

variety of scientific fields; contemporary research is commonly exposed in sessions segregated by discipline. Physical chemists can also publish more perspective or tutorial articles on applying spectroscopy to materials systems.

Developing new functional materials is becoming increasingly important. The fusion of materials synthesis, fabrication, and characterization with time-resolved optical spectroscopy would be a huge step toward advancing the technologies of our everyday world.

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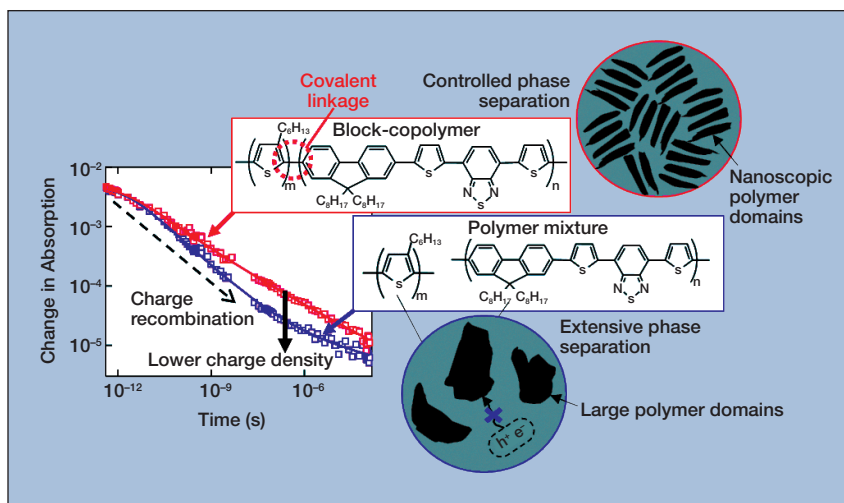


Figure 2. Transient absorption kinetic decays of charge carriers that form in polymer films upon light absorption. Charge recombination is tracked over time, revealing a lower charge density for the polymer mixture at later times. The cartoons illustrate phase separation of the polymer domains that occurs in the films.

Chemical potential and Gibbs free energy

By Long-Qing Chen

Chemical potential is a thermodynamics concept familiar to many, not only in materials science but also in physics, chemistry, chemical engineering, and biology. It is a central concept in thermodynamics of materials because all of the thermodynamic properties of a material at a given temperature and pressure can be obtained from knowledge of its chemical potential. Under the most common thermodynamic condition of constant temperature and pressure, chemical potential determines the stability of substances, such as chemical species, compounds, and solutions, and their tendency to chemically react to form new substances, to transform to new physical states, or to migrate from one spatial location to another.

Chemical potential is considered by many to be one of the most confusing and difficult concepts to grasp, although there appears to be no confusion about temperature, pressure, and electric potential. Chemical potential has been

underappreciated and underutilized in applications of thermodynamics to materials science and engineering. One of the reasons for this is the widespread use of molar Gibbs free energy, partial molar Gibbs free energy, or simply Gibbs energy or Gibbs free energy but with the unit of J/mol. Adding to the confusion is the occasional use of Gibbs potential in place of Gibbs energy or Gibbs free energy, even when it refers to the Gibbs free energy of an entire system rather than on a per mole basis. Another reason why chemical potential is underappreciated is the surprising lack of a unique unit associated with such a quantity of central importance in the thermodynamics of materials.

The two main objectives of this article are to share the author's understanding and interpretation of chemical potential and to make a case that it is the chemical potential, not the Gibbs free energy, that should be employed in the majority of applications of thermodynamics in materials science and engineering.

Definition of potentials

We start with the definitions of different forms of potentials in contrast to their corresponding energies. A potential in physics is defined as the energy stored per unit of matter (i.e., a potential describes the corresponding potential energy intensity). A potential is an intensive property independent of system size. For example, the familiar electric potential, ϕ , is the electrostatic potential energy, U_E , with one unit (e.g., one Coulomb) of charge, q . In its simplest mathematical form, the electrical potential is defined as

$$\phi = \frac{U_E}{q}. \quad (1)$$

Therefore, electrical potential represents the electrical energy intensity. Conceptually, it is fundamentally different from electrical energy, which is proportional to the system size and is an extensive quantity.

Another familiar example for potential is the gravitational potential or gravitational energy intensity, which is

the gravitational potential energy per unit mass. Similarly, temperature, T , which can be considered the thermal potential or thermal energy intensity, is the thermal potential energy, U_T , possessed by one unit of thermal matter, or one unit of entropy S

$$T = \frac{U_T}{S}. \quad (2)$$

Pressure p can be considered as the mechanical potential. It is a measure of mechanical potential energy, U_m , stored per unit volume V , or the mechanical energy intensity

$$p = -\frac{U_m}{V}. \quad (3)$$

Definition of chemical potential

Josiah Willard Gibbs formally introduced the concept of chemical potential approximately 140 years ago in his foundational article.¹ Gibbs not only established the mathematical beauty of thermodynamics by formulating the fundamental equation of thermodynamics of a system but also introduced the concept of chemical potential, which he originally called the intrinsic potential. The establishment of the fundamental equation and introduction of chemical potential marked the birth of chemical thermodynamics and made it possible to apply thermodynamics to materials science and engineering.

In direct analogy to electrical potential, gravitational potential, thermal potential, and mechanical potential, the chemical potential of a chemical substance, μ , can be simply defined as the chemical energy (U_c) possessed by 1 mol of the substance

$$\mu = \frac{U_c}{N}, \quad (4)$$

where N is the number of moles of the substance (i.e., the chemical potential of a chemical substance represents its chemical energy intensity in a given homogeneous system or at a given location of an inhomogeneous system). The chemical energy U_c is the same as the Gibbs free energy G , and Equation 4 holds for each chemical component of a homogeneous multicomponent solution as well as for the entire homogeneous solution.

The definition of chemical potential based on Equation 4 should be significantly easier to comprehend for most people, particularly for beginners in thermodynamics, than using derivatives or rate of increase in an energy function with respect to the addition of a substance, as is often the case. For example, in most textbooks, the chemical potential of a given species i is defined as the rate of increase in the internal energy of the system with respect to the increase in the number of moles of species i under constant entropy, constant volume, and constant number of moles for all species except species i . Alternatively, it is defined as the rate of increase in the Gibbs free energy of the system with respect to the increase in the number of moles of species i under constant temperature, constant pressure, and constant number of moles for all species except species i .

We can draw another analogy for chemical potential to thermal and electrical potentials. The application of an electrical potential difference between two spatial locations or an electrical potential gradient, also referred

to as an electric field, results in electrical conduction, or the transport of electric charges. Imposing a difference in temperature between two locations or a temperature gradient leads to entropy or heat transfer from high-temperature to low-temperature regions. A difference in chemical potential between two locations or a chemical potential gradient is the driving force for the migration of the corresponding chemical species from high chemical potential regions to lower chemical potential regions.

Maxwell recognized the identification of temperature, pressure, and chemical potential as potentials more than 140 years ago: “The pressure is the intensity of the tendency of the body to expand, the temperature is the intensity of its tendency to part with heat, and the potential of any component is the intensity with which it tends to expel that substance from its mass.”²

It should be emphasized that one can associate a chemical potential with any type of substance. It can be a group of atoms, molecules, electrons, electron holes, atomic vacancies, phonons, or photons. The familiar Fermi level in semiconductor device physics or solid-state physics is the chemical potential of electrons.³

Molar Gibbs free energy and chemical potential

To further understand chemical potential (μ) and establish the link between chemical potential and Gibbs free energy (G), we consider the total internal energy, U , of a simple system by adding up the thermal, mechanical, and chemical energy from Equations 2 to 4:

$$U = U_T + U_m + U_c = TS - pV + \mu N. \quad (5)$$

Gibbs defined a simple system as a system without considering the surface, electric, magnetic, and non-hydrostatic mechanical energy contributions.

Equation 5 is precisely the integral form of the fundamental equation of thermodynamics formulated by Gibbs by combining the first and second laws of thermodynamics,¹ which connect the seven basic thermodynamic variables, U , T , S , p , V , μ , and N , of a simple system. We can rewrite

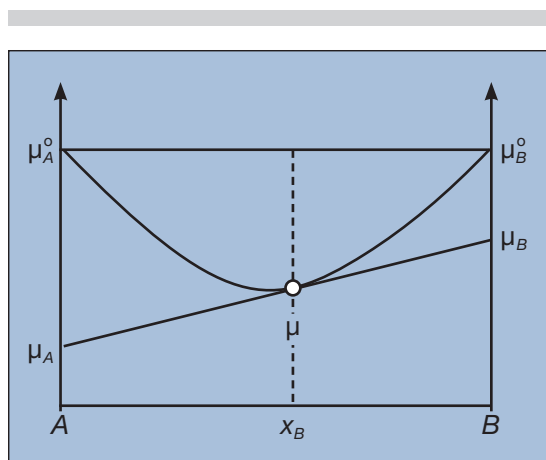


Figure 1. Schematic illustration of the chemical potential μ of a binary solution $A_{x_A}B_{x_B}$ and the chemical potentials μ_A and μ_B of the individual species A and B as a function of composition. μ_A^0 and μ_B^0 are the chemical potentials of pure A and pure B .



Equation 5 in a different form as

$$U - TS + pV = G = \mu N. \quad (6)$$

Equation 6 is another form of the fundamental equation showing that the Gibbs free energy, G , is the chemical energy μN (Equation 4). If we write the chemical potential in terms of Gibbs free energy, we have

$$\mu = \frac{G}{N}. \quad (7)$$

Therefore, the chemical potential of a substance introduced by Gibbs is simply the Gibbs free energy or chemical energy per mole of that substance (i.e., the molar Gibbs free energy is precisely the chemical potential).

Equation 7 suggests that there is no need to introduce the term molar Gibbs free energy. Instead, we should simply use the well-defined chemical potential to replace the term “molar Gibbs free energy” to clearly distinguish between “potential” and “energy.” The fact that we never get confused between electrical potential and electrical energy is because we never call the electrical potential the “molar charge electrical energy.” In electrostatics, we often solve for electrical potential or electric field, but we rarely compute electrical energy. For the same reason, we should have been working mostly with chemical potentials rather than chemical energy in applying thermodynamics to materials equilibrium and processes.

There is a general misconception that Equation 7 holds true only for pure substances or single-component systems. Equation 7 is true regardless of whether the substance is a single component or multicomponent. According to Gibbs, “for the purposes of defining chemical

potential, any combination of elements in a given proportion may be considered a substance, regardless of whether it exists as a homogeneous body.”²¹

We can rewrite the integral form of the Gibbs free energy here for an n -component system,

$$G = \mu N = \mu_1 N_1 + \mu_2 N_2 + \dots + \mu_n N_n, \quad (8)$$

where $\mu_1, \mu_2, \dots, \mu_n$ are the chemical potentials of component 1, 2, ..., and n , respectively, and N_1, N_2, \dots, N_n are the number of moles of component 1, 2, ..., and n , respectively. In Equation 8, $G = \mu N$ can be understood as the total Gibbs free energy or chemical energy of the substance, while $\mu_i N_i$ can be considered the Gibbs free energy or chemical energy possessed by chemical component i in the substance. Therefore, the chemical potential μ of a homogeneous n -component system can be written in terms of chemical potentials for the n individual components, $\mu_1, \mu_2, \dots, \mu_n$,

$$\mu = \mu_1 x_1 + \mu_2 x_2 + \dots + \mu_n x_n, \quad (9)$$

where $x_i (= \frac{N_i}{N})$, where $N = N_1 + N_2 + \dots + N_n$) are mole fractions.

In a simple interpretation, the Gibbs free energy per mole of the homogeneous system is the chemical potential of a homogeneous system at a particular composition (i.e., the chemical energy intensity). The chemical potential of a particular component is the Gibbs free energy per mole of that component in the homogeneous solution. For example, a substance can be a binary solution $A_{x_A} B_{x_B}$ of composition x_A and x_B , with $x_A + x_B = 1$, $\mu = \mu_A x_A + \mu_B x_B$.

The relationship among μ, μ_A , and μ_B can be illustrated using the well-known common tangent construction (see **Figure 1**). In most textbooks, the chemical potential μ of a solution $A_{x_A} B_{x_B}$ is called the molar Gibbs free energy, Gibbs free energy, or Gibbs energy. This can be misleading, because chemical potential is not a form of energy—calling a potential as some sort of energy adds to the confusion and difficulty in understanding the concept of chemical potential.

Unit of chemical potential

The units for energy and for each of the familiar potentials are associated with the names of scientists who introduced or invented them. For example, the unit of energy is Joule; the unit of temperature, the thermal potential, is Kelvin (K); the unit of pressure, the mechanical potential, is Pascal (Pa); and the unit of electric potential is Volt (V) after Volta. However, essentially all textbooks and articles use J/mol (or eV/atom or eV/electron in the physics literature) as the unit for chemical potentials.

To be consistent with the units for the other potentials, it is useful to introduce a unique unit for the chemical potential. Since all the familiar potentials are associated with the names of the scientist who invented them and since Gibbs introduced this important concept of chemical potential, it is only natural and appropriate to adopt the unit “Gibbs” or “ G ” (**Table I**) as the unit of chemical potential to replace the unit of J/mol. Fuchs⁴ as well as Job and Herrmann⁵ already adopted the use of Gibbs as the unit for chemical potential.

Wide adoption of a unique unit for the chemical potential will be helpful for beginners to recognize the analogs of chemical potential to electric potential, temperature, and pressure. Assigning a unique unit for chemical potential will also help to identify whether a thermodynamic quantity is a potential or a form of energy. For example, while chemical potential is measured in Gibbs (=J/mol), Gibbs free energy is measured in Joules (J). Therefore, the molar Gibbs free energy or partial molar Gibbs free energy, which has the unit of J/mol (= Gibbs), should be identified as a chemical potential.

In summary, to facilitate the understanding of and promote applications of chemical potentials, the author makes the following recommendations:

- Introduce a simple definition for chemical potential: “chemical potential of a substance is the chemical energy per mole of the substance.” In this definition, Gibbs free energy is chemical energy, and the substance

Table I

Potential	Units
T – Thermal potential	Kelvin (K)
p – Mechanical potential	Pascal (Pa)
ϕ – Electrical potential	Volt (V)
μ – Chemical potential	Gibbs (G)

can be a pure substance or a multi-component system.

- Use chemical potential to replace the terms “molar Gibbs free energy” and “partial molar Gibbs free energy” as well as “Gibbs energy,” “Gibbs free energy,” “free enthalpy,” and “Gibbs potential” when referring to the Gibbs free energy for 1 mol of a material with the unit of J/mol. If one would like to emphasize the amount of Gibbs free energy stored in 1 mol of matter, its unit should be *J* rather than J/mol.
- Use only the term “Gibbs free energy,” “Gibbs energy,” or “free enthalpy” when referring to the total Gibbs free energy or chemical energy of a material with the unit of *J*, and avoid using the term “Gibbs potential” to clearly distinguish potential from energy.
- Assign a unique unit name to chemical potential replacing its existing unit of J/mol to emphasize its analog to temperature, pressure, and electrical potential. This will also make it easier to recognize molar Gibbs free energy,

which has the same unit as chemical potential, as a chemical potential.

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