carried out to completion if the equilibrium condition cannot be met. For instance, if the container in which the calcite is being heated is open such that the pressure of CO<sub>2</sub> cannot build up and reach  $K^\circ$  or if there is not a large enough amount of starting calcite to reach that pressure.

Another example is the solubility of a mostly insoluble salt. For instance, the solubility reaction in water is:



The equilibrium condition (Eq. 6.165) is:

$$K^\circ = \frac{(a_+)^{\nu_+}(a_-)^{\nu_-}}{a(M_{\nu_+}X_{\nu_-(s)})} \approx \gamma_\pm^\nu \left(\frac{b_+}{b^\circ}\right)^{\nu_+} \left(\frac{b_-}{b^\circ}\right)^{\nu_-} \quad (6.195)$$

where, as above, the activity of the pure solid is assumed equal to one. When this equilibrium constant is written with molality units, it is known as the **solvability product** ( $K_{sp}$ ) of the solid:

$$K_{sp} = \gamma_\pm^\nu (b_+)^{\nu_+} (b_-)^{\nu_-} \quad (6.196)$$

For salts that are only very slightly soluble, the ionic strength of the solution is small and  $\gamma_\pm \approx 1$ . In addition, if the solvent is water,  $b \approx c$ , which leads to the familiar expression:

$$K_{sp} \approx (c_+)^{\nu_+} (c_-)^{\nu_-} \quad (6.197)$$

However, it is important to point out that this equation is not valid if the solvent has a non-negligible ionic strength (for instance, if there are other salts dissolved) or if there is significant ionic association in solution (for example, if the electrolyte is not 1:1).

### 6.8.5 Temperature and Pressure Dependence of the Equilibrium Constant

The temperature dependence of the equilibrium constant:

$$\ln K^\circ = -\frac{\Delta_r G^\circ}{RT} \quad (6.198)$$

is given by the van't Hoff equation (Eq. 4.170):

$$\frac{d \ln K^\circ}{dT} = \frac{\Delta_r H^\circ}{RT^2} \quad (6.199)$$

The derivation is exactly the same as for  $K_p^\circ$  in Section 4.9.3. Same as we did for the Clausius-Clapeyron equation (Eq. 5.15), the van't Hoff equation can be re-written in a more usable form using the chain rule:

$$\frac{d \ln K^\circ}{dT} = \frac{d \ln K^\circ}{d(1/T)} \frac{d(1/T)}{dT} = \frac{d \ln K^\circ}{d(1/T)} \times \left(-\frac{1}{T^2}\right) = \frac{\Delta_r H^\circ}{RT^2} \quad (6.200)$$

from where:

$$\frac{d \ln K^\circ}{d(1/T)} = -\frac{\Delta_r H^\circ}{R} \quad (6.201)$$

Because the standard states of reactants and products depend on pressure in general, the  $K^\circ$ , unlike  $K_p^\circ$ , depends also on pressure, albeit only very slightly.

# Chapter 7

## Electrochemistry

### 7.1 Electrochemical Systems

An **electrochemical system** is a system in which there is a difference in electric potential between phases. The electrochemical systems of interest to us are composed of conducting phases such as metals, electrolytic solutions, molten salts,... and we want to examine the thermodynamics of processes involving movement of charges between different phases, perhaps carrying out work as a result of this movement. A simple example of an electrochemical system is a household battery in which a spontaneous chemical reaction is used to drive electrons from the negative to the positive terminals, effecting work on the environment, like powering an electronic device.

The electric potential at point  $\mathbf{r}$  ( $\phi(\mathbf{r})$ ) is defined as the work required to bring a (positive) unit test charge from infinity to that point. The electric potential energy ( $V$ ) of a particle with charge  $Q$  is therefore:

$$V = Q\phi \quad (7.1)$$

As a consequence of this definition, the work required to move a charge between point  $a$  and point  $b$  is given by the charge  $Q$  times the potential difference ( $\Delta\phi$ ) between those two points:

$$w_{b \rightarrow a} = Q\Delta\phi \quad (7.2)$$

$$\Delta\phi = \phi_a - \phi_b \quad (7.3)$$

This movement is reversible in a thermodynamic sense because the opposite process has opposite work ( $w_{a \rightarrow b} = -w_{b \rightarrow a}$ ).

The force experienced by a charge in an electric field  $\mathbf{E}$  is given by:

$$\mathbf{F} = Q\mathbf{E} \quad (7.4)$$

where the electric field is minus the gradient of the electric potential:

$$\mathbf{E} = -\nabla\phi \quad (7.5)$$

The SI unit of charge is the coulomb (C) and the unit of potential is the volt (V), which is defined as  $1 \text{ V} = 1 \text{ J/C}$  (see Eq. 7.1). The SI unit of electric field is  $\text{V/m}$  (Eq. 7.5) or  $\text{N/C}$  (Eq. 7.4). Negative charges, like electrons, placed in a non-uniform electric field move from regions of low electric potential to regions of high potential following the electric field lines.

The phases present in the electrochemical systems of interest to us are usually good conductors of electricity, which means that charges in the bulk of these phases are relatively free to move

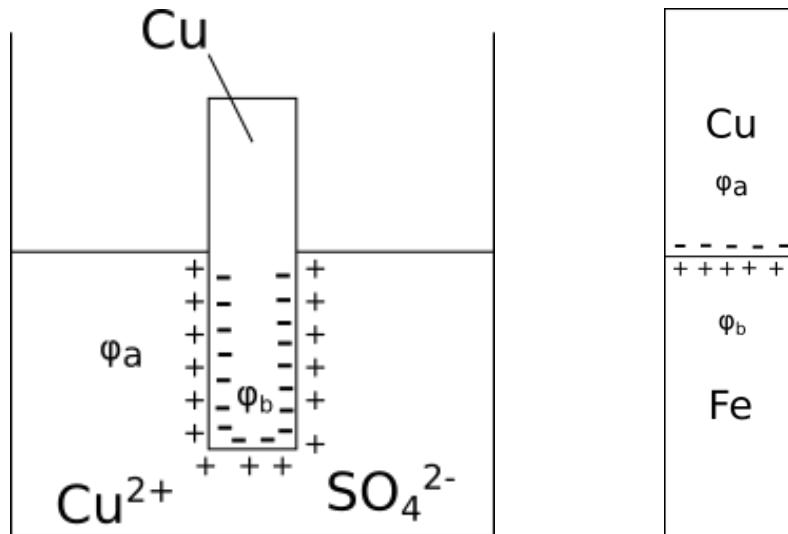


Figure 7.1: Two electrochemical systems. Left: metallic Cu in contact with an aqueous  $\text{CuSO}_4$  solution. Right: two metals (Cu and Fe) in contact. Each phase has a different electric potential ( $\phi_a$  and  $\phi_b$ ).

around. Since a conducting phase in thermodynamic equilibrium must have no net current flowing inside, the net electric forces on all the charges inside the phase must be zero, and therefore the electric field in the interior of a conductor must also be zero (Eq. 7.4). Because the electric field is the gradient of the potential (Eq. 7.5), this means that  $\phi$  must be the same throughout the bulk of a conducting phase in equilibrium. If the phase is charged (i.e. not electrically neutral), then the charges must be distributed over the surface of the phase, to minimize the repulsion between like charges. The electric potential in the interior of a conductor phase in equilibrium is known as the **inner potential** or **Galvani potential**.

## 7.2 The Electrochemical Potential

By definition, an electrochemical system must be composed of at least two phases in contact that have different electric potentials. The electrochemical systems of interest to us have the property that at least one charged species may move between phases in contact. Two examples of such systems are shown in Figure 7.1. The system on the left shows an aqueous  $\text{CuSO}_4$  solution in contact with metallic Cu. In this system, the Cu atoms can drop two electrons in the metal and enter the solution as  $\text{Cu}^{2+}$  cations but the electrons cannot move into the solution. In the system on the right of Figure 7.1, we have two metals (Cu and Fe) in contact and electrons can move from one to the other, but the Fe and Cu atoms cannot. In either of these two examples, because the inner potential of the two phases in contact is different, there is a potential difference that drives the charges from one phase to the other. The charge transfer continues, and both phases become more electrically charged, until the system achieves equilibrium at the point at which the Gibbs free energy of the whole system is a minimum. The electric potential difference between phases is, in general, in the order of a few volts, and it is possible to show that the amount of charged species transferred between phases is so small as to be chemically undetectable.

The potential difference between two phases ( $\Delta\phi = \phi_a - \phi_b$ ) depends on the thermodynamic state: temperature, pressure, the nature of the two phases in contact and their composition, as well as the distribution of charges in the vicinity of the interface between both phases. In general, this potential difference cannot be measured directly because any attempt at doing so necessarily introduces a new interface, and therefore the  $\Delta\phi$  measured no longer corresponds to just the interface under study. For instance, if we attach a potentiometer to each of the phases

in the right system of Figure 7.1, we create two new interfaces (potentiometer/Fe and potentiometer/Cu) with their own  $\Delta\phi$ , which contributes to the overall potential difference. Single interface potential differences can be measured in the particular case when the two phases in contact have similar compositions, and can also be calculated using statistical mechanical models.

Consider a phase  $\alpha$  with potential  $\phi^\alpha$  that undergoes a reversible change in composition. If the components entering the system are uncharged, then the change in Gibbs free energy for this process is given by Eq. 4.108:

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i \quad (7.6)$$

Now assume each component molecule has a charge  $z_i e$ , where  $e$  is the charge of an electron in absolute value ( $e = 1.602\ 176\ 634 \times 10^{-19}$  C) and  $z_i$  is the **charge number** of this species. For instance, an electron has  $z_i = -1$ , a  $Zn^{2+}$  cation has  $z_i = +2$ , and an  $SO_4^{2-}$  anion has  $z_i = -2$ . Since  $z_i e$  is the charge of a single molecule, the charge of an amount  $n_i$  of the component is:

$$Q = n_i N_A \times z_i e = n_i z_i F \quad (7.7)$$

where  $F$  is the **Faraday constant**, the charge of one mole of electrons:

$$F = eN_A = 96\ 485\ C/mol \quad (7.8)$$

When an infinitesimal amount  $dn_i$  of component  $i$  is introduced into the system, the amount of charge added is:

$$dQ = z_i F dn_i \quad (7.9)$$

Since the inner potential of the phase is  $\phi^\alpha$ , this process involves additional non  $p$ - $V$  work equal to (Eq. 7.1):

$$dw_{\text{non-pv}} = \phi^\alpha dQ \quad (7.10)$$

This additional work changes the internal energy via the first law ( $dU = dq + dw$ ) and, therefore, also the Gibbs free energy (Eq. 7.6), which gives:

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i + \phi^\alpha dq = -SdT + Vdp + \sum_i \mu_i dn_i + z_i F \phi^\alpha dn_i \quad (7.11)$$

Rearranging, we find:

$$dG = -SdT + Vdp + \sum_i (\mu_i + z_i F \phi^\alpha) dn_i \quad (7.12)$$

We define the **electrochemical potential**  $\tilde{\mu}_i$  as:

$$\tilde{\mu}_i = \mu_i + z_i F \phi^\alpha \quad (7.13)$$

With this definition, the differential of  $G$  for a phase with nonzero electric potential becomes:

$$dG = -SdT + Vdp + \sum_i \tilde{\mu}_i dn_i \quad (7.14)$$

which is entirely analogous to Eq. 7.6. Note that in the case when the component is not charged ( $z_i = 0$ ) or the inner potential is zero  $\phi^\alpha = 0$ , the electrochemical potential reduces to the usual chemical potential ( $\tilde{\mu}_i = \mu_i$ ) and Eq. 7.14 to Eq. 7.6.

Following the same procedure as in Section 4.8 it is possible to show that  $\tilde{\mu}_i$  replaces  $\mu_i$  in all material equilibrium conditions. In particular, in a closed system, two phases  $\alpha$  and  $\beta$  are in equilibrium if:

$$\tilde{\mu}_i^\alpha = \tilde{\mu}_i^\beta \quad (7.15)$$

for each species  $i$  in the two phases (compare to Eq. 4.131). If there is a reaction happening in a closed system, the equilibrium condition is:

$$\sum_i \nu_i \tilde{\mu}_i = 0 \quad (7.16)$$

which is the analogue of Eq. 4.145 for electrochemical systems. An electrochemical system is said to be in **electrochemical equilibrium** if Eqs. 7.15 and 7.16 hold for all phases in contact and, as a consequence, there is no net flow of charges within the system.

In the particular case when all the species involved in the reaction are in the same phase  $\alpha$ , we have:

$$0 = \sum_i \nu_i \tilde{\mu}_i = \sum_i \nu_i (\mu_i + z_i F \phi^\alpha) = \sum_i \nu_i \mu_i + \sum_i \nu_i z_i F \phi^\alpha \quad (7.17)$$

$$= \sum_i \nu_i \mu_i + F \phi^\alpha \left( \sum_i \nu_i z_i \right) \quad (7.18)$$

but for any chemical reaction the sum of the charges of the reactants equals the sum of the charges of the products, and therefore:

$$\sum_i \nu_i z_i = 0 \quad (7.19)$$

Hence, the equilibrium condition for a chemical reaction in an electrochemical system (Eq. 7.16) reduces to the usual equilibrium condition (Eq. 4.145):

$$\sum_i \nu_i \tilde{\mu}_i = \sum_i \nu_i \mu_i = 0 \quad (7.20)$$

if all the species involved in the reaction are in the same phase.

Lastly, consider again the systems in Figure 7.1. In equilibrium, the  $\text{Cu}^{2+}$  cations (left system,  $z_i = +2$ ) and the electrons (right system,  $z_i = -1$ ) follow Eq. 7.15:

$$\tilde{\mu}_i^\alpha = \tilde{\mu}_i^\beta \quad (7.21)$$

$$\mu_i^\alpha + z_i F \phi^\alpha = \mu_i^\beta + z_i F \phi^\beta \quad (7.22)$$

Rearranging, we find:

$$\mu_i^\alpha - \mu_i^\beta = z_i F (\phi^\beta - \phi^\alpha) \quad (7.23)$$

Therefore, if the component is uncharged ( $z_i = 0$ ) or if the electric potential of the two phases in contact is equal ( $\phi^\beta = \phi^\alpha$ ), the phase equilibrium condition reduces to the usual expression (Eq. 4.131):

$$\mu_i^\alpha = \mu_i^\beta \quad (7.24)$$

Instead, in the systems depicted in Figure 7.1, when the two phases are first put in contact, there is a flow of charge that changes the electric potential of both phases until both sides of Eq. 7.23 (and also Eq. 7.15) equalize.

## 7.3 Electrochemical Cells

### 7.3.1 Definitions

The electrochemical systems we are interested in comprise two or more interfaces, and involve a **reduction-oxidation (redox) reaction**, which is a chemical transformation in which

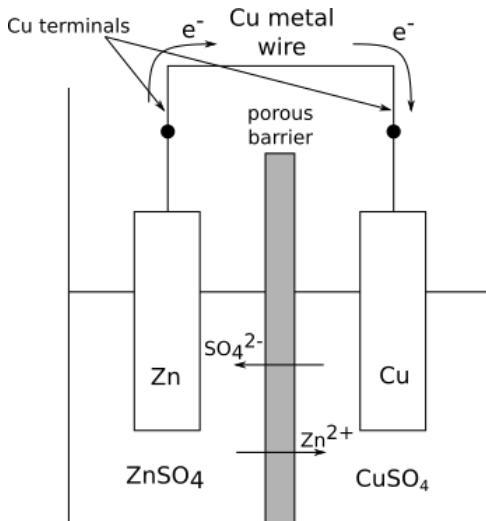
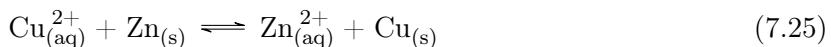
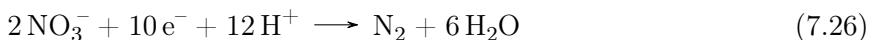


Figure 7.2: A Daniell cell. Zn oxidizes on the left electrode and the electrons travel through the wire to the right electrode, where Cu is reduced.

electrons are transferred between reactants and products. A simple example of a redox reaction happens between metallic Zn in contact with a CuSO<sub>4</sub> solution:



In this reaction, the metallic Zn slowly dissolves and metallic Cu is deposited from the solution. The species that loses electrons (Zn in this case) is **oxidized** and the species that gains electrons (Cu<sup>2+</sup>) is **reduced**. Conversely, the Zn in this example can be thought of as a **reducing agent** or **reductant** and the Cu<sup>2+</sup> is the **oxidizing agent** or **oxidant**. While the above is a particularly simple electron transfer reaction, other redox reactions involve more extensive chemical changes in reactants and products that result from the electron transfer and involve a mechanism with multiple steps. For instance, the reduction of nitrate anions in solution gives:



Redox reactions are essential in many fields, particularly in biochemistry where they are involved in many biologically important processes such as cell respiration.

Now we separate the species involved in the redox reaction (Eq. 7.77) into two different containers as shown in Figure 7.2. The left container has metallic Zn in contact with a ZnSO<sub>4</sub> solution. The right container has metallic Cu in contact with a CuSO<sub>4</sub> solution. Both metals are connected via a copper wire through which the electrons can flow. Because the overall reaction (Eq. 7.77) is spontaneous, electrons move over the copper wire joining the two cells, carrying out the reaction. During the reaction, a Zn atom releases its two electrons and dissolves as Zn<sup>2+</sup> in the solution. The electrons travel through the wire to the right container and react with a Cu<sup>2+</sup> atom close to the surface, depositing the neutral Cu atom on the metal. Since two electrons have migrated from the left to the right container, the right container is now negatively charged. To prevent a build up of charge that would change the inner potentials of each phase and stop the reaction (Eq. 7.16), the wall separating the two containers is porous so SO<sub>4</sub><sup>2-</sup> anions and Zn<sup>2+</sup> cations can travel through it, balancing the charges and maintaining the electrical neutrality of each phase. The existence of the porous union between the two aqueous solutions closes the circuit and allows the reaction to happen.

Since the redox reaction is physically separated into two distinct compartments where reduction and oxidation take place, we can talk about the corresponding **half-reactions**, which

in this case are:



Half-reactions are customarily expressed as reductions (with the electrons as reactants). The overall redox reaction (Eq. 7.77), which is a combination of one half-reaction minus the other, is called the **cell reaction**:



The two species involved in a half-reaction are known as a **redox couple**. In the examples above, the redox couples are  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Zn}^{2+}/\text{Zn}$ .

The union of the compartments containing the two half reactions **electrochemical cell**. For instance, the system in Figure 7.2 is an electrochemical cell known as the Daniell cell. If the redox reaction happening in an electrochemical cell is spontaneous, the cell operates as a **galvanic cell** (or **voltaic cell**). In a galvanic cell, the electric potential in the container where oxidation takes place is lower than the container where the reduction happens. If the circuit is closed, electrons flow through the wire, perhaps effecting some work on the environment. It is also possible to apply a reverse electric potential to the two terminals of an electrochemical cell such that the electrons flow in the opposite direction. This results in the cell carrying out a reaction that would normally not be spontaneous. In this case the system acts as an **electrolytic cell** and the process is known as **electrolysis**. A common example is the electrolysis of water to form  $\text{H}_2$  and  $\text{O}_2$  by using an electrical current:



which gives the global equation:



In the rest of this chapter, we will consider only galvanic cells. A particular type of galvanic cell is a **fuel cell**, in which the reactants are continuously fed to each electrode from outside the cell.

An electrochemical cell must contain at least one phase that conducts electricity by the movement of ions in its interior, known as an ionic conductor or **electrolyte**. Otherwise, electrons would flow within the cell and carry out the spontaneous redox reaction, even if there is no wire connecting the terminals. Electrolytes are often solutions, as in the case of the Daniell cell (Figure 7.2), but they can also be solids (solid-state electrolyte), gels (as in a lithium-ion battery), or ionic liquids such as molten salts, the only condition being that they conduct electricity through ionic mobility. The cell also comprises electronic conductors, which conduct electricity by the movement of electrons, and are often, but not necessarily, metals. The electronic conductors in direct contact with the electrolyte where the redox half-reactions occur are known as **electrodes**, and the combination of electrode plus electrolyte forms an **electrode compartment** or **half-cell**. Electrodes may be inert, when they do not participate in the reaction other than by carrying the electrons, but they can also act as catalysts or they can be involved in the reaction as reactants or products, as is the case in the Daniell cell (Figure 7.2).

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The term “electrode” is often used to describe the whole half-cell, not just the electronic conductor. For instance, the “silver chloride electrode” typically refers to the metal ( $\text{Ag}$  or  $\text{Pt}$  coated with  $\text{Ag}$ , plus deposited  $\text{AgCl}$ ), to the solution (water saturated with  $\text{KCl}$  and dissolved  $\text{Ag}^+$  cations), to the casing that contains both elements, and to the filter that allows the exchange of ions with the

external electrolyte. It is usually clear which meaning of the term “electrode” is being used based on the context.

The electrode where the oxidation takes place is known as the **anode** and the electrode where the reduction happens is the **cathode**. In the Daniell cell, the anode is on the left (oxidation:  $\text{Zn} - 2\text{e}^- \rightarrow \text{Zn}^{2+}$ ) and the cathode is on the right (reduction:  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ ).

Lastly, the half-cell may be connected to the rest of the electrochemical system through additional phases. For convenience, metals, known as **terminals**, are often connected to the electrodes to which the wire is connected. In the rest of the chapter, for simplicity, we will assume the terminals of both half-cells are made of the same metal, and therefore can be assumed to have the same composition. The electrolyte can be separated from other electrolytes in the cell by an interface known as a **liquid junction**. The porous union between the electrolytes in a Daniell cell (Figure 7.2) is a liquid junction. A **salt bridge** is a double liquid junction built with concentrated KCl solution in agar gel that is useful because it has a very small potential across the interface, we discuss salt bridges later.

### 7.3.2 Cell Potential

For a galvanic cell, we define the **cell potential** (also the **electromotive force**, or **emf**),  $E_{\text{cell}}$ , as the difference in electric potential between the cathode and the anode terminals when no current is flowing through the cell:

$$E_{\text{cell}} = \phi(T_{\text{cathode}}) - \phi(T_{\text{anode}}) \quad (7.33)$$

The cell potential has the same units as the electric potential, volts (V) in the SI. The zero-current condition can be achieved by opening the circuit (i.e. by disconnecting the terminals) or by applying an electric potential to the terminals that is equal, but reverse, to their cell potential, such that the cell is at equilibrium. The latter method is used by a **potentiometer**, which is a device used to measure cell potentials that draws zero current from the cell when it is in operation. The zero-current condition is important to the definition of cell potential because, if a non-zero current is flowing, the electric potential between the terminals decreases as a result of the resistance of the cell to the charge flow (the **internal resistance**). The study of cells and electrodes with non-zero current, and therefore of the rate of the redox reactions and half-reactions happening at them, is the purview of **electrochemical kinetics**, which is an important field for many analytical techniques (e.g. voltammetry). In the rest of this chapter, we consider all the cells are under open-circuit (zero current) conditions.

The cell potential given by Eq. 7.33 can also be interpreted as the sum of the potential differences across all the interfaces in the galvanic cell. This happens because a galvanic cell conducts electricity by moving charges through conducting phases which, as noted in Section 7.1, have constant  $\phi$  throughout their bulk. For instance, consider a cell:



where  $\text{T}$  are the anode ( $a$ ) and cathode ( $c$ ) terminals,  $\text{E}$  are the electrodes, and  $\text{I}$  is a shared electrolyte (ionic conductor). Then the cell potential can be written:

$$\begin{aligned} E_{\text{cell}} &= \phi(T_c) - \phi(T_a) \\ &= [\phi(T_c) - \phi(E_c)] + [\phi(E_c) - \phi(I)] + [\phi(I) - \phi(E_a)] + [\phi(E_a) - \phi(T_a)] \end{aligned} \quad (7.34)$$

Note that, by Eq. 7.23, the electric potential difference across each of the interfaces composing the cell is directly proportional to the chemical potential difference for the electrically charged species able to cross the interface, and therefore the cell potential could also be written as a sum of chemical potential differences across all interfaces in the cell.

### 7.3.3 Cell Notation

Conventions exist regarding how to write text diagrams that represent electrochemical cells and half-cells (some of them contained in the IUPAC gold book):

1. The anode (oxidation reaction) is written on the left of the diagram. The cathode (reduction) is written on the right. The terminals are often omitted.
2. A phase boundary is indicated by a vertical bar (|). If the phase boundary is between two liquids (a liquid junction), a dashed vertical bar is used (|̄).
3. A double vertical dashed line (||) represents a liquid junction that gives a negligible contribution to the cell potential (e.g. a salt bridge). (Sometimes a double vertical bar (|||) is used instead.)
4. Two species in the same phase are separated by a comma.
5. The aggregation state of each phase (s,l,g,aq) is indicated in parentheses. If the species are reactive and not in their standard states (1 bar for gases and 1 mol/kg for solutions), their pressures or concentrations are indicated in parentheses.

Since the cathode is on the right of the diagram and the anode is on the left, Eq. 7.33 can be written as:

$$E_{\text{cell}} = \phi_{\text{R}} - \phi_{\text{L}} \quad (7.35)$$

where “R” represents the right terminal and “L” is the left terminal in the cell diagram.

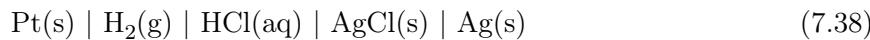
Applying these rules, the Daniell cell in Figure 7.2 is represented:



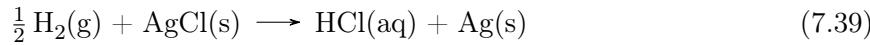
If, instead of being separated by a porous union the two compartments were separated by a salt bridge, it would be:



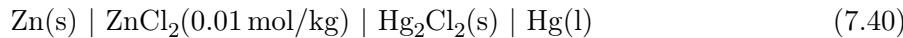
Another example is the “Harned cell”, where the anode is the standard hydrogen electrode and the cathode is the silver chloride electrode (see below), used for the calibration of the latter:



where the cell reaction is:



and the two electrodes share the same electrolyte. An example of a cell involving the calomel electrode:



where, again, the two half-cells share electrolyte. The cell reaction is:



### 7.3.4 Reversible Cells and Reversible Electrodes

The fundamental equation for the change in Gibbs energy (Eq. 7.14) is only valid for a reversible process so, in order to be able to apply it to a galvanic cell, the cell needs to be able to operate reversibly. Consider an electrochemical cell that is held in equilibrium (zero-current) by applying an electrical potential to its terminals that is the exact opposite of the cell potential. A small change in the applied potential disrupts equilibrium and makes charge flow

through the cell. A **reversible cell** is one in which the cell at equilibrium can be made to operate as a galvanic cell (carrying out the spontaneous reaction) by an infinitesimal change in the applied electric potential and then it can be made to operate as an electrolytic cell (carrying out the reverse reaction) by applying an infinitesimal change in the applied electric potential of opposite sign, making the electrochemical cell follow the same sequence of thermodynamic states in the opposite direction.

For example, the Daniell cell in Figure 7.2 is not a reversible cell. Assume the cell is forced to have zero current by an external electric potential that exactly opposes the cell potential. The applied potential is changed infinitesimally so that the cell operates like a Galvanic cell:



As it operates, the metallic Zn at the anode oxidizes to  $\text{Zn}^{2+}$  and dissolves in the electrolyte, and the  $\text{Cu}^{2+}$  in the electrolyte reduces to Cu and is deposited at the cathode. The anode compartment becomes positively charged and the cathode compartment is negatively charged as a consequence,  $\text{Zn}^{2+}$  cations (and  $\text{SO}_4^{2-}$  anions) cross the porous barrier into the other compartment. Now we operate the Daniell cell in reverse:



by infinitesimally changing the applied electric potential in the opposite direction. The role of cathode and anode are reversed, Cu is oxidized to  $\text{Cu}^{2+}$ , which dissolves, and  $\text{Zn}^{2+}$  reduces to Zn and is deposited. While these steps are the reverse of the previous ones with the cell operating as a galvanic cell, in this case the Cu compartment becomes positively charged and, consequently,  $\text{Cu}^{2+}$  cations cross the porous barrier into the Zn compartment. Note this last step is not the reverse of the same step with the cell operating under the opposite potential (it was  $\text{Zn}^{2+}$  crossing the barrier), and therefore the cell is not reversible. The irreversibility of the Daniell cell arises from the fact that there is a liquid junction connecting two different electrolytes. Therefore, for a cell to be reversible the two electrodes must share the same electrolyte, which must be the only electrolyte in the cell. We will see later how to take into account the irreversibility caused by a liquid junction.

A necessary condition to build a reversible cell is that both electrodes are themselves reversible. A **reversible electrode** is defined similarly to a reversible cell: it is an electrode which, by infinitesimally changing the applied potential, can be made to operate in either direction, following the same sequence of the thermodynamic states. Since a reversible electrode must be able to carry out both the direct and the reverse half-reactions, all reactants and products must be present in the compartment of a reversible electrode. Common types of reversible electrodes are:

**Metal/metal ion electrodes.** A metal M is in contact with a solution containing its cations ( $\text{M}^{z+}$ ).



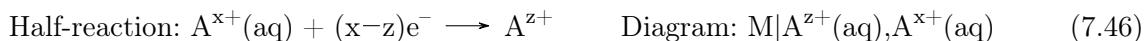
Example: the  $\text{Zn}/\text{Zn}^{2+}$  and  $\text{Cu}/\text{Cu}^{2+}$  electrodes in the Daniell cell.

**Amalgam electrodes.** An amalgam (solution of M in Hg) in contact with a solution containing the metal ions ( $\text{M}^{z+}$ ).



This electrode is typically used for metals that react with the electrolyte and therefore cannot be built as metal/metal ion electrodes. For instance, the  $\text{Na}(\text{Hg})/\text{Na}^+$  electrode (metallic sodium reacts with water).

**Redox electrodes.** The electrode half-reaction occurs between two species in solution and the metal is inert.



The name is slightly misleading since all electrodes involve a redox half-reaction of some sort. Example:  $\text{Fe}^{3+}/\text{Fe}^{2+}$ .

**Metal/insoluble salt.** A metal M in contact with its mostly insoluble salt MX and in contact with a solution of  $X^-$  anions.



These electrodes have the advantage that they can be utilized without a liquid junction and are therefore useful for building reversible cells. If the solution is saturated in  $X^-$  anions, their contribution to the cell potential is stable, making them useful as **reference electrodes**. Two popular examples are the (**saturated calomel electrode**) ( $\text{Hg}(\text{s})|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Cl}^-(\text{aq})$ ) and the more environmentally friendly (**saturated silver chloride electrode**) ( $\text{Ag}(\text{s})|\text{AgCl}(\text{s})|\text{Cl}^-(\text{aq})$ ). In the saturated versions of these electrodes, the solution is saturated by putting it in contact with excess solid KCl with  $\text{Cl}^-$  concentration at about 4.5 M.

**Gas electrodes.** A gas  $X_2$  in contact with an inert metal and a solution containing its ions ( $X^+$  or  $X^-$ ).



An example of gas electrode is the **hydrogen electrode** ( $\text{Pt}|\text{H}_2(\text{g})|\text{H}^+(\text{aq})$ ) in which hydrogen is bubbled through an acidic solution in contact with Pt and that is used to define the standard electrode potentials, and the chlorine electrode ( $\text{Pt}|\text{Cl}_2(\text{g})|\text{Cl}^-(\text{aq})$ ).

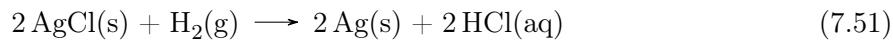
**Ion-selective membrane electrodes.** These electrodes comprise a solid membrane whose potential difference is sensitive to the activity of a particular ion on both of its sides. The most popular membrane electrode is the **glass electrode**, which has a bulb of thin glass whose potential difference is dictated by the concentration of  $\text{H}^+$ , and is therefore used to measure pH. Other ion-selective membrane electrodes are used to determine concentrations of ions that are difficult to measure by chemical means, including  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NO}_3^-$ .

## 7.4 The Nernst Equation

Consider the reversible cell:



with its terminals in open-circuit. The cell reaction is:



Since the cell is in open-circuit, the electrons cannot travel from one terminal to the other outside the system so, instead of the above, we consider the **electrochemical reaction**:



where the number of electrons at the right (R, cathode) and left (L, anode) terminals required to carry out the reaction are noted explicitly. We define the **charge number** (or **electron**

**number),  $n$** , as the number of electrons transferred for every step of the electrochemical reaction as written. In the example above,  $n = 2$ .

Because the cell is reversible, the equilibrium equations in Section 7.2 apply and all adjacent phases are in electrochemical equilibrium. In particular, the equilibrium condition is (Eq. 7.16):

$$\sum_i \nu_i \tilde{\mu}_i = 0 \quad (7.53)$$

where the sum  $i$  goes over the molecular species as well as the electrons on both sides of the electrochemical reaction. Separating the electrons from the molecular species (“mol”):

$$n\tilde{\mu}_{e^-}(L) - n\tilde{\mu}_{e^-}(R) + \sum_i^{\text{mol}} \nu_i \tilde{\mu}_i = 0 \quad (7.54)$$

where we used that the stoichiometric coefficients of the electrons on the left electrode is  $+n$  and for the electrons on the right electrode it is  $-n$ . Using the definition of electrochemical potential (Eq. 7.13), we have:

$$\begin{aligned} \sum_i^{\text{mol}} \nu_i \tilde{\mu}_i &= n(\mu_{e^-}(R) - F\phi_R) - n(\mu_{e^-}(L) - F\phi_L) \\ &= n(\mu_{e^-}(R) - \mu_{e^-}(L)) - nF(\phi_R - \phi_L) \end{aligned} \quad (7.55)$$

We assumed the metals the terminals are made of are the same, so a reasonable approximation is to assume their temperature, pressure, and composition is equivalent and therefore the two chemical potentials for the electrons are equal. Therefore the first term in the equation above vanishes:

$$\sum_i^{\text{mol}} \nu_i \tilde{\mu}_i = -nFE_{\text{cell}} \quad (7.56)$$

where we used the definition of the cell potential for a conventional cell diagram ( $E_{\text{cell}} = \phi_R - \phi_L$ , Eq. 7.35). For the molecular species, either the species are neutral, in which case  $\tilde{\mu}_i = \mu_i$  because  $z_i = 0$ , or they are ionic, in which case they must be within the only electrolyte present in this cell, because the cell is reversible. We have seen in Section 7.2 that the electroneutrality of a chemical reaction and the fact that the ionic spaces are all within the same phase means that:

$$\sum_i^{\text{mol}} \nu_i \tilde{\mu}_i = \sum_i^{\text{mol}} \nu_i \mu_i \quad (7.57)$$

and therefore Eq. 7.56 reduces to:

$$\sum_i^{\text{mol}} \nu_i \mu_i = -nFE_{\text{cell}} \quad (7.58)$$

Note the left hand side is the difference between products and reactants of the chemical potentials in the cell reaction. Equation 7.58 is valid only for a reversible cell with terminals that have the same composition and at zero current (open circuit).

For a homogeneous system undergoing a reversible composition change at constant temperature and pressure caused by a chemical reaction (Eq. 4.120):

$$dG = \sum_i \mu_i dn_i^\alpha = \sum_i \nu_i \mu_i d\xi \quad (7.59)$$

where we used the extent of the reaction differential (Eq. 4.141). Therefore, the left hand side in Eq. 7.58 equals the derivative of  $G$  with respect to the extent of the reaction:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_i^{\text{mol}} \nu_i \mu_i = -nFE_{\text{cell}} \quad (7.60)$$

where the sum runs over the species in the cell reaction (i.e. the same as in the electrochemical reaction minus the electrons). Note the partial derivative on the left hand side of Eq. 7.60 is zero for a reaction at equilibrium, because  $G$  is a minimum and  $\sum_i \nu_i \mu_i = 0$ . Therefore, if the cell reactions is at thermodynamic equilibrium,  $E_{\text{cell}} = 0$ . In contrast, a reversible electrochemical cell may still be at electrochemical equilibrium if the circuit is open and no electrons are flowing, even if the cell potential is not zero.

In many sources, the left hand side of equation 7.60 is written as:

$$\Delta_r G = -nFE_{\text{cell}} \quad (7.61)$$

This is somewhat inconsistent with our definition of  $\Delta_r G^\circ$ , which is the difference in  $G$  between products and reactants in their standard states (Eq. 4.155):

$$\Delta_r G^\circ = \sum_i \nu_i \mu_i^\circ \quad (7.62)$$

Note the chemical potentials for both reactants and products in Eq. 7.60 are calculated at the same extent  $\xi$  within the reacting mixture, not for pure separated products or reactants. Therefore, we follow Levine's recommendation and prefer using  $dG/d\xi$  for this quantity.

For the species in the electrolyte, the chemical potentials are given by (Eq. 6.84):

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

where  $a_i$  are the Henry's law activities in the molality scale, as usual for electrolytes.

Substituting in Eq. 7.58:

$$\begin{aligned} -nFE_{\text{cell}} &= \sum_i \nu_i \mu_i = \sum_i \nu_i (\mu_i^\circ + RT \ln a_i) = \sum_i \nu_i \mu_i^\circ + RT \sum_i \nu_i \ln a_i \\ &= \Delta_r G^\circ + RT \ln \left( \prod_i a_i^{\nu_i} \right) = \Delta_r G^\circ + RT \ln Q^\circ \end{aligned} \quad (7.63)$$

where we dropped the superscript "mol" for simplicity—all summations run over molecular species from now on—and we used the definition of the standard reaction Gibbs free energy (Eq. 4.155) for the cell reaction and defined the **standard reaction quotient** ( $Q^\circ$ ) for the cell reaction as:

$$Q^\circ = \prod_i a_i^{\nu_i} \quad (7.64)$$

by analogy with Eq. 4.173. We define the **standard cell potential** as:

$$E_{\text{cell}}^\circ = -\frac{\Delta_r G^\circ}{nF} \quad (7.65)$$

from where Eq. 7.63 is rearranged to give:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q^\circ = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \left( \prod_i a_i^{\nu_i} \right) \quad (7.66)$$

This is the **Nernst equation**, which relates the cell potential to the activities of reactants and products involved in the cell reaction.

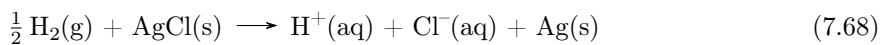
There are several things to note about the Nernst equation:

- The Nernst equation written as in Eq. 7.66 is valid only for reversible cells. In particular, the cell must have a single electrolyte and no liquid junctions. Also, the Nernst equation is valid only when no current is flowing through the cell, either because the cell is in open circuit (the terminals are not connected) or because an external electric potential is being applied that exactly matches minus the cell potential.
- In general, a galvanic cell in a zero current (open circuit) state is in electrochemical equilibrium (no current is flowing) but not in thermodynamic equilibrium, because the cell reaction can still occur. Only when  $Q^\circ = K^\circ$  and  $a_i = a_i^{\text{eq}}$  does the cell reaction achieve material equilibrium, in which case the two terms on the right hand side of the Nernst equation cancel out and  $E_{\text{cell}} = 0$ .
- The value of the cell potential is independent of how we write the cell reaction. This is because the electron number ( $n$ ) in the denominator of the second term in Eq. 7.66 can enter the logarithm and divide the exponents of the activities.
- The standard cell potential (Eq. 7.5) is simply a way to rewrite the standard reaction Gibbs free energy. This means that  $E_{\text{cell}}^\circ$  can be calculated from the  $\Delta_r G^\circ$  (for instance, from standard formation free energies of reactants and products) or, much more commonly,  $\Delta_r G^\circ$  for chemical reactions can be calculated from the corresponding  $E_{\text{cell}}^\circ$  obtained from potentiometric measurements. In particular, a positive  $E_{\text{cell}}^\circ$  corresponds to an exergonic reaction ( $\Delta_r G^\circ < 0$ ) and a negative  $E_{\text{cell}}^\circ$  corresponds to an endergonic reaction ( $\Delta_r G^\circ > 0$ ). In particular,  $E_{\text{cell}}^\circ$ , like  $\Delta_r G^\circ$ , depends on temperature and only very slightly on pressure, and not on the composition of the cell.
- The cell potential on the left hand side of the Nernst equation (Eq. 7.66) is still the sum of the electric potential differences across all interfaces in the reversible cell (Eq. 7.34)

**Example.** For the Harned cell:



with cell reaction:



the Nernst equation gives the cell potentials as:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \left( \frac{a(\text{H}^+)a(\text{Cl}^-)}{a(\text{H}_2)^{1/2}} \right) \quad (7.69)$$

Note the activities of the pure solids are approximately one and  $a(\text{H}_2) = f(\text{H}_2)/p^\circ$  where  $f(\text{H}_2)$  is the fugacity of the gas, equal to its pressure if we assume the gas is ideal.

Using the relation between  $\Delta_r G^\circ$  and the equilibrium constant (Eq. 6.164), the Nernst equation (Eq. 7.66) can be written as:

$$E_{\text{cell}} = -\frac{\Delta_r G^\circ}{nF} - \frac{RT}{nF} \ln Q^\circ = \frac{RT}{nF} \ln \left( \frac{K^\circ}{Q^\circ} \right) \quad (7.70)$$

Therefore, a positive cell potential ( $E_{\text{cell}} > 0$ ) indicates that  $Q^\circ < K^\circ$  and the cell reaction shifts towards the products when the circuit is closed. Conversely, if  $E_{\text{cell}} < 0$ ,  $Q^\circ > K^\circ$  and the reaction shifts towards the reactants.

The Nernst equation can be modified in the case when the cell has a liquid junction. We define the **(liquid) junction potential** as:

$$E_J = \phi_{\text{junction},R} - \phi_{\text{junction},L} \quad (7.71)$$

where the potentials refer to the phases on the right and left of the liquid junction as written in the cell diagram. It is possible to show that, if the cell has a liquid junction, the Nernst equation reads:

$$E_{\text{cell}} = E_{\text{Nernst}} + E_J = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \left( \prod_i a_i^{\nu_i} \right) + E_J \quad (7.72)$$

Junction potentials are in the order of tens of mV, a small but not negligible quantity. A junction potential can be minimized by using a **salt bridge** to connect the two electrolytes. A salt bridge typically consists of a jelly (agar gel) with a concentrated solution of a salt whose anion and cation have approximately the same mobilities in the electrolyte solvent (usually, KCl). The salt bridge introduces two more or less equivalent interfaces to the two electrolytes which approximately cancel out. The use of a salt bridge brings the junction potential down to 1–2 mV.

It is possible to build an electrochemical cell where the two half-reactions are the same and the half-cells only differ in the concentrations of the various species. This is a **concentration cell** and, since the cell reaction has the same reactants and products, it has  $\Delta_r G^{\circ} = E_{\text{cell}}^{\circ} = 0$ . For a concentration cell the Nernst equation simplifies to:

$$E_{\text{cell}} = -\frac{RT}{nF} \ln \left( \prod_i a_i^{\nu_i} \right) \quad (7.73)$$

If the two half-reactions are different, as in any of the examples above, the cell is known as a **chemical cell**. An example of a concentration cell is:



## 7.5 Standard Electrode Potentials

Standard cell potentials (and therefore  $\Delta_r G^{\circ}$ ) can be calculated as the sum of contributions from each of the electrodes (half-cells) in a galvanic cell. Measuring potentials for individual electrodes is difficult so, in order to assign them individual potential values, we assign a fixed potential to an arbitrarily chosen electrode, which by convention is the hydrogen electrode ( $\text{Pt}|\text{H}_2(\text{g})|\text{H}^{+}(\text{aq})$ ). The **standard electrode potential** (also **standard reduction potential**,  $E^{\circ}$ ) is the standard cell potential of the galvanic cell that has the hydrogen electrode on the left (anode) and the electrode under study on the right (cathode):



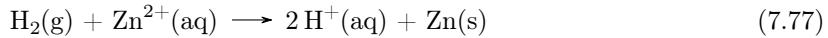
Therefore, by this convention, **all standard electrode potentials are reduction potentials**.

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**Example.** The standard electrode potential of the metal/metal ion electrode  $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})$  is the standard cell potential of the cell:



which is  $E^{\circ} = -0.76 \text{ V}$  at room temperature. The standard electrode potential has opposite sign to the  $\Delta_r G^{\circ}$  for the corresponding cell reaction:



and, since  $E^{\circ}$  is negative, it indicates that this reaction is not spontaneous or, equivalently, that  $\text{H}_2$  is not a reducing agent powerful enough to reduce  $\text{Zn}^{2+}$ .

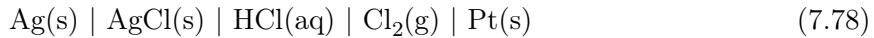
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Table 7.1: Standard electrode potentials for a few common redox pairs at room temperature in water. More values can be found in Bratsch, “[Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K](#)”, *J. Phys. Chem. Ref. Data* **18** 1 (1989).

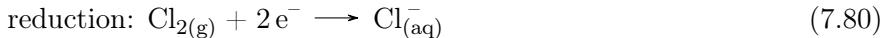
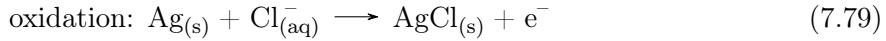
Half reaction	$E^\circ$ (V)
Strongly oxidizing	
$\text{F}_{2(\text{g})} + 2 \text{e}^- \rightarrow 2 \text{F}_{(\text{aq})}^-$	2.87
$\text{Au}_{(\text{aq})}^+ + \text{e}^- \rightarrow \text{Au}_{(\text{s})}$	1.69
$\text{Cl}_{2(\text{g})} + 2 \text{e}^- \rightarrow \text{Cl}_{(\text{aq})}^-$	1.36
$\text{O}_{2(\text{g})} + 4 \text{H}_{(\text{aq})}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}_{(\text{l})}$	1.23
$\text{Br}_{2(\text{l})} + 2 \text{e}^- \rightarrow 2 \text{Br}_{(\text{aq})}^-$	1.08
$\text{Ag}_{(\text{aq})}^+ + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}$	0.80
$\text{Hg}_{2(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow 2 \text{Hg}_{(\text{l})}$	0.79
$\text{Fe}_{(\text{aq})}^{3+} + \text{e}^- \rightarrow \text{Fe}_{(\text{aq})}^{2+}$	0.77
$\text{O}_{2(\text{g})} + 2 \text{H}_2\text{O}_{(\text{l})} + 4 \text{e}^- \rightarrow 4 \text{OH}_{(\text{aq})}^-$	0.40
$\text{Cu}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$	0.34
$\text{Hg}_2\text{Cl}_{2(\text{s})} + 2 \text{e}^- \rightarrow 2 \text{Hg}_{(\text{l})} + 2 \text{Cl}_{(\text{aq})}^-$	0.27
$\text{AgCl}_{(\text{s})} + \text{e}^- \rightarrow \text{Ag}_{(\text{s})} + \text{Cl}_{(\text{aq})}^-$	0.22
$2 \text{H}_{(\text{aq})}^+ + \text{e}^- \rightarrow \text{H}_{2(\text{g})}$	0.00
$\text{Pb}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Pb}_{(\text{s})}$	-0.13
$\text{Sn}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Sn}_{(\text{s})}$	-0.14
$\text{PbI}_{2(\text{s})} + 2 \text{e}^- \rightarrow \text{Pb}_{(\text{s})} + 2 \text{I}_{(\text{aq})}^-$	-0.37
$\text{Fe}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}_{(\text{s})}$	-0.44
$\text{Zn}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Zn}_{(\text{s})}$	-0.76
$2 \text{H}_2\text{O}_{(\text{l})} + 2 \text{e}^- \rightarrow \text{H}_{2(\text{g})} + 2 \text{OH}_{(\text{aq})}^-$	-0.83
$\text{Al}_{(\text{aq})}^{3+} + 3 \text{e}^- \rightarrow \text{Al}_{(\text{s})}$	-1.66
$\text{Na}_{(\text{aq})}^+ + \text{e}^- \rightarrow \text{Na}_{(\text{s})}$	-2.71
$\text{Ca}_{(\text{aq})}^{2+} + 2 \text{e}^- \rightarrow \text{Ca}_{(\text{s})}$	-2.87
$\text{Li}_{(\text{aq})}^+ + \text{e}^- \rightarrow \text{Li}_{(\text{s})}$	-3.05
Strongly reducing	

A few standard electrode potentials at room temperature in water for common redox pairs are shown in Table 7.1. Extensive tabulations of standard electrode potentials exist in textbooks and in the specialized literature.

The standard electrode potentials in Table 7.1 can be combined to calculate the standard cell potential for a galvanic cell. For instance, consider we have the galvanic cell with diagram:



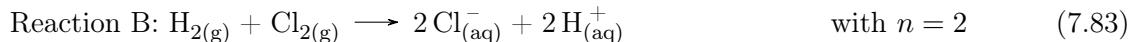
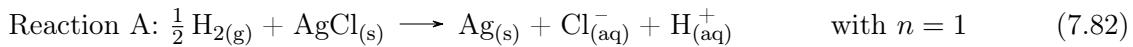
The oxidation and reduction half-reactions are:



with an overall reaction:



The oxidation and reduction half-reactions can be related to the corresponding standard electrode potentials by considering their combination with the standard hydrogen electrode:



For these reactions the standard reaction Gibbs energy is related to the corresponding standard cell potential by (Eq. 7.81):

$$\Delta_r G_A^\circ = -FE_{\text{cell}}^\circ(\text{A}) = -FE^\circ(\text{AgCl/Ag}) \quad (7.84)$$

$$\Delta_r G_B^\circ = -2FE_{\text{cell}}^\circ(\text{B}) = -2FE^\circ(\text{Cl}_2/\text{Cl}^-) \quad (7.85)$$

where we used the fact that the standard electrode potentials of the two redox pairs are, by definition, equal to the standard cell potentials of these reactions. The overall reaction for this process (Eq. 7.81) can be written as a linear combination of reactions A and B. Applying Hess' law we have:

$$\Delta_r G^\circ = \Delta_r G_B^\circ - 2\Delta_r G_A^\circ = -2FE^\circ(\text{Cl}_2/\text{Cl}^-) + 2FE^\circ(\text{AgCl/Ag}) \quad (7.86)$$

The cell in Eq. 7.78 has  $n = 2$  because two electrons are transferred between anode and cathode every step of the reaction. Therefore, the standard cell potential for this cell is:

$$E_{\text{cell}}^\circ = -\frac{\Delta_r G^\circ}{2F} = E^\circ(\text{Cl}_2/\text{Cl}^-) - E^\circ(\text{AgCl/Ag}) \quad (7.87)$$

so the standard cell potential of the cell in Eq. 7.78 can be written as the standard potential of the electrode on the right (cathode) minus that of the electrode on the left (anode). In general:

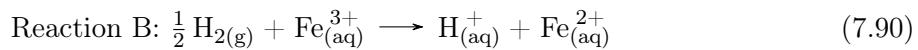
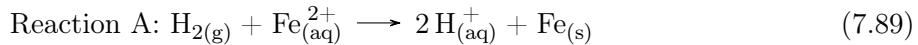
$$E_{\text{cell}}^\circ = E^\circ(\text{R}) - E^\circ(\text{L}) \quad (7.88)$$

where the “R” refers to the right electrode in the cell diagram (the cathode) and the “L” to the left electrode (the anode). Note that this equation does not involve the electron number ( $n$ ) of the overall reaction or the half-reactions.

Since a reaction with  $E_{\text{cell}}^\circ > 0$  is exergonic ( $\Delta_r G^\circ < 0$ ), Eq. 7.88 indicates that a cell reaction is more spontaneous the higher the standard potential of the cathode (right electrode) and the lower the standard potential of the anode (left electrode). Consequently, species higher up in Table 7.1, with very positive  $E^\circ$ , tend to reduce while species down in the table, with negative  $E^\circ$ , tend to oxidize. If a species A is lower in the table than another species B, then A reduces

B. For instance, zinc ( $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76$ ) reduces  $\text{H}^+$  in aqueous solution to  $\text{H}_2$  ( $E^\circ(\text{H}^+/\text{H}_2) = 0.00$ ), which explains why an acidic solution in contact with metallic zinc bubbles hydrogen. However, note that even if a reaction is thermodynamically favored it may not happen due to slow kinetics.

Lastly, two standard electrode potentials can be combined to generate a third potential. For instance, Table 7.1 gives the electrode potentials for the  $\text{Fe}^{2+}/\text{Fe}$  ( $-0.44 \text{ V}$ ) and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ( $0.77 \text{ V}$ ) pairs, corresponding to the standard cell potentials of the cell reactions:



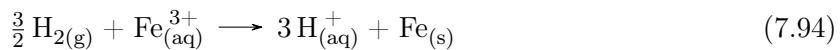
for which:

$$\Delta_r G_A^\circ = -2FE_{\text{cell}}^\circ(\text{Fe}^{2+}/\text{Fe}) \quad (7.91)$$

$$\Delta_r G_B^\circ = -FE_{\text{cell}}^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) \quad (7.92)$$

$$(7.93)$$

If we want, the standard electrode potential of the  $\text{Fe}^{3+}/\text{Fe}$  pair, we need the standard cell potential for the reaction:



which can be calculated by noting that this reaction is a combination of reaction B plus A:

$$E^\circ(\text{Fe}^{3+}/\text{Fe}) = -\frac{\Delta_r G^\circ}{3F} = -\frac{\Delta_r G_A^\circ + \Delta_r G_B^\circ}{3F} = \frac{2}{3}E_{\text{cell}}^\circ(\text{Fe}^{2+}/\text{Fe}) + \frac{1}{3}E_{\text{cell}}^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) \quad (7.95)$$

or, moving the electron number of the  $\text{Fe}^{3+}/\text{Fe}$  pair ( $n = 3$ ) to the left-hand side:

$$3 \times E^\circ(\text{Fe}^{3+}/\text{Fe}) = 2 \times E_{\text{cell}}^\circ(\text{Fe}^{2+}/\text{Fe}) + 1 \times E_{\text{cell}}^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) \quad (7.96)$$

In general, if the half-reaction C with electron number  $n_C$  can be written as a combination of half-reaction A ( $n_A$ ) and B ( $n_B$ ), the corresponding standard electrode potential is:

$$n_C E^\circ(\text{C}) = n_A E^\circ(\text{A}) + n_B E^\circ(\text{B}) \quad (7.97)$$

In this case, unlike what happened with the standard cell potentials, the electron numbers need to be taken into account.

## 7.6 Equilibrium Constants and Reaction Properties from Cell Potentials

The standard cell potential is directly related to the standard reaction Gibbs energy (Eq. 7.5):

$$E_{\text{cell}}^\circ = -\frac{\Delta_r G^\circ}{nF} \quad (7.98)$$

and, in turn,  $\Delta_r G^\circ$  is related to the equilibrium constant of the cell reaction (Eq. 6.164):

$$\Delta_r G^\circ = -RT \ln K^\circ \quad (7.99)$$

Putting the two together we get:

$$E_{\text{cell}}^\circ = \frac{RT \ln K^\circ}{nF} \quad (7.100)$$

Potentiometric measurements are a very common way of obtaining accurate equilibrium constants for chemical reactions. For instance, consider the disproportionation reaction:



which is the cell reaction for the following two electrodes:



The standard cell potential for the overall reaction is:

$$E_{\text{cell}}^\circ = E^\circ(\text{R}) - E^\circ(\text{L}) = 0.52 \text{ V} - 0.16 \text{ V} = 0.36 \text{ V} \quad (7.104)$$

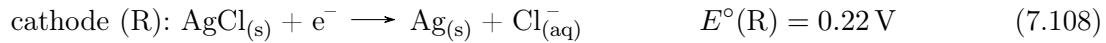
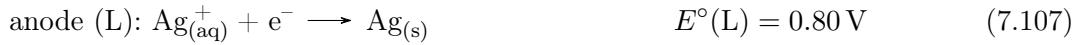
and we have that the equilibrium constant is:

$$\ln K^\circ = \frac{nFE_{\text{cell}}^\circ}{RT} = \frac{1 \times 96\,485.3 \text{ C} \times 0.36 \text{ V}}{8.314 \text{ J/K/mol} \times 298.15 \text{ K}} = 14.01 \quad (7.105)$$

This method can be applied even if the reaction under consideration is not redox. For instance, the solubility product of AgCl, which is the equilibrium constant for the reaction:



can be calculated by noting that this is the cell reaction corresponding to the following two half-reactions:



whose standard electrode potentials can be consulted in Table 7.1. The corresponding standard cell potential is:

$$E_{\text{cell}} = E^\circ(\text{R}) - E^\circ(\text{L}) = -0.58 \text{ V} \quad (7.109)$$

and the solubility product at room temperature is:

$$\ln K_{\text{sp}}^\circ = \frac{nFE_{\text{cell}}^\circ}{RT} = \frac{1 \times 96\,485.3 \text{ C} \times (-0.58 \text{ V})}{8.314 \text{ J/K/mol} \times 298.15 \text{ K}} = -22.57 \quad (7.110)$$

or  $K_{\text{sp}}^\circ = 1.57 \times 10^{-10}$ .

Potentiometric measurements are also an accurate way of determining other reaction properties besides  $\Delta_r G^\circ$ , such as  $\Delta_r H^\circ$  or  $\Delta_r S^\circ$ . For instance, the standard reaction entropy is:

$$\Delta_r S^\circ = - \left( \frac{\partial \Delta_r G^\circ}{\partial T} \right)_p = nF \left( \frac{\partial E_{\text{cell}}^\circ}{\partial T} \right)_p$$

where the temperature derivative of the standard cell potential is known as the **temperature coefficient** of the galvanic cell, which can be determined experimentally by measuring  $E_{\text{cell}}^\circ$  at different temperatures. The standard reaction enthalpy is:

$$\Delta_r H^\circ = \Delta_r G^\circ + T\Delta_r S^\circ = -nFE_{\text{cell}}^\circ + nFT \left( \frac{\partial E_{\text{cell}}^\circ}{\partial T} \right)_p = nF \left[ T \left( \frac{\partial E_{\text{cell}}^\circ}{\partial T} \right)_p - E_{\text{cell}}^\circ \right]$$

Potentiometric techniques are also very useful in the determination of ionic activities in solution (for instance, the potentiometric determination of the pH using a glass electrode), activity coefficients, as well as for quantitatively measuring the concentration of a redox active species using potentiometric titrations.

## Appendix A

# Summary of Standard States

The following table has been adapted from Levine's *Physical Chemistry*, 6th edition, Table 11.1. It specifies the standard state used by convention for various substances. Because the activity is defined as:

$$a_i = \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right)$$

it is always true that:

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

and the standard states in the table complete the definition of  $a_i$  by setting the value of  $\mu_i^\circ$  to the chemical potential of some standard state of substance  $i$  chosen by convention. The argument inside the logarithm in the last column is equal to the activity for that particular choice of standard state.

The following limiting behaviors apply:

- In real gases or gas mixtures,  $\phi_i \rightarrow 1$  and  $f_i \rightarrow p_i$  as  $p_i \rightarrow 1$ , where  $p_i = x_i p$  is the partial pressure.
- In a solution under the Raoult's law convention,  $\gamma_{i,R} \rightarrow 1$  as  $x_i \rightarrow 1$  for each component  $i$ .
- In a solution under the Henry's law convention, the activity coefficient of every component tends to one at infinite dilution ( $x_A \rightarrow 1$ ) regardless of the chosen scale, including the solvent. Namely:  $\gamma_{A,H}^\infty = \gamma_{i,H}^\infty = \gamma_{i,b}^\infty = \gamma_{i,c}^\infty = \gamma_\pm^\infty = 1$ .

For the ideal models, the following statements apply under any conditions:

- In an ideal gas or ideal gas mixture,  $\phi_i = 1$  and  $f_i = p_i = x_i p$ .
- In an ideal solution,  $\gamma_{i,R} = 1$  and  $a_i = x_i$  for each component  $i$ .
- In an ideal-dilute solution,  $\gamma_{A,H} = \gamma_{i,H} = \gamma_{i,b} = \gamma_{i,c} = \gamma_\pm = 1$ .

Substance	Standard State	Chemical potential
Gas (pure or in a gas mixture)	Pure ideal gas at 1 bar and $T$	$\mu_i = \mu_i^\circ(T) + RT \ln\left(\frac{f_i}{p^\circ}\right)$
Pure liquid or pure solid	Pure substance at 1 bar and $T$	$\mu_i = \mu_i^\circ(T) + \int_{p^\circ}^p V_{m,i} dp$
<i>Solution, Raoult's law convention:</i>		
Solution component	Pure $i$ at $T$ and $p$ of solution	$\mu_i = \mu_i^*(T, p) + RT \ln \gamma_{i,R} x_i$
<i>Solution, Henry's law convention:</i>	Pure A at $T$ and $p$ of solution	$\mu_A = \mu_A^*(T, p) + RT \ln \gamma_{A,H} x_A$
Non-electrolyte solute, mole fraction scale	Fictitious state with $x_i = 1$ and $\gamma_{i,H} = 1$	$\mu_i = \mu_{i,H}^\circ(T, p) + RT \ln \gamma_{i,H} x_i$
Non-electrolyte solute, molality scale	Fictitious state with $b_i = b^\circ$ and $\gamma_{i,b} = 1$	$\mu_i = \mu_{i,b}^\circ(T, p) + RT \ln \left(\gamma_{i,b} \frac{b_i}{b^\circ}\right)$
Non-electrolyte solute, molarity scale	Fictitious state with $c_i = c^\circ$ and $\gamma_{i,c} = 1$	$\mu_i = \mu_{i,c}^\circ(T, p) + RT \ln \left(\gamma_{i,c} \frac{c_i}{c^\circ}\right)$
Electrolyte solute, molality scale	Fictitious state with $\nu_{\pm} b_i = b^\circ$ and $\gamma_{\pm} = 1$	$\mu_i = \mu_i^\circ(T, p) + \nu RT \ln \left(\nu_{\pm} \gamma_{\pm} \frac{b_i}{b^\circ}\right)$