

EQUILIBRIUM IN MULTIPHASE REACTING SYSTEMS

Renato Rota

Dipartimento Di Chimica Materiali Ingegneria Chimica, Politecnico di Milano, Italy

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Summary

After a short introduction, the basic laws of thermodynamics are reviewed. From these laws, the equilibrium conditions for multiphase reaction systems are deduced, both in the form involving entropy and in alternative forms involving internal energy, Helmholtz energy, and Gibbs energy. Then, two basic constraints, that is the closed system and the non-negativity ones, are discussed. In this context, the extent of reaction concept is introduced. The equilibrium problem is then posed and solved following two different approaches: stoichiometric and non-stoichiometric, respectively. Both these approaches require the evaluation of the chemical potential, which is the topic of the next sections. Pure fluids and solutions are discussed, together with the use of volumetric equations of state and activity coefficient models. The next section introduces the equilibrium constant concept and discusses its dependence on temperature and pressure, as well as its relation with the reaction difference of Gibbs energy and the choice of the reference state. Finally, several applications are discussed. In particular, reacting systems without phase equilibrium, phase equilibrium involving vapor-liquid, liquid-liquid and solid-liquid phases, as well as multiphase reacting systems are illustrated with the help of numerical examples.

1. Introduction

In the following sections we deal with equilibrium conditions in closed systems, that is, locally stable equilibrium states. While the rigorous definition of a thermodynamic system is given elsewhere (see Thermodynamic systems and state variables; here it suffices to remind that a closed system is a portion of matter that does not exchange mass with its surroundings), it is worth discussing what equilibrium conditions means. With this statement we indicate a thermodynamic state (also for definition of thermodynamic states see Thermodynamic systems and state variables) that is independent of time, its previous history as well as position within it, and it is also resistant to limited-amplitude fluctuations in state variable values. This definition clearly distinguishes an equilibrium condition from non-equilibrium steady and unsteady state conditions, as well as from metastable equilibrium conditions.

In what follows there is no attempt to discuss all the possible equilibrium conditions of a thermodynamic system, but rather to constrain the discussion to a few common peculiar situations. Then we will not consider any surface or tensile effect (that is, the only external mechanical stress considered is that of a uniform external pressure) as well as any potential field (e.g., gravitational or electrical). Moreover, we will also disregard nuclear and macroscopic kinetic energy effects.

Apart from these simplifications, there are two more constraints that are intrinsic in the systems we are dealing with, that is the mass conservation (arising from the closed-system assumption) and the non-negativity constraint forcing the number of moles of each species to be equal or greater than zero.

The aforementioned assumptions define the problem we have to face. What we need is to relate quantitatively the variables that describe all the homogeneous phases in the system to compute the equilibrium values of some of them when the values of all the other variables are given. With homogeneous phase we mean a portion of matter where all the intensive properties (in particular, temperature, pressure and composition; this last usually expressed as mole fractions) are everywhere the same (for definition of intensive and extensive variables see *Thermodynamic systems and state variables*). The various phases present in the system can exchange mass and energy one another (that is, they can be considered as open systems). Moreover, the various chemical species can react, that is, can exchange atoms one another.

To solve this problem through thermodynamics a three-step procedure is required, as illustrated in Figure 1.

Starting from a problem in the real world (say, computing the equilibrium composition of an homogeneous mixture of carbon monoxide, carbon dioxide and oxygen at a given temperature and pressure), the first step (step A in Figure 1) is to translate this problem in the abstract world of thermodynamics. Thermodynamics simply provides a mathematical framework where this kind of problems can be solved, and in fact the mathematical solution of the abstract problem is the second step (step B in Figure 1). The final step (step C in Figure 1) is to translate back the solution provided by thermodynamics into the real world. Since the fundamental works of J.W. Gibbs at the end of XIX century steps A and B can be considered solved. We know how to translate the equilibrium problem in thermodynamic language as well as to solve it. Much more problems arise from the recovering into the real world the solutions obtained through thermodynamic relations. This is a field not yet completely elucidated, but unfortunately it is essential for obtaining numerical answers to design problems.

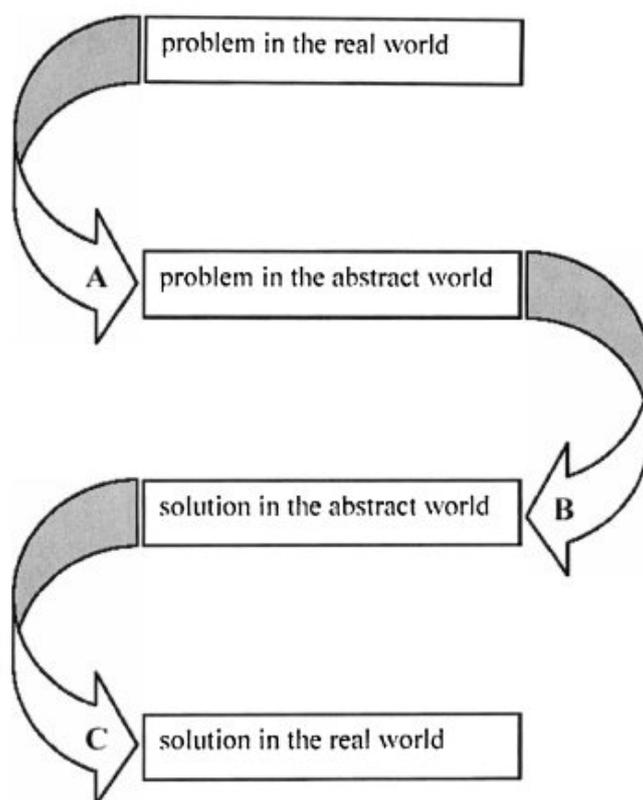


Figure 1 – Three-step procedure for solving the equilibrium problem through thermodynamics.

In the following we will assume already known some basic concepts related to state functions and thermodynamic laws as well as to thermodynamic transformations and relations (see Thermodynamic systems and state variables) and we will begin with the mathematical definition of equilibrium conditions (that is, step A and B in Figure 1). Then we will go through some relevant situations for discussing how to recast the results from thermodynamics into the real world.

2. Equilibrium conditions from thermodynamic laws

Thermodynamics is a law-based science, in the sense that from few simple laws it allows to derive a mathematical framework useful to solve practical problems. These laws cannot be proved in the mathematical sense. They rather represent postulates whose validity lies in the absence of contrary experimental evidences.

The first law defines the internal energy as a state function able to explain how energy can be stored in a system. It followed from the famous series of experiments carried out by J.P. Joule in the XIX century. However, it can be also formalized in a more modern way through an energy balance, whose general formulation is:

$$[acc] = [in] + [prod] \quad (1)$$

Here [acc] is the accumulation term, that is, the time derivative of the energy enclosed in the system boundary, [in] is the power entering (or exiting, when negative) the

system through its boundary, while [prod] refers to energy production.

Considering the constraints discussed in the previous section, for a closed system equation (1) leads to the following relation (see Figure 2):

$$\frac{dU}{dt} = \dot{Q} + \dot{W} \quad (2)$$

where U is the internal energy, while \dot{Q} and \dot{W} are the heat and work power entering the system, respectively.

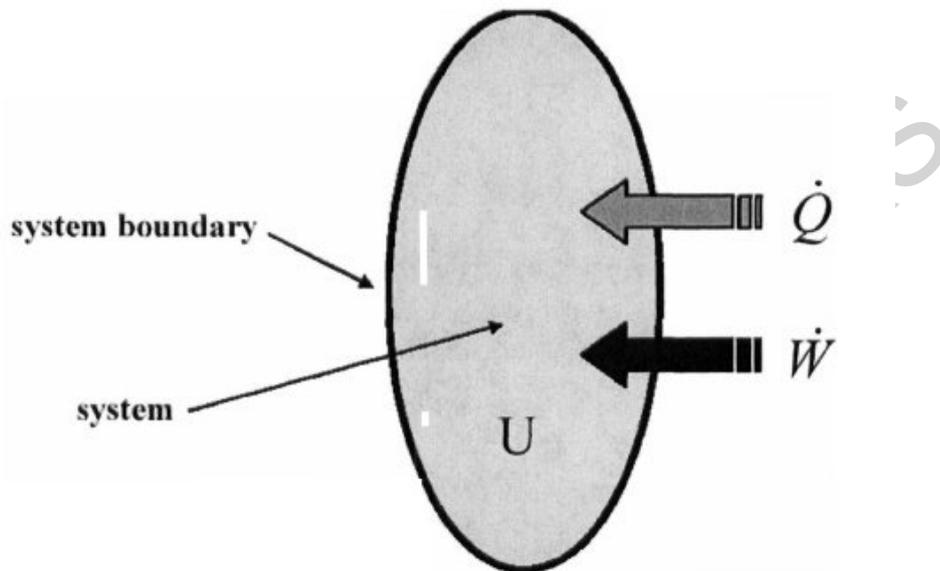


Figure 2 – closed system exchanging energy (that is, work and heat) through its boundary.

This equation can be recast in the following one:

$$dU = \dot{Q}dt + \dot{W}dt = dQ + dW \quad (3)$$

which is the mathematical expression of the “first law (or principle) of the thermodynamics.” It simply states that the total energy is constant, although it can assume different forms.

As the first principle postulates the existence of the internal energy to explain the possibility of storing energy in a system, the second law defines the entropy as a way to describe the direction of spontaneous transformations. The entropy of a system is a state function whose change in a reversible transformation (that is, a transformation involving only states no more than infinitesimally displaced from equilibrium, see Thermodynamic systems and state variables) is defined (for a closed system) as the ratio of the heat exchanged to the system temperature:

$$dS = \frac{dQ_{rev}}{T} \quad (4)$$

where S is the entropy of the system.

Entropy allows identifying the direction of any spontaneous process. Let us consider for the sake of example the heat exchange between two heat reservoirs (that is, ideal systems able to exchange heat without changing their temperature). It is a common experience that heat is always transferred from the hotter body to the colder one: this is the direction of the spontaneous process. The change of entropy of the hotter reservoir, whose temperature is T_1 , when exchanging an amount of heat equal to Q is given by:

$$\Delta S_1 = \frac{-|Q|}{T_1} \quad (5)$$

The entropy variation of a heat reservoir at temperature equal to T is always given by Q/T regardless the transformation is reversible or not since the heat exchange process does not influence its temperature. In other words, the effect of heat exchange on the reservoir is not influenced by the temperature of the other system to (or from) which the heat is transferred. The minus sign in equation (5) arises from the fact that heat exits the hotter reservoir.

Analogously, entropy change for the colder reservoir at T_2 is given by:

$$\Delta S_2 = \frac{|Q|}{T_2} \quad (6)$$

The total change of entropy is then given by (note that $T_1 > T_2$ for a spontaneous process):

$$\Delta S_t = \Delta S_1 + \Delta S_2 = \frac{-|Q|}{T_1} + \frac{|Q|}{T_2} = |Q| \left(\frac{T_1 - T_2}{T_1 T_2} \right) > 0 \quad (7)$$

Only in the limit of $T_1 \rightarrow T_2$ (that is, reversible processes) the total entropy change is equal to zero. This result can be demonstrated for any spontaneous process leading to the mathematical formulation of the “second law (or principle) of the thermodynamics”:

$$\Delta S_t \geq 0 \quad (8)$$

The statement of the second law is that every process proceeds in a direction leading to an increase of the total entropy, being the limit value of zero achieved only by reversible processes.

The total change of entropy refers to any closed system plus its surroundings, that is, to a system whose internal energy and volume are constant. Consequently, for any

spontaneous process proceedings towards the equilibrium state (with the constraints of constant internal energy and volume) the entropy can only increase, reaching a maximum value at the equilibrium. This results in a criterion for assessing equilibrium conditions when the constraints of constant volume and internal energy are enforced, that is:

$$dS|_{U,V} \geq 0 \quad \xrightarrow{\text{equilibrium}} \quad \max(S) \quad \text{at} \quad U, V = \text{const} \quad (9)$$

Consequently, pressure, temperature and composition of each phase in a closed system at constant volume and internal energy will change up to the maximum value of entropy (compatible with the enforced constraints, that is, constant volume, internal energy and mass) will be reached: this is the equilibrium state.

2.1 Alternative relations

Let us consider a closed system with uniform temperature and pressure containing an arbitrary number of species and phases in a non-equilibrium condition. It follows that the species will migrate from one phase to another and they will react up to the equilibrium condition. All these changes are spontaneous, that is, irreversible. Let us assume the system in thermal and mechanical equilibrium with its surroundings, so as any heat exchange and expansion work takes place reversibly. It follows that the total infinitesimal change of entropy for the surroundings is equal to:

$$dS_{surr} = \frac{dQ_{surr}}{T_{surr}} = \frac{-dQ}{T} \quad (10)$$

where the minus sign accounts for the fact that heat entering the surroundings exits the system. The second law requires that:

$$dS_t = dS + dS_{surr} \geq 0 \quad (11)$$

that is, introducing equation (10):

$$TdS \geq dQ \quad (12)$$

Introducing the first law (equation (3)) together with the assumption of considering only expansion work (that is, $dW = -PdV$) we obtain:

$$TdS - dU - PdV \geq 0 \quad (13)$$

It must be stressed that since equation (13) involves only state functions it must be satisfied for any transformation in a closed system with uniform temperature and pressure, regardless the system is in equilibrium with its surroundings or not. This is the usual way to generalize results in thermodynamics, which explains the great importance of state functions.

In equation (13) the inequality defines the direction of any spontaneous change leading towards the equilibrium state, which is characterized by the equality. From this equation the equilibrium condition for a closed system with constant volume and internal energy, that is equation (9), follows directly. However, also other relations characterizing equilibrium conditions with different constraints can be easily deduced. For instance, considering a closed system with constant entropy and volume it follows that:

$$dU|_{S,V} \leq 0 \quad \xrightarrow{\text{equilibrium}} \\ \min(U) \quad \text{at} \quad S, V = \text{const} \quad (14)$$

that is, equilibrium conditions at constant volume and entropy require the internal energy to be minimum.

When considering a closed system with constant temperature and volume equation (13) can be recast in the following one:

$$TdS - dU = d(TS - U) \geq 0 \quad (15)$$

The term between brackets is the ‘‘Helmholtz energy,’’ $F=U-TS$, thus leading to the following equilibrium condition for a closed system with constant temperature and volume:

$$dF|_{T,V} \leq 0 \quad \xrightarrow{\text{equilibrium}} \\ \min(F) \quad \text{at} \quad T, V = \text{const} \quad (16)$$

This means that equilibrium conditions at constant volume and temperature require the Helmholtz energy to be minimum.

Finally, let us keep constant the most common variables used in practice (since they can be easily measured), that is temperature and pressure. In this case, equation (13) leads to:

$$d(TS) - dU - d(PV) = d(TS - U - PV) = \\ d(TS - H) \geq 0 \quad (17)$$

where the enthalpy, $H=U+PV$, has been introduced. The term between brackets is the ‘‘Gibbs energy,’’ $G=H-TS$, thus leading to the following equilibrium condition for a closed system with constant temperature and pressure:

$$dG|_{T,P} \leq 0 \quad \xrightarrow{\text{equilibrium}} \\ \min(G) \quad \text{at} \quad T, P = \text{const} \quad (18)$$

This is the most important relation for practical purposes, stating that equilibrium conditions for a closed system at constant temperature and pressure require the Gibbs energy to be minimum, that is (as necessary condition):

$$dG|_{T,P} = 0 \quad (19)$$

This result is rather general since it states that an equilibrium state for a closed system has a minimum value of the total Gibbs energy with respect to all possible changes at given temperature and pressure values. In other words, we can write an expression for the Gibbs energy as a function of the number of moles of the various species in all the phases and look for a set of such number of moles minimizing the total Gibbs energy. This procedure applies to problems involving non-reacting phase equilibrium, homogeneous chemical-reaction equilibrium, as well as simultaneous phase and chemical equilibrium. The various expression characterizing equilibrium conditions are summarized in Table 1.

Constraints	Thermodynamic potential	Equilibrium condition
$U, V = \text{const}$	$dS _{U,V} \geq 0$	$\max(S)$
$S, V = \text{const}$	$dU _{S,V} \leq 0$	$\min(U)$
$T, V = \text{const}$	$dF _{T,V} \leq 0$	$\min(F)$
$T, P = \text{const}$	$dG _{T,P} \leq 0$	$\min(G)$

Table 1– Thermodynamic potentials characterizing the equilibrium state for a closed system with different constraints.

Obviously, the Gibbs energy minimum has to fulfil the constraints of mass conservation and non-negativity discussed previously. While the non-negativity constraint follows straightforwardly, the mass conservation one deserves some non-trivial problems, in particular when reacting systems are considered. This is the topic discussed in the next section.

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Biographical Sketch

Renato Rota was born in June, the 8th, 1961, and he is married with two sons. He took his degree in Chemical Engineering in 1986 at the Politecnico of Milano, Italy. From 1986 to 1988 he worked at the chemical engineering company Snamprogetti S.p.A. He got a position for a three-years “Corso di Perfezionamento” (that is, Ph.D.) at the Scuola Normale Superiore di Pisa in 1988. He was a visiting student at the Purdue University (USA) in 1988/99. From 1990 to 1998 he worked at the Politecnico di Milano as a researcher, doing research and teaching in several courses (e.g., Applied Physical Chemistry; Thermodynamics; Applied Chemical Kinetics; Fundamentals of Technology). From 1998 he is a professor of Chemical Engineering Thermodynamic and Safety and Reliability in the Process industries at the Politecnico di Milano. He won in 1986 the National Award "ENIChem - Piano giovani" reserved to Degree Thesis and in 1996 the VIII National Award "Federchimica - per un futuro intelligente," reserved to chemical researchers and professors. His scientific work is summarized in about 150 publications.