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Triple points as pernts

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Abstract

The concept of a triple point in phase theory is elucidated, and it is revealed that the temperature and pressure are not fixed by the presence of three phases at equilibrium for any real substance. The multidimensional range of temperatures, pressures, and compositions over which three phases are at equilibrium is likened to a pernt, the latter a concept previously defined to describe indistinct, usually high-order, phase transitions. Phase diagrams are presented to demonstrate that no system can be one-component within the triple pernt. Some chemical systems with demonstrably large triple pernts are discussed.

INTRODUCTION

In 1965, Giauque et al. [1] ascended to that rarest form in scientific writing, humor, to introduce and define the concept of pernt as a special kind of indistinct point. Their point, their rhetorical one, was serious. They had in mind certain types of gradual phase transitions in which the transition temperatures and pressures are indistinct, even in the idealized models by which we understand them; a point is not better called a pernt simply because of imprecision in measurements or in setting the conditions of the transition. Some examples they gave are: Curie pernt, lambda pernt, ferroelectric pernt, and Néel pernt. Others, also usually associated with high-order transitions, come quickly to mind.

This paper elucidates the concept of a triple point in phase theory and reveals it to be a pernt. A triple pernt will be thought of as the range of temperatures, pressures, and compositions over which three given phases are at equilibrium. In the course of this demonstration it will be realized that first-order two-phase transition points are also pernts, except under exact and restrictive conditions, and in some chemical systems such conditions may not exist. Examples will be given of substances whose triple pernts are large and cause distinct and important effects. It will, of

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course, be recognized that in the cases of chemical elements and many compounds (e.g., water) the triple pernts are small and nearly indistinguishable from points. In the particular case of water, the solid–liquid–vapor triple pernt is small enough to be used as a standard point on the absolute temperature scale [2].

PERNTS

The phase rule requires in a one-component system that if three phases are present at equilibrium, then the temperature (T) and pressure (P) are fixed; the specification of one component necessarily establishes the composition (X). Such a situation defines a triple point of a one-component system. The three phases might be solid, liquid, and vapor; every sufficiently chemically stable pure substance is considered to have such a point as one of its properties.

The previous paragraph contains a hidden presumption which leads to logical problems when the facts of chemical stoichiometry are introduced [3]. The presumption is that one-component systems exist; in fact, none does. It is indeed possible to conceptualize an ideal chemical compound with exact X, e.g. water H_2O, and then, with sufficient effort, to establish and maintain that X for the substance in the form of a given phase, e.g. the liquid, to any degree of accuracy at any T and P where the phase is stable. But it is also possible, in concept and in reality, in the case of our example or in any other case, to induce variations in X by means of stresses in the direction of either element (or component) along the X axis. Even chemical elements can be stressed along the nucleus–electron X axis. Unless effort is exerted to maintain a specified X, then natural forces resulting from differing dependences of chemical potentials of the constituents on T and P will cause changes in X when the values of these variables are changed. Thus the concept of a one-component system is strictly an ideal one, and any real system, at least to some extent, is multicomponent [3].

The condition of forced constant X cannot be maintained in general, even in an ideal case, for all phases in the P–T–X vicinity of a first-order phase transition. That fact is revealed in the necessary form of the phase diagram in the vicinity of a triple point as shown schematically in Fig. 1; the case illustrated there, triple point with condensed-phase, ℓ, condensed-phase, $\mathscr{k}$, and vapor at equilibrium is sufficiently general for illustration. Figure 1 is a three-dimensional equilibrium phase diagram; the P axis is represented at only three discrete values. No proportionality between distance and value on any axis is implied, but the relation is intended to be monotonic. Regions representing condensed phases are shaded. The vapor lies above the looping curved line. Other regions contain two phases. Horizontal straight lines represent three phases.

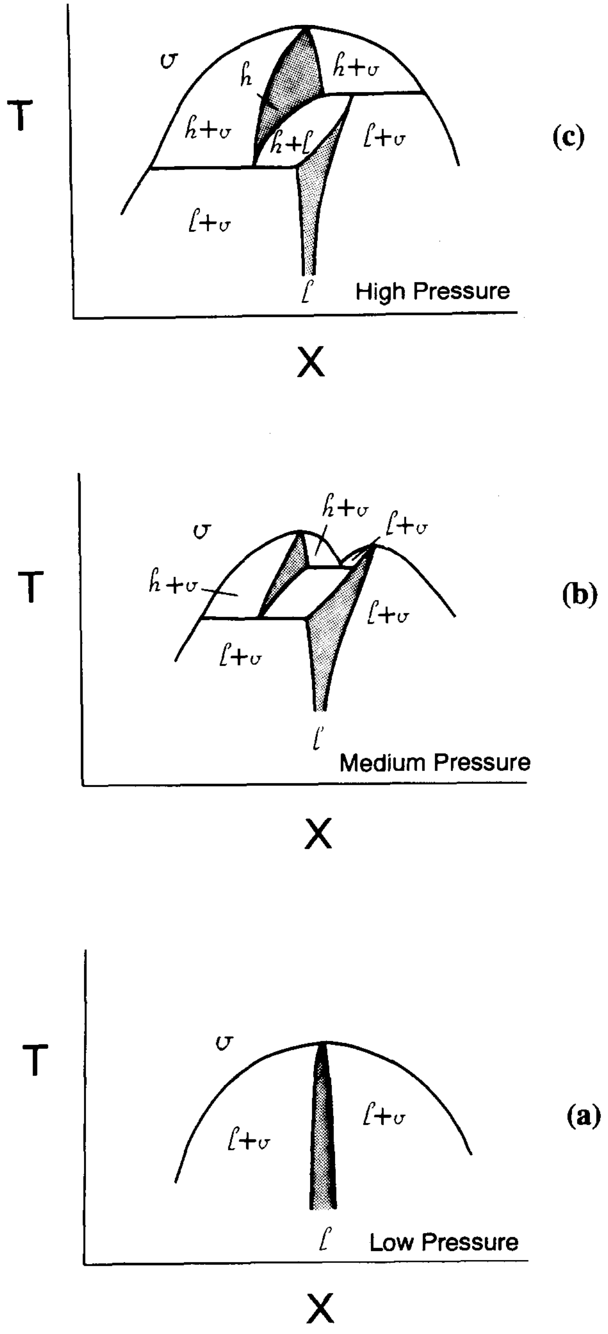

Fig. 1. Schematic temperature–composition phase diagrams at (a) low, (b) medium, and (c) high pressures in the vicinity of a triple point. Shaded areas are regions of stability of two condensed phases: ℓ, the low temperature phase; 𝒽, the high temperature phase. Alternatives including congruent condensed-phase transformation in the high pressure case are given in Figs. 2 and 3.

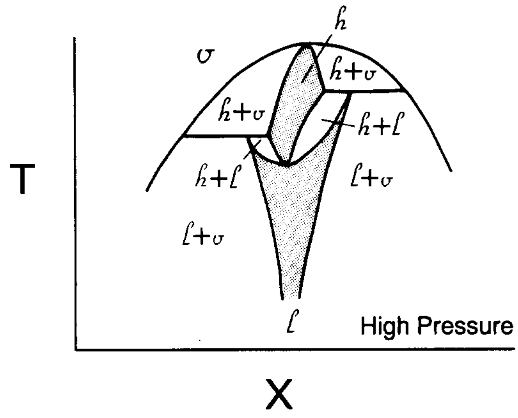

Fig. 2. Schematic temperature–composition phase diagram at high pressure in the vicinity of a triple pernt: a case with congruent condensed-phase transformation.

At low P, only phase ℓ is stable in the condensed phase. At each low P, a T and X can be set such that ℓ transforms congruently to the vapor, i.e. vaporizes congruently as shown at the maximum point of phase ℓ. An example of this case would be solid water at P below 4.5 Torr. With increasing P, at some intermediate P at a specific X and T, phase ℏ first will appear at a single point on the phase diagram. At higher intermediate P, such as the one shown in Fig. 1, ℏ will exist over a range of T and X. At appropriate values of T and X, either ℓ or ℏ can vaporize congruently at the maximum points of the phases. At high P, either condensed phase can exist if X and T are appropriately set, but only ℏ can vaporize congruently.

Figures 2 and 3 illustrate possible variations at high pressures on the necessary general form in Fig. 1. At sufficiently high pressure, a substance

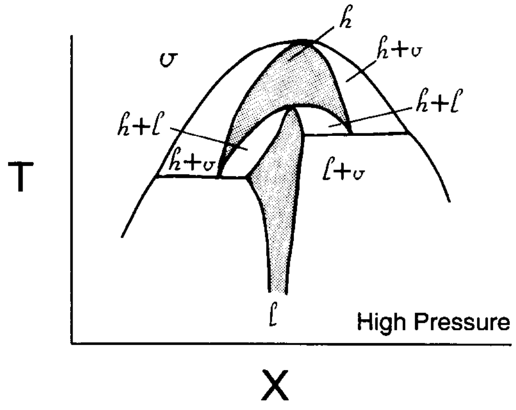

Fig. 3. Schematic temperature–composition phase diagram at high pressure in the vicinity of a triple pernt: a case with congruent condensed-phase transformation.

with a phase diagram such as either of these could have a congruent transformation of phase ℓ to phase k under the restriction that X be set exactly to the correct value. But the necessary X for congruent transformation would be different at every P.

The disproportionations, miscibility gaps, and variations in miscibilities shown in Figs. 1–3 are forced. The chemical potentials of the constituents of a phase are determined by chemical properties and by the independent variables X, T, and P. When two phases are at equilibrium, the chemical potential of each constituent must be the same in both phases. If the experimenter sets T, P, and the overall X, then the X of each of the two phases adjusts independently in order to keep all chemical potentials equal across the phase boundary; the features shown schematically in Figs. 1–3 occur as a result. Examination and extension of these principles reveal that similar variations must occur around any first-order phase transition. A wonderful illustration of the response of a chemical system to these forces is in the melting of CdTe as represented by Zanio [4] on the basis of work by Smith [5] and de Nobel [6]. With the permission of the publisher, the phase diagram of Cd–Te in the vicinity of the melting point of CdTe is reproduced in Fig. 4. Similar effects have been seen in

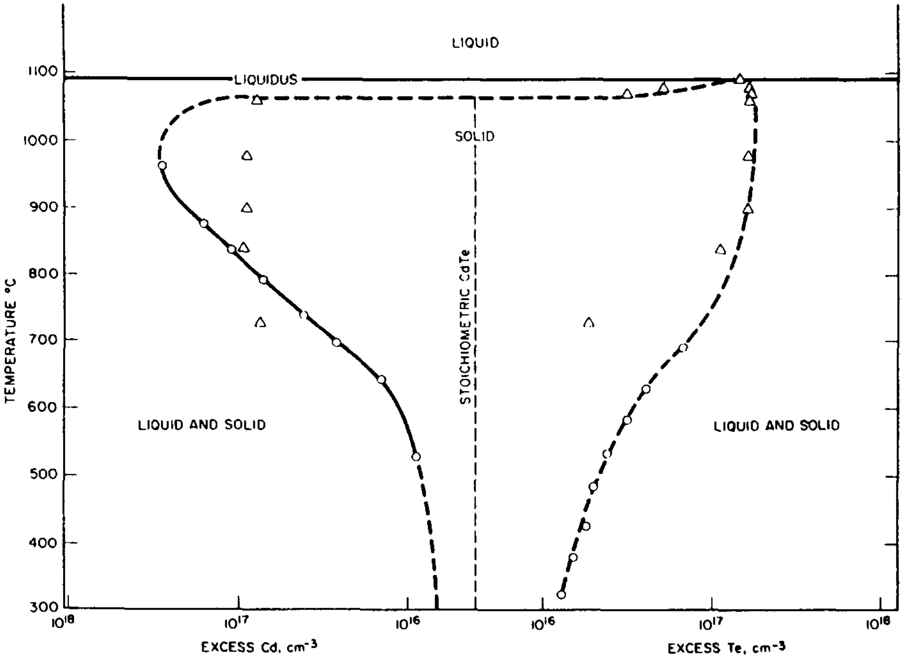

Fig. 4. Temperature–composition phase diagram on a logarithmic scale, showing the extent of the electrically active homogeneity region as interpreted through defect models. —— most reliable data; ○, Smith [5]; △, de Nobel [6].

other systems, for which the desire to grow pure crystals from the melt has inspired sufficiently careful work.

One sees from the phase diagrams in Figs. 1–3 that three phases are at equilibrium over some ranges of T, P, and X. The sizes of these ranges determine the size of the triple pernt. Prominent among the factors influencing the size of the triple pernt are the widths of the phases ℓ and k along the X axis at values of T and P well away from the phase transition, i.e. the variability of the chemical composition of the substance involved. In the case of the example above (water) the variability in X on the oxygen–hydrogen X axis is small and the size of the triple pernt is consequently small. The necessary stoichiometric variations of elements along the nucleus–electron X axis at phase transitions, too, are small, even for metals. The variations around the solid–liquid equilibrium of CdTe, though not directly measurable, have drastic effects on the melting point and on the electronic and optical properties.

Gallium sesquisulfide is an example of a substance with directly measurable stoichiometric variations around a large solid–liquid–vapor triple pernt. The chemistry of this substance around its triple pernt has been extensively studied [7–9], though the triple pernt has not been discussed previously.

The principal vapor species in equilibrium with condensed gallium sesquisulfide are $Ga_2S(g)$ and $S_2(g)$, and at equilibrium the substance vaporizes congruently [10]. In a closed system, the partial pressures of the two species would be nearly equal, as determined by the stoichiometry of the condensed phase, which varies by a small amount around the ideal $Ga_2S \cdot S_2$ [7]. An anomalous variation of the partial pressures of the two principal species was observed by Roberts and Searcy [7] during a study by Knudsen-effusion mass spectrometry. Their abstract states

> In a limited temperature range the partial pressure of gallium subsulfide (Ga_2S) above gallium sesquisulfide (Ga_2S_3) increases when the temperature is decreased. The anomaly in the partial pressure is caused by changes with temperature in the equilibrium compositions of two solid phases that coexist at 1228 ± 3 K. At this temperature the solids differ in sulfur content by 0.4 atomic percent sulfur.

The remarkable phenomenon discovered by Roberts and Searcy arose as a result of their observing a triple pernt; two condensed phases and the vapor were in the effusion cell. The reported difference in compositions of the condensed phases was due to the forced disproportionation at the triple pernt. The anomaly they reported arose because of an extraordinary interaction of the properties of the effusion cell with those of the effusing substance [9]. Specifically, the composition of a vapor at equilibrium with its condensed phase in an effusion cell is dependent on the relative molecular weights of the effusion vapor species and on the chemical and thermodynamic properties of the system. This imposed vapor composition restricts the number of thermodynamic states available to the system in the effusion cell. In the vicinity of the triple pernt, gallium sesquisulfide is unable to accomplish the required phase disproportionations while maintaining equilibrium vapor composition during effusion. Put simply, the equilibrium constant of the vaporization reaction cannot be obeyed as the system transforms from its high temperature form to its low temperature form in an effusion cell, and thus the system cannot follow an equilibrium path through the transformation.

Recently it has been shown that a similar anomaly occurs as the temperature of gallium sesquisulfide in an effusion cell is increased through the triple pernt [9]. Moreover, because the system is not at equilibrium, it is possible during the decreasing-temperature transformation to cause the total vapor pressure to increase with decreasing temperature and vice versa. There is some possibility that the high temperature form of gallium sesquisulfide observed by Roberts and Searcy was the liquid and not a solid [9].

Effects similar to those in gallium sesquisulfide have been observed in studies of gallium sesquiselenide [11, 12], indium sesquiselenide [13], and the manganese-monosulfide–gallium-sesquisulfide system [14]. Dieleman et al. [12], having studied effusion of gallium sesquiselenide, proposed a phase diagram including features like some in Fig. 3. Many substances undergo condensed-phase transitions in the range of effusion studies and hence exhibit the effects from triple pernts. Understanding the nature of the triple pernt and accounting for its possible effects is necessary in interpreting the results of many effusion studies.

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