

# Gibbs Phase Rule

## General Stuff, Definitions, and How It Works

### Science

**Josiah Willard Gibbs** (February 11, 1839 - April 28, 1903), an American scientist working at Yale University, is one of the unsung heroes of Materials Science (then called physics, chemistry, and mathematics). His work on the applications of thermodynamics is at the core of Materials Science. He created statistical mechanics (a term he coined) together with James Clerk **Maxwell** and Ludwig **Boltzmann**. He also invented modern vector calculus (independently of Oliver Heaviside), an indispensable tool in all of science.

● Having duly praised old Gibbs, I now must add that his hero status wasn't recognized right away. He not only published in very obscure journals, he also did his best to write as incomprehensible as possible <sup>1</sup>. His work only received wide recognition in Europe after it was translated into German by **Wilhelm Ostwald** (and into French by Henri Le Chatelier). Recognition in the United States came even later, possibly because around 1880, when his major work was done, Americans didn't much care for science and research. They were preoccupied with killing, or at least ripping off, all those Indians, Southerners, Yankees, former slaves, etc. They also couldn't read German.

Gibbs deduced what is still known as *Gibbs phase rule* all over the world. It is an extremely simple rule or equation, but of overbearing importance as soon as we look at any material that is not just a simple phase.

I need to clarify terms before I can get to the phase rule proper. This is best done by looking at an example. Of course, I pick our old friend, the carbon steel or pure iron (Fe) with at most about 2 % of pure carbon (C).

We need to clarify the parameters that we must use to describe the [system](#) iron - carbon. What we have are:

● **Components (C)**. Our model system carbon steel system has *two* components: iron (Fe) and carbon (C). The number of system components thus is **C = 2**. That's why we call it a *binary* system. If we would look at real steel, we might have far more components, e.g. iron, carbon, manganese, silicon, and nickel: C = 5. Since Gibbs phase rule applies to *any* system, we keep in mind that there is no limit on components.

● **Phases (P)**. What is a phase? Here is the definition [given in the backbone](#):

**A phase is a region of space where all physical properties (e.g. density, hardness, chemical composition) of a material are essentially uniform.**

Robert P. Baumann, whose book "Modern Thermodynamics with Statistical Mechanics" (McMillan Publ. Co.) I used for this module, states:

*"A phase is a homogeneous sample of matter, or a collection of equivalent homogeneous samples".*

In [Eric J. Mittemeijer's](#) wonderful book we read:

*"A phase is a macroscopically homogeneous body exhibiting uniform physical and chemical properties".*

Aha! That one needs that many big words to state the obvious should make you a bit suspicious. And indeed, I have witnessed full-grown Mat. Sci. Profs battling ferociously about something or other being a true phase or not. No matter, it is reasonably clear what constitutes a phase for the example we are looking at here. Here is a list of possible phases in our system iron with a little bit of carbon:

- bcc iron with some dissolved carbon, also known as ferrite.
- fcc iron with some dissolved carbon, also known as austenite.
- hexagonal iron with some dissolved carbon - not forbidden but doesn't exist
- Liquid iron/carbon.
- Cementite or Fe<sub>3</sub>C.
- Any other well-defined iron carbon compounds (Fe<sub>x</sub>C<sub>y</sub>), should they exist (they don't).
- Carbon with some dissolved iron it. Does exist but is usually not found.
- Whatever else you can make with carbon and iron.

In other words, knowing the number of components doesn't tell *you* how many phases you may find in your system. I told you that there is no hexagonal iron with some dissolved carbon but are you sure I didn't lie? Note also that a phase can contain any number of components as long as they are "randomly mixed" on an atomic level. Note also that "[magnetic ferrite](#)" below the [Curie temperature](#) is, nominally, a *different* phase from non-magnetic ferrite above the Curie temperature. However, since these two phases have rather similar properties as far as we care, we usually count them as just one phase. Now you get a first idea why the concept of phases can get a bit confusing at times.

● **Degrees of Freedom (F).** If we take a real piece of material from our model system Fe - C and look at it, we see a piece of steel. If we look at it a bit closer, we see either one phase (for example liquid steel or ferrite) or a mixture of several phases. If you read and understood the backbone part, you know that we see at most a mixture of two phases because [I told you so](#). But that is what we want to *prove* here. I thus leave the number of phases open for the time being.

Now let's consider that we do something to our system. We might, for example, lower the temperature *T*, increase the pressure *p*, change the composition *c<sub>C</sub>:c<sub>Fe</sub>* by adding more carbon or taking out some carbon (it's easy; we are dealing with a brain system here!), add a magnetic field, whatever. The point marking the state of the system in some phase diagram then moves to a different position and we get a different system - but do we also get different phases? That is the big question that Gibbs phase rule will answer.

Of course we already know parts of the answer. If you start with the one-phase system "liquid carbon steel" and then decrease the temperature, it will eventually freeze and then you have changed the phase. However, if it is hot enough to start with, you can change the *temperature*, the *pressure* and the *composition* to some degree, and you will still have the same phase: liquid steel. We have obviously three *degrees of freedom F* or three *variables* that we can use to play with our system, without changing the phases it consists of.

On the other hand, if the system happens to be right at the boundary between liquid and solid, you can't change the temperature without producing either pure liquid or pure solid. At least one degree of freedom is lost in this case.

It took the genius of Josiah Willard Gibbs to realize that the three parameters given above are related by an extremely simple equation, the **Gibbs phase rule**:

$$P + F = C + 2$$

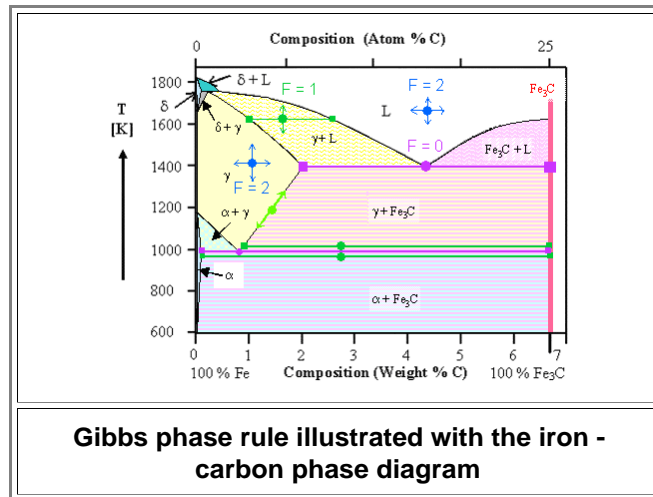
● What does Gibbs phase rule mean? Let's see. For our model system we have *C = 2* or two components. The sum of the number of phases and degrees of freedom thus equals four; *P + F = 4*. That gives us the following options for our two component system "carbon steel":

Number of <i>components</i> : <i>C = 2</i> Possible <i>variables</i> : Temperature <i>T</i> , Pressure <i>p</i> and Composition <i>c<sub>C</sub>:c<sub>Fe</sub></i>				
Number of phases <i>P</i>	1	2	3	4
Degrees of freedom <i>F</i>	3	2	1	0

● The first interpretation is simple. If, for example, we only have *one* phase, like liquid steel or ferrite, we can change all three variables (*T*, *p*, and the *composition c<sub>C</sub>:c<sub>Fe</sub>*) and still have only one phase. Of course, if we change the variables, we move to another point in a *three*-dimensional phase diagram where the variables define the axis. The system is characterized by a point in the phase diagram, and as we change the variables, the point moves to some other place inside a *volume* that characterizes the particular one-phase state. If we change the variables a lot, we will eventually reach a boundary and the validity range of Gibbs phase rule. *Three*-dimensional phase diagrams, with the pressure *p* as third axis, are perfectly sensible and useful things to have. They are just not very *practical* as long as we keep the pressure constant. That's why we usually just give *two*-dimensional phase diagrams with temperature *T* and compositions *c<sub>1</sub>:c<sub>2</sub>* as axes. In other words: assuming that the *pressure is constant* reduces the maximum degrees of freedom by one. Gibbs phase rule reduces to *P + F = C + 1*, and we end up with the following table:

Pressure <i>p = const.</i> Number of <i>components</i> : <i>C = 2</i> Possible <i>variables</i> : Temperature <i>T</i> and Composition <i>c<sub>1</sub>:c<sub>2</sub></i>			
Number of phases <i>P</i>	1	2	3
Degrees of freedom <i>F</i>	2	1	0
Representation in phase Diagram	Area(s)	Line	Point

Let's look at the relevant phase diagram for our system to see what that means:



The colored dots represent some specific state of our system. We can be either inside an area, on a line, or on a point where lines meet. Let's go through these options.

● If we are inside an *area* we could be either inside a single phase area or an mixed phase area. What we get is clear:

- **Single phase area:** We have  $P = 1$  and thus  $F = 2$ . We can change the composition *and* the temperature and still keep a single phase.
- **Two phase area:** We have  $P = 2$  and thus  $F = 1$ . Indeed, since we have a structure decomposed into the two phases on the left and right of the *tie line*, we can *either* change the temperature (than the new compositions is given and not independent) *or* the composition (than the temperature for this composition is given and not independent).
- **Three phase area** We have  $P = 3$  and thus  $F = 0$ . That means it ain't an area. *It's a point*. You can't change anything, and that means anything is is fixed. Three phases can *only* coexist at a *point* in a binary phase diagram - as they do indeed at the violet circles.
- **Four-phase area** We have  $P = 3$  and thus  $F = -1 = ???$ . That simply means it *can't be done*. You can never have four phases coexisting in a system of two components that is in equilibrium.

And now I have proved the assertion made in the backbone!

What about being *right* on a *horizontal* line? Well - there is no such thing, *except* at the points marked by a *violet circle*. There you have three phases coexisting and thus no degree of freedom; I covered that already. Composition and temperature are fixed and you invariably are at an intersection of three lines.

- The phases with their *precise* composition are what you have at the intersection point, and to the left and right of it; as marked by squares in the phase diagram above. Three phases can only coexist with those three *different* compositions.
- If you look at a point *somewhere else* on a horizontal line, for example as shown for the line separating  $\gamma + \text{Fe}_3\text{C}$  and  $\alpha + \text{Fe}_3\text{C}$ , you simply can't have that exact state. The system is unstable in this case and will be thrown either into the  $\gamma + \text{Fe}_3\text{C}$  or into the  $\alpha + \text{Fe}_3\text{C}$  area. Tiny fluctuations will do that: it takes only an infinitesimal amount of energy to kick you off a mathematical line, after all. You might imagine that your system fluctuates back and forth between the two areas. So you are always in a two phase region in this case, with one degree of freedom. It is obvious, that this degree of freedom is now only a change in the composition because changes of temperature will get you "off-line".
- That makes also clear what is going to happen if your system is positioned on one of the inclined lines. You can't really be *exactly* on the line; you are a little bit to the left or right. If you want to stay "on" that line (meaning close to it), you can only move up and down that line. That is one degree of freedom but with a defined direction. If you change one variable by an arbitrary amount, you must change the other one by a defined amount.
- Why can't the system be exactly on a line? Gibbs phase rule doesn't say that. You have to look at the *derivation* of Gibbs phase rule to figure that out. That's one of the reasons why we don't just feed the final formulae to our students but run them through the intricacies of derivations, proofs, exceptions, etc. It is one thing to cook a fantastic meal following precise instructions, it is another thing to create *new* fantastic meals. Writing a cookbook with new good recipes is far more difficult than cooking from an existing one.  
Below, where I derive Gibbs phase rule, I will show why the system cannot be exactly on a line.

You might be inclined to think that Gibbs phase rule is not all that hot, actually. Just looking at that binary phase diagram could have told you all of the above directly.

- Well, you are wrong. It is obvious, indeed, that there is only one degree of freedom in a two-phase region because we have the splitting into the two composition there. Right. But *why* do we have a splitting into two different compositions? Because of Gibbs phase rule.
- But yes, I admit, that Gibbs phase rule is not all that hot for binary systems because the way we draw and interpret phase diagrams has already incorporated the important points. As soon as you look into ternary, quaternary, and so on systems,, however, it is absolutely essential to use the phase rule if you want to keep your brain from toying with the self-destruct option by alloying large amounts of alcohol.

### Derivation of Gibbs Phase Rule

I'll show you in a kind of short-cut way how one can derive Gibbs phase rule. That's kind of me considering the alternative 3).

The first major point is to figure out what questions we need to ask to get to the phase rule.

- We want to look at a *system* with **C** components that is in equilibrium. We want to find out the *state* of that system when it is in equilibrium ("nirvana"). The state is described completely by a *point* in a generalized phase diagram that can have several axes.

One axis is always the temperature **T**. Other axes define the compositions. For a binary system I only need a **c<sub>1</sub>:c<sub>2</sub>** axis, but in a ternary system I would also need to define **c<sub>1</sub>:c<sub>3</sub>** or **c<sub>2</sub>:c<sub>3</sub>** by an axis. It is important to realize that I only need **C – 1** axes for **C** components because all concentrations must add up to 100 %, meaning that I always can calculate one if I know all the others.

- The *free enthalpy* **G** (also known as **Gibbs enthalpy**, that's why it is always abbreviated with **G**) for some phase **P<sub>i</sub>** that I can form with my **C** components then is a function of **(C – 1) + 2** variables. I need to specify **C – 1** composition variables plus the **2** standard variables temperature **T** and pressure **p**.

At equilibrium, **G** must have an absolute minimum, meaning that the variation of **G** with respect to all variables must be zero; **dG = 0** obtains. That demands that all or at least some of the variables have some fixed values. They are then no longer variables but the *unknowns* in some equations. Solving the equations in order to get numbers for the unknowns is what we want to do. The solutions would actually *produce* a phase diagram, because they tell us for any point in such a diagram what we should find.

Just for the hell of it, let's write that down for the phase **P<sub>1</sub>**:

$$dG_{P_1} = \frac{\partial G}{\partial c_1} \cdot dc_1 + \frac{\partial G}{\partial c_2} \cdot dc_2 + \dots + \frac{\partial G}{\partial c_{C-1}} \cdot dc_{C-1} + \frac{\partial G}{\partial T} \cdot dT + \frac{\partial G}{\partial p} \cdot dp = 0$$

This doesn't look like a normal equation with some **x** or **y** as unknowns, but suspiciously like a partial differential equation that only its mother could love. Never mind; it is still an equation or function with variables that turn into unknowns if you try to apply it to some real problem.

The partial derivatives of **G** with respect to the component concentration (the  $\frac{\partial G}{\partial c}$ ) have a name, they are called the "**chemical potentials**" of the respective component. That tells you that *we* do love that baby, we even gave names to all of its many heads!

Since I may have **P** different phases, I have now **P** equations for equilibrium with altogether **P(C – 1) + 2** unknowns. The question now is how to solve these equations.

If you know anything about equations, you realize that we have a lot more unknowns than equations. That means we have a problem. Basic math tells you that you can only solve a system of equations if you have as many equations as unknowns. We need more equations

The second major point thus is to find more equations. What we need to consider is that all those phases are not independent since we require equilibrium not just for each phase on its own, but for the whole *system*. The easiest way to deal with that is to look at what happens when you move from one phase in system to another one. In doing that you are crossing a *phase boundary*. Now consider yourself to be a particle of component 1, or 4, or whatever, that moves over from phase 1 to phase 2. If you are at nirvana (= equilibrium), you must not notice that you switched phases. If you would notice, something has changed and since nirvana is the best of all states, it could only have become worse.

- What that means in cold math is that your chemical potential must not change. In equations we have:

$$\frac{\partial G_{P_1}}{\partial c_1} = \frac{\partial G_{P_2}}{\partial c_1} \quad \frac{\partial G_{P_1}}{\partial c_4} = \frac{\partial G_{P_2}}{\partial c_4}$$

- How many of those equations do we have? We have  $P - 1$  possible boundaries between  $P_1$  and one of the other  $P$  phases and thus  $P - 1$  equations describing equilibrium between phase 1 and all the others for one component. How about the boundary between and  $P_3$ , or all the other ones between phase two and the rest, omitting phase  $P_1$ ? They are not included in the count above, neither are the ones between  $P_3$  and  $P_4$ , and so on. We do not need to consider these. It is easy to show that if we have equilibrium between  $P_1$  and  $P_3$ , and between  $P_1$  and  $P_4$ , we automatically have equilibrium between  $P_3$  and  $P_4$ , and so on.
- So for one component we have  $P - 1$  equations, for  $C$  components we have a grand total of  $C(P - 1)$  equations. We still have  $P(C - 1) + 2$  unknowns. Let's see what the balance looks like and subtract the number of equations from the number of unknowns:

$P(C - 1) + 2 - C(P - 1) = C - P + 2 = F$		
No. unknowns	No. equations	Degrees of freedom

▶ The balance obviously just gives Gibbs phase rule. Why is that?

- If  $F$  would be zero, we have an equal number of equations and unknowns, meaning that one and only one unique solution exists that gives precise values for all concentrations, the temperature, and the pressure. Only for those values could our  $C$  components -  $P$  phases system achieve nirvana. If  $F$  would be negative, meaning that we have more equations than unknowns, solutions do not exist. This can never happen if we describe a real system. "Real" means that you can see it, touch, and so on, and since the system exists, so must solutions to the equations describing it.
- If  $F$  is positive, we have more unknowns than equations. Then you cannot find a unique solution - but you now have the *freedom* to assign arbitrary values to some unknowns, thus reducing the number of unknowns. If you assign some number to  $F$  unknowns, the number of remaining unknowns equals the number of equations and now you can find the solution for all the remaining unknowns. So it is clear now, why  $F$  is called "degree of freedom".
- Note that there is a difference between *knowing* that solutions to some equations must exist, and actually *finding* those solutions. We have actually derived Gibbs phase rule without ever *solving* an equation. If we would do that (it is not easy!) we would essentially calculate the phase diagram. The lines in the phase diagram than mark the conditions where then equations actually have no solutions but become unstable. Infinitesimal changes of conditions throw the mathematical system either into solution kind 1 or solution kind 2. That's pretty common in slightly more advanced math and nothing to worry about. And that's why there cannot be a state point *exactly* on the lines of a phase diagram.

▶ Pretty tricky, right?

- As C. Kittel puts it, in the preface to his classic: "Introduction to Solid State Physics":  
*"A vague discomfort at the thought of the chemical potential is still characteristic of a physics education. This intellectual gap is due to the obscurity of the writings of J. Willard Gibbs who discovered and understood the matter 100 years ago."*  
 The eminent **Ostwald** reminisced in his "Lebenslinien" on his decision to translate Gibbs' work. After some difficulty procuring a copy, he had even further difficulty understanding it. He soon found that the only way to study Gibbs' papers was to translate word by word because the text was already so terse that no abbreviated summary of the content was possible. Ostwald openly admitted that he had not been able to understand all of the mathematics, and he believed that not one flaw - either in logic, mathematics, or in scientific assumptions - had yet been found there
- Easy to remember with the little (dirty) line: Paul f...s Carla twice.
- Duhem (another hero of thermodynamics), for example, criticized the phase rule because he doubted that the independent variables for the components of each of the phases of the system must be identical with the independent variables of the system. Duhem admitted that Gibbs had dealt with this problem in a few lines, but proposed to do it "with all possible rigor". Forty-two pages later he concluded: "Thus are rigorously established the various propositions contained in the phase Rule of J. Willard Gibbs". It is not easy reading!  
 Source: Edward E. Daub; "Gibbs Phase Rule: Centenary Retrospect"; Journal of Chemical Education **53** (1976) 747