Re: triple points

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- *From*: d.086@xxxxxxxxxxx
- *Date*: 16 Feb 2007 20:21:38 −0800

On Feb 16, 6:24 pm, "rge11x" <rge...@xxxxxxxxxxxx> wrote:

> On Feb 16, 8:50 pm, d...@xxxxxxxxxxx wrote:
>
>> On Feb 16, 10:11 am, Ian Gay <g...@xxxxxxx> wrote:
>>
>>> "rge11x" <rge...@xxxxxxxxxxxx> wrote
>>> innews:1171330368.262333.142470@xxxxxxxxxxxxxxxxxxxxxxxxxxxx:
>>>
>>>> According to the phase rule of Gibbs the
>>>> degrees of freedom d of a
>>>> single component system with one
>>>> mechanical interaction (pressure)
>>>> is d=3−M
>>>> where M is the number of phases present.
>>>> Now when there are three
>>>> phases, M=3, the degrees of freedom is d=0.
>>>>
>>>> The way the phase rule is derived, counting
>>>> number of constraints
>>>> against the number of parameters making up
>>>> the energy
>>>> differential, would really imply that when
>>>> M=3 the topological
>>>> dimension of the free parameters must be 0,
>>>> not that there is a
>>>> single such point. That is, one might also
>>>> have more than one

discrete, not connected, "triple points". After all, a set of simultaneous nonlinear equations can have several solutions. This surely would be very weird material because to have a second "triple point" it would have to solidify from a gas as one increases the temperature beyond the first.

My question: is there a material exhibiting such behavior, and if not, then what physical principle excludes it from happening?

Thanks

I think most follow−ups to this post have missed the point. The condition for simultaneous equilibrium of phases 1,2,3 (i.e. a triple point) is (writing u for chemical potential)

u1(T,P) = u2(T,P) = u3(T,P)

Mathematically, if u1, u2, u3 are arbitrary functions, it is not necessary that these two equations have a single solution point.
Geometrically, each of the u(T,P) functions is a surface in 3−dimensional space; the equilibrium point corresponds to the simultaneous intersection of the 3 surfaces. There can easily be more than one such point; consider as an example two planes and a sphere.

However, u(T,P) is not an arbitrary mathematical function. It is constrained by thermodynamics. The question is, do the constraints

guarantee that there can be only one triple point for a given
set of
3 phases?

This is not discussed in any of my thermodynamics texts.
One obvious
constraint is, since entropy and volume are positive, that u
always
has a positive derivative with respect to P, and negative with
respect to T. I don't think that's enough to give the above
guarantee.

Anyone got other ideas?

Ian

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If the chemical potential u, of each phase always has positive derivative with respect to P, and negative with respect to T, then u is monotonic wrt P and T. That's merely tautological. However, it is noteworthy that a monotonic function may be transformed into a linear function by some transformation of coordinate system. E.g. an exponential function is plotted as a straight line on log−linear paper. If there exists some nonlinear transformation of u, P and T in which u1(T,P), u2(T,P) and u3(T,P) map into planar surfaces then there can be at most one real solution to u1=u2=u3. This is not a proof it is hand waving. However, in contrast to mathematics where functions can be 'diabolical', in thermodynamics functions are 'well behaved'. So the argument given is meant to convince if not prove the point.

There seems to be some disparity regarding the definition of triple point. Take a look at the phase diagram for water found at:http://mutuslab.cs.uwindsor.ca/schurko/introphyschem/lectures/240_l14...

There is only one triple point labeled as such. However, it is reasonable to define a triple point as the temperature and pressure at which any three phases can coexist in equilibrium. The 'triple points' that can be identified on the phase diagram for water are:

Ice I/liquid/vapour
Ice I/Ice II/Ice III
Ice I/Ice III/liquid
Ice II/Ice III/Ice V
Ice III/Ice V/liquid
Ice V/Ice VI/liquid

Ice IV does not appear on the phase diagram; it is metastable within the phase diagram. See:http://www.lsbu.ac.uk/water/ice_iv.html

If we assign chemical potentials according to u1(Ice I), u2(liquid), u3(vapour), u4(Ice II), u5(Ice III), u6(Ice V), u7(Ice VI) then the various 'triple points' are each solutions of one of:

u1=u2=u3
u1=u4=u5
u1=u5=u2
u4=u5=u6
u5=u6=u2 or
u6=u7=u2

In these different equations, there is no example where two equations share the same three indices. Given the argument above it is reasonable to say that given three phases of one pure component, at most one triple point can occur.

That multiple triple points of the same phases, i.e., multiple solution sets of the same system of simultaneous equations do not seem to happen on the phase diagrams I have so far seen made me think, that if true in general, it must be a property, a special restriction, of the type of functions allowed by physics. Certainly, systems of

> equations may have no solution, but if they do have one or multiple discrete solution sets, at least from a mathematical point of view these are both 0 degree freedom. I do not believe that monotonicity in each variable is enough to exclude multiple solutions, there must be more to it and I am still puzzled.− Hide quoted text −
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Maybe an appeal to a higher authority would help. The wikipedia entry for Gibbs phase rule says, ...

"Consider water, the H2O molecule, C = 1.

.. when three phases are in equilibrium, P = 3, there can be no variation of the (intensive) variables ie. F = 0. Temperature and pressure must be at exactly one point, the 'triple point' (temperature of 0.01 degree Celsius and pressure of 611.73 pascals). Only at the triple point can three phases of water exist at the same time. At this one point, Gibbs rule states: F = 1 − 3 + 2 = 0" ...

This seems to say F=0 <=> exactly one point.

I'm sure a convincing argument of why this is so can be constructed, perhaps exploring the topological requirements of a phase diagram. Perhaps Josiah Gibbs had a proof that he left in the margins of a page.

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