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"THERMODYNAMICS OF A MAGMATIC GAS PHASE" 50 YEARS LATER: COMMENTS ON A PAPER BY JOHN VERHOOGEN (1949)

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ABSTRACT

In 1949 John Verhoogen published a paper entitled *Thermodynamics of a Magmatic Gas Phase* in The University of California Publications in the Geological Sciences. This paper documented the first sophisticated application of thermodynamics to a problem in igneous petrology. In that paper, Verhoogen examined many aspects of the behavior of a magmatic gas phase: development and composition of a gas phase, deposition from a gas phase, variation of vapor pressure over a cooling magma. He also discussed two other possible processes in magmas: distillation and crystallization of indifferent states. Distillation occurs when a constituent has a higher concentration in the vapor than in the melt. The volatile constituents of magmas, H_2O, CO_2, and H_2S, obviously fit the definition of constituents that undergo distillation. Verhoogen did not discuss the reverse process, partitioning of a constituent into the melt rather than the gas phase. HF is a constituent that undergoes reverse distillation; its concentration is higher in a melt than in a gas phase. Volatile constituents that undergo reverse distillation cause magmas to vesiculate at shallower depths than those that undergo distillation. Indifferent states occur during processes that change the masses of the phases of a system but leave their compositions unchanged. Univariant systems and azeotropes are familiar examples of indifferent states. At the time Verhoogen wrote his paper, there were limited amounts of experimental data on $NaAlSi_3O_8$–H_2O and not much else. Thermodynamic databases constructed in the last decade provide the tools needed to explore processes described by Verhoogen 50 years ago.

Keywords: thermodynamics, igneous petrology, magmatic gas phase, distillation, indifferent states.

SOMMAIRE

En 1949, Jean Verhoogen publia un article intitulé *Thermodynamics of a Magmatic Gas Phase* dans la revue The University of California Publications in the Geological Sciences. Dans cet article, il documenta la première application sophistiquée de l'approche thermodynamique à un problème en pétrologie ignée. Il examina plusieurs aspects du comportement d'une phase vapeur: développement et composition de la phase vapeur, précipitation à partir de celle-ci, variation en pression exercée par celle-ci en contact avec un magma au cours de son refroidissement. De plus, il discuta deux autres processus possibles dans un magma: distillation et cristallisation selon les états indifférents. La distillation a lieu dans les cas où un composant possède une concentration plus élevée dans la phase gazeuse que dans le bain fondu. Les composants volatils du magma, par exemple H_2O, CO_2, et H_2S, répondent clairement à la définition des composants sujets à une distillation. Verhoogen n'a pas traité du processus contraire, le partage d'un composant dans le bain fondu plutôt que dans la phase gazeuse, par exemple le composant HF, dont le comportement est en fait une distillation inverse: sa concentration est plus élevée dans le bain fondu que dans la phase gazeuse.

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Les composants volatils qui ont cette propriété provoquent une saturation du bain fondu en phase gazeuse à plus faible profondeur que dans les cas sujets à une distillation. Les états indifférents apparaissent où il y a changement des masses des phases d'un système sans changement en composition. Les systèmes univariants et ceux qui contiennent un azéotrope sont des exemples familiers d'états indifférents. A l'époque de Verhoogen, il y avait un peu d'information expérimentale à propos du système $NaAlSi_3O_8$–H_2O, et très peu sur les autres systèmes importants. Les banques de données thermodynamiques devenues disponibles au cours de la dernière décennie fournissent les outils nécessaires pour explorer à fond les processus décrits il y a cinquante ans par Verhoogen.

(Traduit par la Rédaction)

Mots-clés: thermodynamique, pétrologie ignée, phase gazeuse magmatique, distillation, états indifférents.

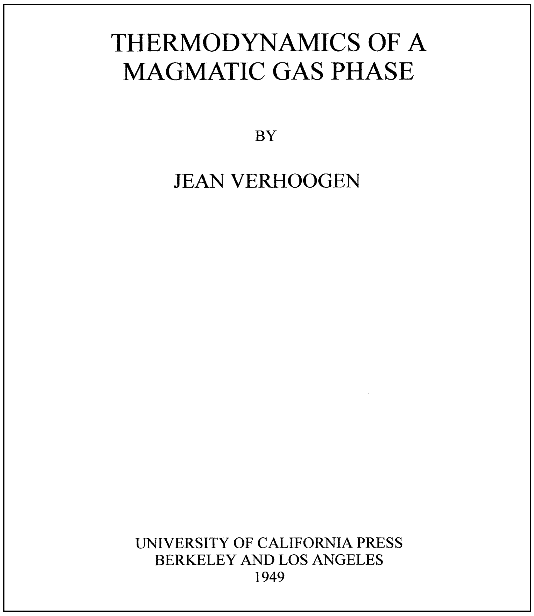
INTRODUCTION

In 1949, John Verhoogen published a paper entitled *Thermodynamics of a Magmatic Gas Phase* in *The University of California Publications in the Geological Sciences* (Fig. 1). The paper, 44 pages long, contained 90 numbered equations, more that were not numbered, and no figures. This paper was the first sophisticated application of thermodynamics to a problem in igneous petrology.

Verhoogen (Fig. 2) was born in Brussels, Belgium in 1912. He made major contributions to igneous and metamorphic petrology, to our understanding of continental drift and plate motion, to our understanding of the heat budget of the Earth, and to the study of rock magnetism. Verhoogen died in 1993.

As a graduate student at the University of Liège, Verhoogen learned thermodynamics from Professors Prigogine and Defay. These professors wrote a treatise, *Thermodynamique chimique conformément aux méthodes de Gibbs et de Donder*. D.H. Everett translated the 1950 edition into English (Prigogine & Defay 1954). Much of *Thermodynamics of a Magmatic Gas Phase* is based on the work of Prigogine & Defay, which Verhoogen acknowledged in his paper. Several of the ideas and concepts expressed by Verhoogen in *Thermodynamics of a Magmatic Gas Phase* are more completely developed by Prigogine & Defay (1954).

In *Thermodynamics of a Magmatic Gas Phase*, Verhoogen examined several aspects of the behavior of a magmatic gas phase. Table 1, which shows the table of contents of his paper, lists the topics he discussed. In this paper, I will look at a few topics introduced by



THERMODYNAMICS OF A
MAGMATIC GAS PHASE

BY

JEAN VERHOOGEN

UNIVERSITY OF CALIFORNIA PRESS
BERKELEY AND LOS ANGELES
1949

FIG. 1. Facsimile of the cover page of Verhoogen's 1949 paper.

FIG. 2. John Verhoogen in 1958 as the recipient of the Arthur L. Day Medal from the Geological Society of America.

TABLE 1. TABLE OF CONTENTS FOR
Thermodynamics of a Magmatic Gas Phase
(Verhoogen 1949)

Verhoogen into igneous petrology. Some have been studied thoroughly, whereas some have been ignored.

To describe gas phase phenomena, calculations were made with a modified version of the thermodynamic database constructed by Ghiorso & Sack (1995), a solubility model for CO_2 in a silicate melt developed by Papale (1999), and some speculations on the behavior of volatile substances in silicate melts on my part.

FUNDAMENTAL RELATIONS

The first section of *Thermodynamics of a Magmatic Gas Phase* provides a complete coverage of the fundamental relations of thermodynamics. In eight pages, Verhoogen developed the relationships between Gibbs energy and chemical potentials, entropy, and volume. Partial molar quantities are defined, and their place in thermodynamic theory explained. Finally, he derived versions of the Gibbs phase rule and Duhem's theorem.

Definition of equilibrium

There is really nothing new in fundamental relations in classical thermodynamics since Gibbs. However, petrologists have become more precise about the relationship between thermodynamic calculations and real processes. Anderson (1996) and Greenwood (1989), in particular, have emphasized that thermodynamics provides a model to compare with reality. I would like to extend this idea to the concept of equilibrium. I suggest that the concept of equilibrium belongs to the thermodynamic model rather than to reality.

Thermodynamic systems can be described in two different ways. There is, first, the real collection of atoms, molecules, phases, and energy that constitutes the real world. Then there is the mathematical structure that represents the real world. The literature contains several definitions of equilibrium in thermodynamic systems. Some definitions are phrased in terms of the behavior of the real collection. Other definitions are mathematical statements. Prigogine & Defay (1954, p. 69, Eq. 6.23) use the value of a linear combination of chemical potentials to describe the equilibrium condition:

$$\sum_i \nu_i \mu_i = 0 \tag{1}$$

where ν_i is a stoichiometric coefficient and μ_i is the chemical potential of the chemical entity i. Verhoogen (1949, Eq. I.14) also described this criterion as the equilibrium criterion. Equation (1) represents the equilibrium for a chemical transformation that can be symbolized:

$$\sum_i \nu_i x_i = 0 \tag{2}$$

where x_i is a chemical formula, and Equation (2) represents a balanced chemical transformation. This criterion for equilibrium will hereafter be called the First Statement.

Denbigh (1981) described thermal equilibrium with his zeroth law: ".... if bodies A and B are each in thermal equilibrium with a third body, they are also in thermal equilibrium with each other." In other words, bodies in equilibrium, at least bodies in thermal equilibrium, have the same temperature. Later in his text, Denbigh (1981, p. 263) stated that equality of chemical potentials for a component is the only proper criterion for equilibrium with respect to diffusion. This is the same statement as that of Verhoogen (1949). The criterion is a particular application of the first statement.

Nordstrom & Munoz (1985) stated that equilibrium occurs when the equality holds in the Clausius equation:

$$dQ - TdS \geq 0 \tag{3}$$

where Q is the heat gained by the system, T is the temperature in Kelvin, and S is entropy. Equality holds for reversible processes.

Anderson & Crerar (1993) defined equilibrium with two statements: 1) "A system at equilibrium has none of its properties changing with time, no matter how long it is observed." 2) "A system at equilibrium will return to that state after being disturbed, that is, after having one or more of its parameters slightly changed, [they will] then change back to the original values." Other statements of equilibrium postulate a minimum for thermodynamic potentials that depend on a particular set of variables. For example, equilibrium obtains if the Gibbs energy for a system is a minimum at some fixed values of pressure and temperature.

All of these statements are correct in that, if the criteria hold, then the system is at equilibrium. However, except for the definition used by Prigogine & Defay (1954) and Verhoogen (1949), the statements are sufficient rather than necessary criteria for equilibrium in chemical systems. In some systems, the other statements will be incorrect, whereas the statement by Prigogine & Defay (1954) and Verhoogen (1949) (the First Statement) will still be correct. If the other statements obtain, then so does the First Statement. The converse is not true. The First Statement can obtain although one or more of the others do not obtain. Appendix A contains counter examples of the sufficient statements.

In summary, the sufficient statements are:

1. Equilibrium systems do not change, no matter how long they are observed.
2. At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction.
3. When infinitesimally perturbed, equilibrium systems return to their original equilibrium state.
4. A minimum in the value of a thermodynamic potential occurs at equilibrium.
5. Equilibrium systems are at constant temperature.

Usually, the systems that contain one phase are not described with chemical potentials. Consequently, the First Statement is not often applied to such systems. The first statement applies, however, even in the trivial case of one phase. Suppose two grains of kyanite, *a* and *b*. Then,

$$\mu^{a}{}_{Al_2SiO_5} - \mu^{b}{}_{Al_2SiO_5} = 0 \qquad (4)$$

To quote Verhoogen (1949, p. 94) "At equilibrium, the chemical potential of all constituents must be the same in all phases."

Representations of equilibrium by linear combinations of chemical potentials equal to zero do, in fact, provide convenient methods for defining equilibrium systems. Equilibrium systems are those parts of reality that can be adequately and appropriately represented by such linear combinations. The non-equilibrium parts must be represented by linear combinations of chemical potentials different from zero. Describing systems in terms of equality and inequality constraints puts the initial focus on whether or not that part of reality can be described in terms of equilibrium thermodynamics or whether the description must be a dynamic one. The causes for the differences can then be interpreted in terms of geometrical walls, membranes and barriers to the transfer of matter and energy.

Although many equilibrium thermodynamic systems cannot be realized in nature, they often provide adequate representations of reality. If even part of a natural system can be adequately approximated by an equilibrium system, then significant simplification over a dynamic model usually follows. Consequently, a precise definition of equilibrium leads to precise descriptions of representations of reality and a better understanding of processes that affect chemical systems.

Equilibrium systems are in many cases equated with parts of reality characterized by reversible reactions or changes. Although systems containing reversible processes are systems at equilibrium, the converse need not be true. Some systems containing irreversible processes can be analyzed and described with equilibrium statements. One such set of systems is the set that contains isenthalpic changes. Examples include expansion of gases into a vacuum (the Joule–Thompson effect; see Lewis & Randall 1961, p. 48), adiabatic decompression during uplift (Waldbaum 1971), and rapid ascent of nephelinites (Nicholls 1990, Trupia & Nicholls 1996). Such systems should be distinguished from systems described by what are called irreversible thermodynamics (*e.g.*, the Soret effect).

Duhem's Theorem

Verhoogen (1949, p. 98) introduced this remarkable theorem to petrology. Duhem's Theorem is another phase rule. The familiar Gibbs Phase Rule is:

$$F_G = c - \phi + 2$$

where F_G is usually called the degrees of freedom of the thermodynamic model, c is the number of components, and ϕ is the number of phases in the model. Degrees of freedom often cause confusion. Actually, the degrees of freedom express the number of variables one must fix or set before all the other variables describing the model can be calculated. The remarkable feature of Duhem's Theorem is that the degrees of freedom are 2 if the composition of the thermodynamic model is known. This means that one can often specify temperature and pressure and then calculate all other properties of the model, including phase compositions and relative abundances of those phases. Thermodynamic models thus have a large number of independent properties that can be compared with nature. If the calculated properties of the model adequately describe the properties of the real system, one gains insight into processes of rock formation.

Both Verhoogen (1949) and Prigogine & Defay (1954) derived Duhem's Theorem in terms of masses of the components forming a system. Their derivations had the unfortunate result of preventing the significance of Duhem's Theorem from being appreciated. Finding or knowing the masses of components composing a rock body, for example, can be fraught with difficulty. Consequently, petrologists looked to the Gibbs Phase Rule for insight because it invokes only intensive variables, such as concentrations; extensive variables, such as masses of the components, need not be considered. The requirement that the masses of the components be known is too stringent. The weaker requirement that the composition of the system be known is sufficient. Whether the system is the size of a batholith or a laboratory crucible, if the system is at equilibrium, then the properties of the phases are independent of size. The size of the system can be arbitrarily set and all the properties calculated except the two that are required by Duhem's Theorem (Nicholls 1990).

As an example of the guidance Duhem's Theorem can give, consider the problem of calculating the saturation conditions of a phase in a melt. Duhem's Theorem states that one need fix only two variables to calculate the state of the model system if the composition of the system is known. The state of the system is known when the temperature, pressure, compositions of all the phases, and the relative amounts of all the phases are known. One variable to fix is the pressure. The saturation state at a fixed pressure can then be calculated. However, temperature cannot be arbitrarily fixed because an arbitrary temperature may not be on the saturation surface at a fixed pressure. Consequently, the temperature must be a calculated quantity. Also, the composition of the saturating phase must be a calculated quantity because, again, an arbitrary composition may not be the composition of the saturating phase at a fixed pressure. Constraining the system to a saturation state implicitly fixes the amount of the saturating phase at

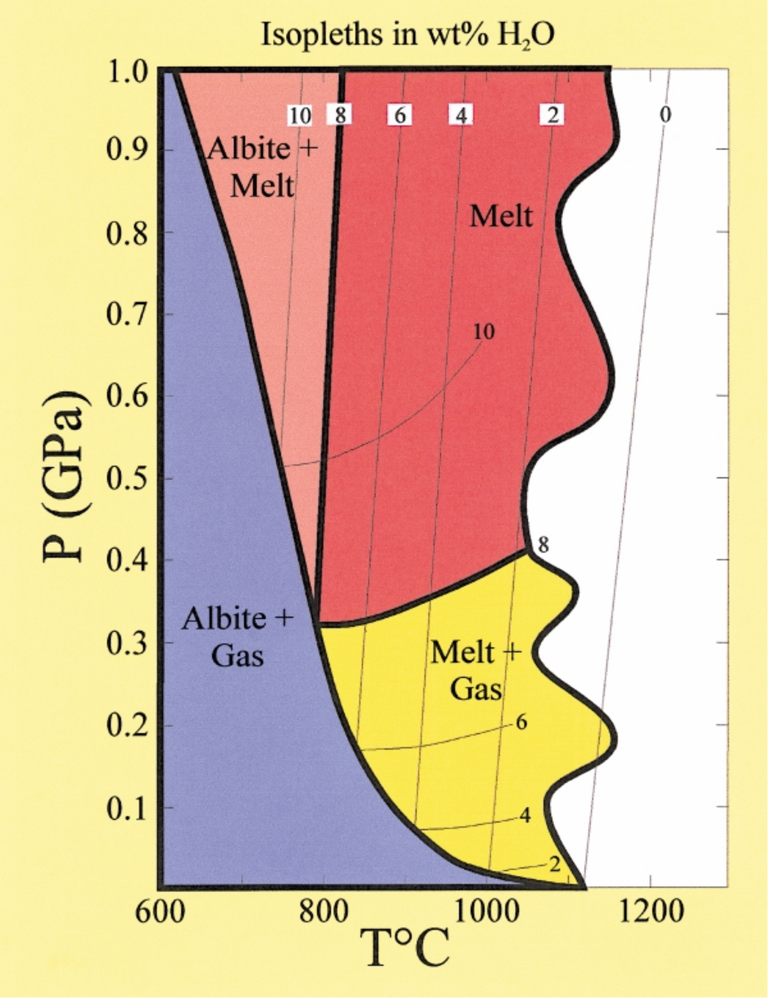


FIG. 3. P–T diagram for the system $NaAlSi_3O_8$–H_2O, which serves as a model for a magmatic system that can coexist with a gas phase.

zero, which fixes the second variable required by Duhem's Theorem. The melt is forced to have the same composition as the system, which is a composition that is known by hypothesis. A solution composed of n components has $n - 1$ independent compositional variables because the mole fractions sum to one. For each of the n components, one can write a form of the First Statement. This procedure provides a system of n equations, which can be solved for the $n - 1$ independent compositional variables and the saturation temperature. In summary, Duhem's Theorem guarantees that no matter what the chemical complexity of the solid solution or the melt, one can calculate the composition of the saturating phase and the temperature of saturation at a fixed pressure.

DEVELOPMENT OF A GAS PHASE

The system $NaAlSi_3O_8$–H_2O as a model

Several petrologists have used the system $NaAlSi_3O_8$–H_2O as a model system for the generation of a magmatic gas phase (Goranson 1938, Burnham 1974, Nicholls 1980). A calculated P–T diagram is shown on Figure 3. At a fixed H_2O concentration, the diagram can be divided into four areas: melt (red), melt plus gas phase (yellow), melt plus solid (tan), and solid plus gas phase (blue). The nearly vertical lines, labeled with wt% H_2O contents in the melt, are the coordinates where solid albite crystallizes from a melt containing dissolved H_2O. The heavy line labeled 8 separating the red and tan regions is the liquidus curve for an H_2O-undersaturated melt that is in equilibrium with albite. The line separating the P–T region of melt (red) from melt plus gas phase (yellow) marks the P–T coordinates of vesiculation in the model system on release of pressure. The solidus, the line separating the blue region from the others, where melt, gas, and solid coexist, appears as a line in a P–T section, but is an area in a T–X section. This univariant line represents a set of indifferent states, a topic for later discussion.

If a melt is originally at a temperature greater than the solid–melt isopleth, then on cooling, albite will crystallize when the P–T coordinates coincide with the solid–melt isopleth. If the magma cools at constant pressure, the H_2O concentration in the melt will increase, and the concentration of albite (condensed component) will decrease. For P–T coordinates on the univariant, three-phase curve, gas, melt, and solid coexist. As the temperature or pressure drops, the amount of gas and solid will increase at the expense of melt. The P–T coordinates remain on the univariant curve until all the melt has crystallized and evaporated. At any instant, a magma will contain a fixed amount of volatile species dissolved in the melt.

In order for a gas phase to form, pressure–temperature conditions will have to coincide with the appropriate vesiculation isopleth (Fig. 3). As the P–T conditions drop below the isopleth, the melt loses H_2O to the gas phase, and the concentration of H_2O in the melt decreases. If the pressure drops a small amount, then the amount of gas phase will be small. In order to produce a large amount of gas from an undersaturated magma, the pressure drop must be large. Most large plinian eruptions, such as occurred at Mount St. Helens, probably are initiated by a large change in pressure. The Mount St. Helens eruption is considered to have resulted from the pressure release caused by the landslide that immediately preceded the eruption. Volcanic activity at Mount St. Helens was the subject of Verhoogen's Ph.D. thesis at Stanford University, which was later published in *The University of California Publications in the Geological Sciences* (Verhoogen 1937).

The isopleths carry into multivariate systems. The liquidus and vesiculation curves, in particular, have analogues in multicomponent systems. The positions of the liquidus and vesiculation curves depend on the concentrations of the condensed components and the concentrations of the volatile components. The latter can have a significant effect on the location of the vesiculation curves. If the vesiculation curves are displaced to lower pressures, then magmas must move up in the Earth (or other planets) to form a gas phase. If the vesiculation curves are displaced to higher pressures, then a gas phase will separate at greater depths. The saturation or vapor pressure of a gas phase depends, among other factors, on the volatile species dissolved in a magma. Some volatile species will displace the vesiculation curves to higher pressures, and others species will displace them to lower pressures. CO_2 and HF are examples that cause the contrasting effects relative to the H_2O vesiculation curve (Fig. 4).

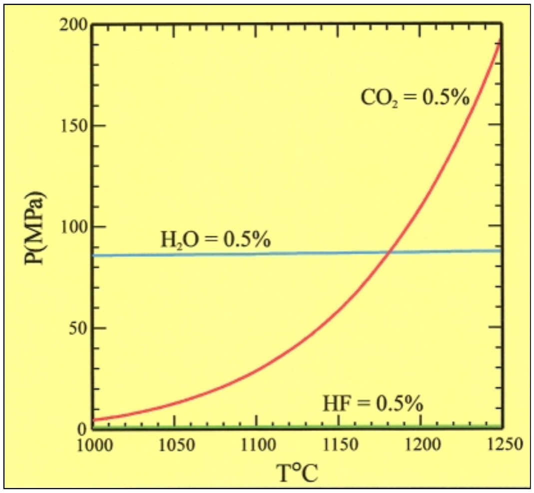


FIG. 4. P–T diagram showing the vesiculation curves for 0.5 wt% volatile species dissolved in a melt with the composition of an alkali olivine basalt from Hawai'i.

In the section on Development and Composition of a Gas Phase, Verhoogen (1949) provided general relations between the thermodynamic properties of the melt and gas phases. He pointed out that the properties of the pure components are not reliable indicators of the properties of the components in the melt or gas phase solutions.

DISTILLATION

Verhoogen (1949) defined distillation from a magmatic gas phase as a process that occurs when the concentration of a constituent increases in the gas phase and decreases in the silicate melt. H_2O and CO_2 will undergo distillation where both are dissolved in the melt. Rhyolitic melts in hydrothermal experiments show disproportionately larger amounts of vesiculation if CO_2 is added to melts saturated with H_2O (Ian Carmichael, pers. commun.).

The opposite effect, increasing concentration in the melt and decreasing concentration in the gas phase, can also occur. Most constituents display this behavior (*e.g.* SiO_2, TiO_2, *etc.*). One unexpected constituent that undergoes reverse distillation is HF. Appendix B contains the details of the calculation.

Figure 4 shows the vesiculation pressures of an HF-bearing melt with the composition of an alkali olivine basalt from Hawai'i. An HF-bearing melt will vesiculate at pressures approximately one-tenth the pressures of vesiculation of the equivalent H_2O-bearing melt. HF increases the solubility of H_2O in silicate melts and raises the saturation temperatures of (OH, F)-bearing solids. This latter effect is shown for apatite on Figure 5.

Zoning of apatite is a consequence of the partitioning of HF into the melt and its retention by the melt during crystallization. Fluorapatite typically is brown, whereas hydroxyapatite is clear (Fig. 6A). Apatite microphenocrysts in intermediate to felsic volcanic rocks commonly have a clear center and a brown rim that results from the increasing HF concentration brought about by fractional crystallization.

Even a small concentration of HF can affect the eruption of intermediate to felsic rocks. The Craters of the Moon lava field, in Idaho, comprises minor basalt and larger numbers of intermediate and felsic lava flows of trachybasalt, tristanite, and trachyte (Stout *et al*. 1994). The rocks have SiO_2 concentrations as high as 63% and feldspar contents as high as 80% by volume (Stout *et al*. 1994, Fig. 6). Melts with these concentrations should have viscosities similar to those of rhyolitic melts, yet the morphology of the flows suggests a viscosity similar to that of basaltic melts (Fig. 7). For example, basalts with a SiO_2 content near 45% and a liquidus temperature near 1250°C have a viscosity of approximately 3×10^2 Pa s (Shaw 1972). Rhyolites with a SiO_2 content near 65% have a viscosity near 3×10^6 Pa s at their liquidus temperatures (1050°C). Trachytes from the Craters of the Moon, Idaho, with a SiO_2 content near 63%, should have a viscosity near 5×10^6 Pas at their liquidus temperature (1050°C).

INDIFFERENT STATES

In part V of his 1949 paper, Closed Systems, Verhoogen introduced the concept of indifferent states to petrology. A chemical system is in an indifferent state if the concentrations of the phases in the system change but the compositions of the phases do not. Examples of systems in an indifferent state include systems with two or more polymorphs. Two polymorphs coexist along a univariant line. In crossing from one side of the line to the other, the relative proportion of the two phases changes but, being polymorphs, their compositions do not change. In the writings on indifferent states, pressure and temperature have been considered constants. In this example, they do not have to be constant. However, in the general case, pressure and temperature have to be constrained to constant values to satisfy the definition of an indifferent state. An example is provided by a system with two solid solutions, a pure solid, and a melt. There is one degree of freedom under the Gibbs Phase Rule, and the compositions of the solids change along the univariant curve. Another common example of a system with an indifferent state is one with an azeotrope (Fig. 8). Azeotropes can occur at minimum or maximum temperatures at constant pressure. Like univariant curves with solutions, an azeotrope is in an indifferent state if the pressure and temperature are constant because the composition of the azeotrope changes with pressure and temperature (*e.g.*, Denbigh 1981, p. 221).

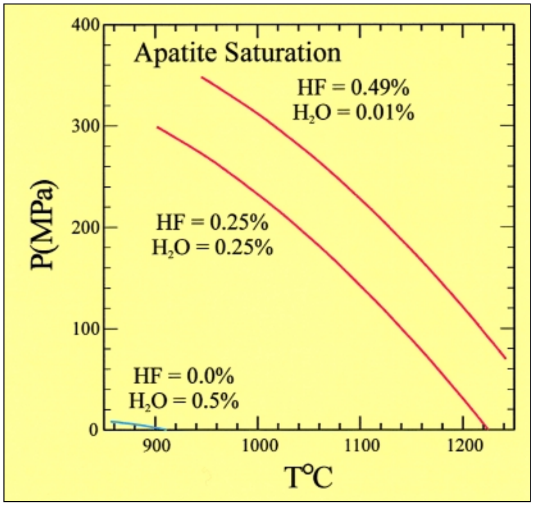


FIG. 5. P–T diagram for apatite saturation as a function of H_2O and HF concentration in a melt with the composition of an alkali olivine basalt from Hawai'i.

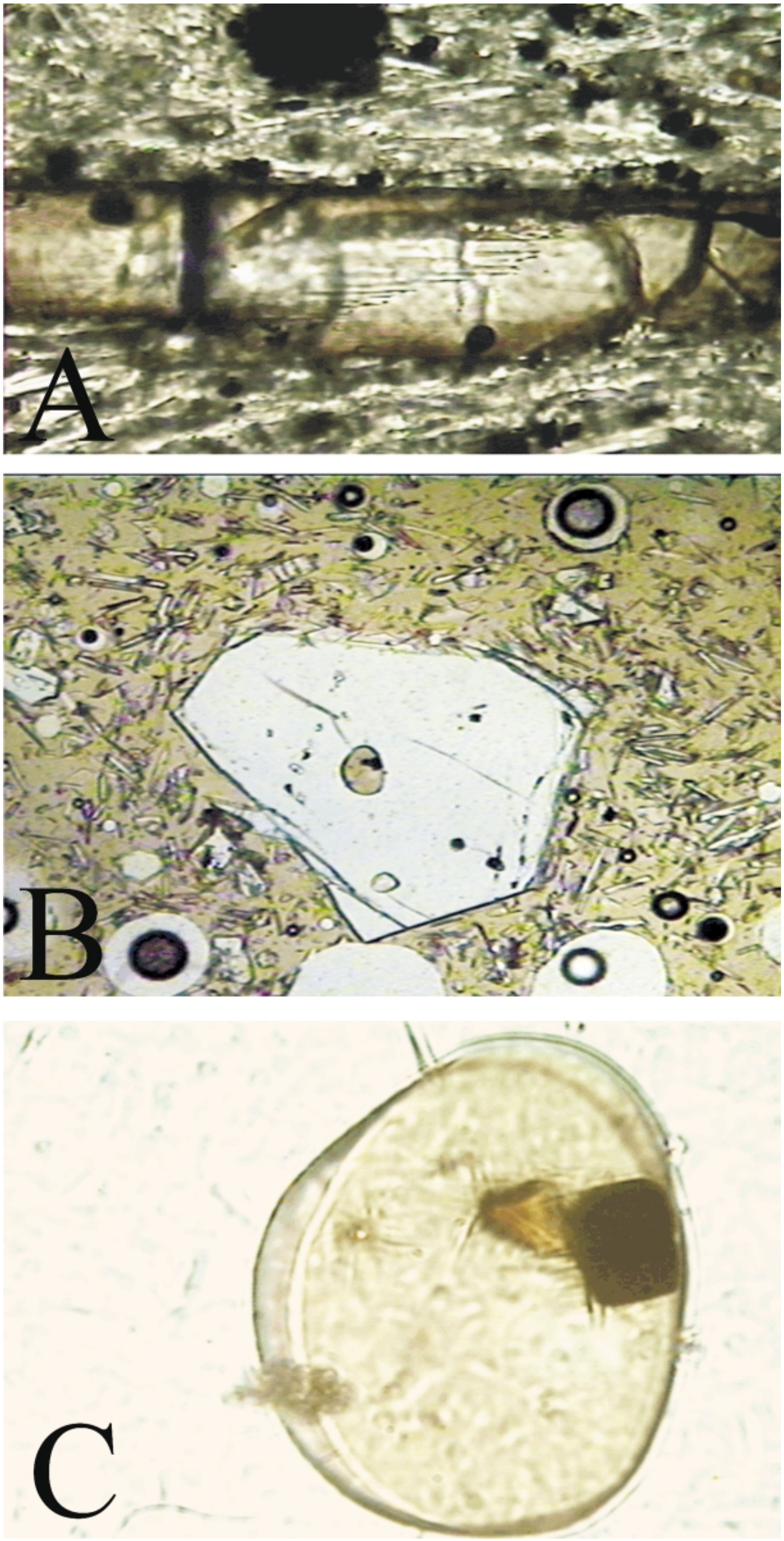


FIG. 6. A. Photomicrograph of an apatite microphenocryst in a hawaiite from Kohala volcano, Hawai’i. B. Olivine phenocryst in glassy picrite (oceanite) from Kīlauea volcano, Hawai’i. C. Glass inclusion from olivine phenocryst in Figure 6B. Spinel (black) and augite (?) inclusions in the glass.

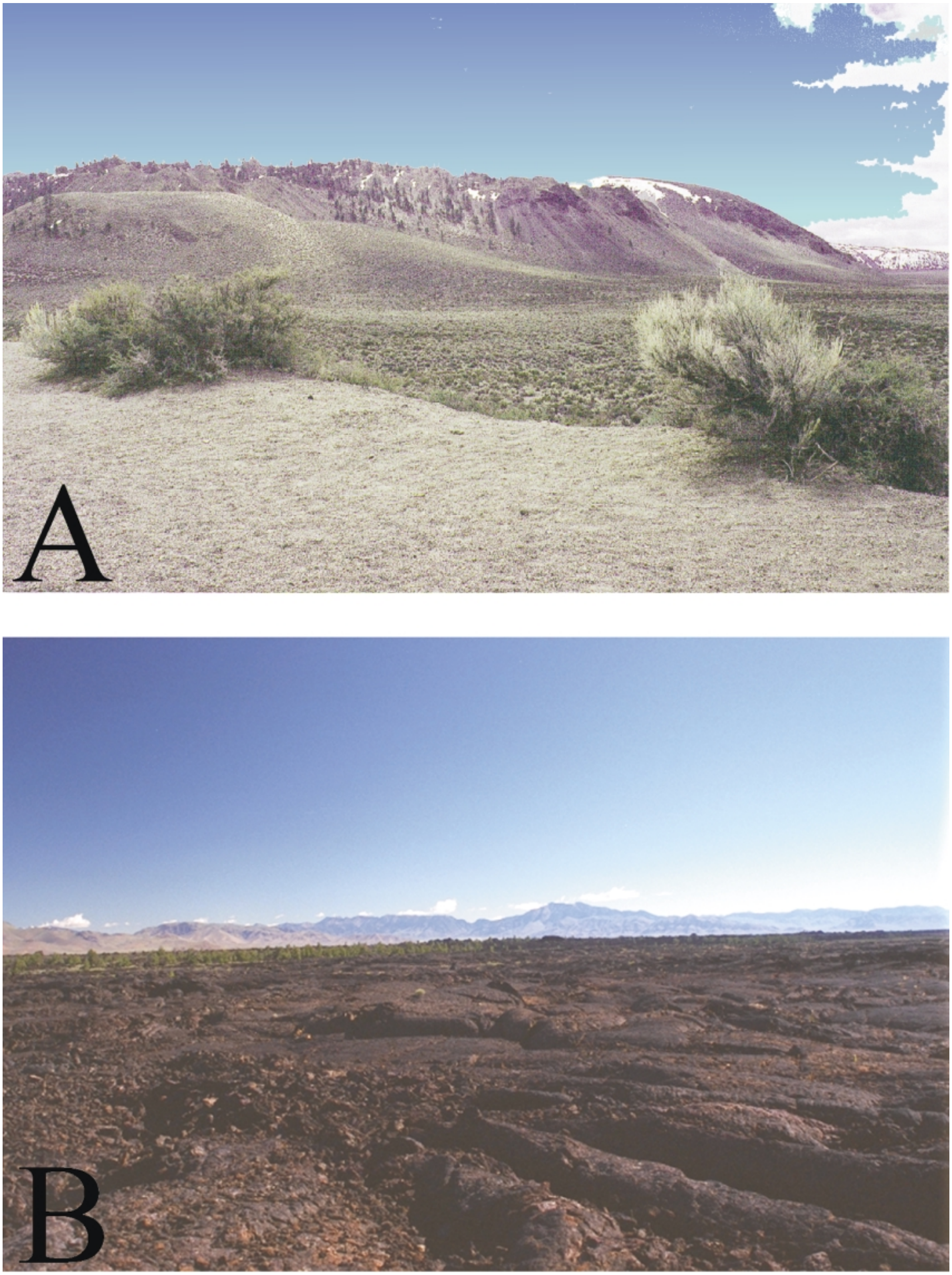


FIG. 7. View of contrasting morphology of flows in rhyolite domes (Mono Craters, California) and trachybasalt flows (Craters of the Moon, Idaho).

The concept of general conditions for indifferent states in petrological systems has not been explored since Verhoogen (1949). Although typical indifferent states occur in simple systems (Fig. 8), I do not know whether analogous features occur in complex systems. I also do not know whether processes of melting and crystallization will bring the system to a maximum or minimum in temperature (Fig. 8). Consequently, what follows is speculation on my part.

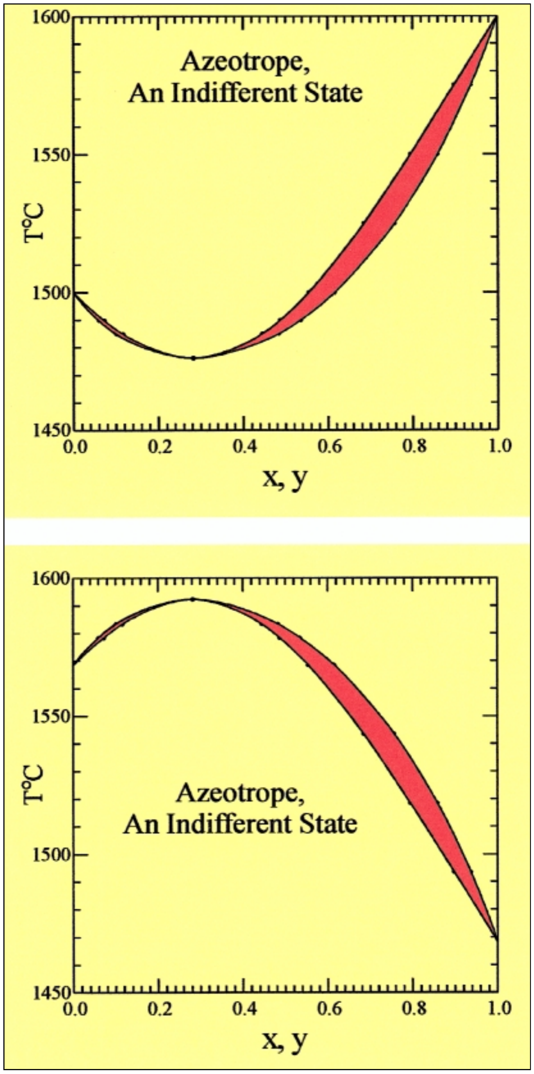


FIG. 8. Binary systems with azeotropes. A system with the composition of the azeotrope is in an indifferent state at the pressure and temperature of the azeotrope. A system in an indifferent state can change from completely melted to all solid without changing pressure and temperature. The azeotrope temperature can be either a maximum or a minimum at constant pressure. Maximum temperatures are rare in chemical systems relevant to the formation of rock-forming minerals.

Indifferent states may be significant in partial melting of mantles of rocky planets. The primary melts supplied to Kīlauea volcano, Hawai'i are, at least in some instances, picritic (Nicholls & Stout 1988, Wright 1971). Within the glassy picrites that were erupted from Kīlauea volcano in 1968 are olivine phenocrysts with glass inclusions (Fig. 6B). Included within the glass inclusions are inclusions of spinel and augite (?) (Fig. 6C). On a plot of (Fe + Mg)/K *versus* Si/K, the rock compositions define a fractionation path controlled by olivine from picrite to olivine tholeiite (Fig. 9). Joining the fractionation path controlled by olivine is a fractionation path controlled by olivine, plagioclase, and augite from olivine tholeiite to tholeiite (Fig. 9). Data points representing the compositions of the glass included in olivine fall below the extension of the olivine – plagioclase – augite fractionation path (dashed line, Fig. 9). After being trapped, the glass (melt) inclusion was affected by plating of olivine on the wall of the inclusion and by crystallization of the minerals in the inclusion. Consequently, the closest point on the fractionation path where the inclusion could have been trapped is directly above the data point. For the extreme glass composition, the melt at the time of trapping contain approximately 18% MgO. This is a minimum estimate, and the primary melt may have had a higher concentration of Mg. One can calculate a composition from a mixture of olivine, orthopyroxene, and clinopyroxene that has the same composition as a picrite with 18% MgO. If spinel is included in the assemblage, the MgO concentration must be near 22%. Consequently, the mass-balance criterion for an indifferent state in the source region beneath Hawai'i is satisfied. Whether the temperature and pressure at which this indifferent state could exist is a subject for future research, as is whether the actual mantle composition is close to the requirement for an indifferent state.

If an indifferent state exists in the upper mantle, it could play a part in the formation of large igneous provinces. Large igneous provinces are massive emplacements of mafic extrusive and intrusive rocks in the crust. Examples are the Columbia River basalts, the Kerguelen Plateau, and the Deccan Traps (Coffin & Eldholm 1994). One of the largest is the approximately 120 Ma Ontong–Java province. The volume of magma extruded to form this province was $55 \pm 20 \times 10^6$ km^3 (Coffin & Eldholm 1994). This volume is equivalent to a sphere with a diameter between 405 and 470 km. If the magmas of the Ontong–Java province formed by partial melting of the mantle, then a large part of the low-velocity zone must have been affected. If the primary melts were basaltic, then they would have formed by small amounts of partial melting, and the volume of low-velocity zone affected would be large. At larger amounts of partial melting, a smaller volume would be affected, but the primary melts would be picritic or approach a

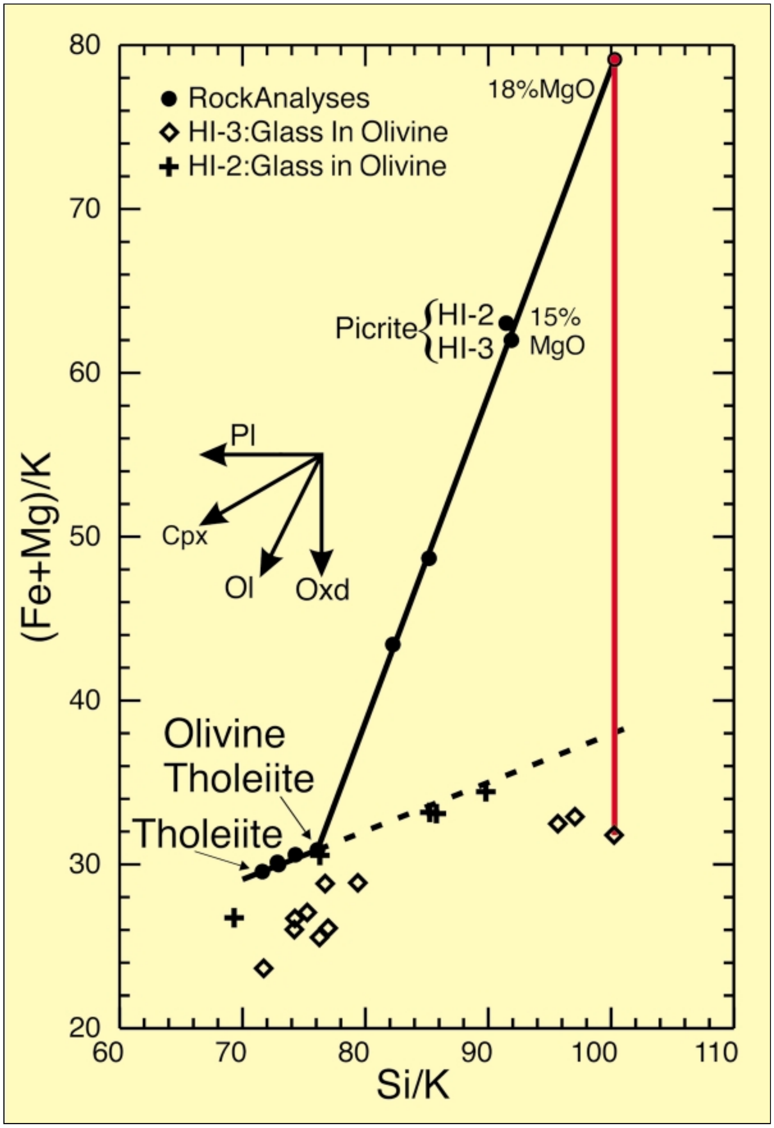


FIG. 9. (Fe + Mg)/K *versus* Si/K plot depicting the formation of basaltic melts from picritic melts by fractionation of olivine at Kilauea Volcano, Hawaii. The compositions of the glass inclusions are consistent with melts with a minimum of 18% MgO being precursors to the melts that erupted at the surface with 15% MgO.

picritic composition, and these would have to fractionate to a basaltic composition before eruption. If the source region for the Ontong–Java magmas was in an indifferent state, the melting would be 100%, and the volume affected by the melting process would be minimal. I would like to stress, again, that the idea of an indifferent state in the mantle is complete speculation.

An indifferent state may also play a role in the formation of amphibolites in a regional metamorphic terrane. Basaltic melts can crystallize directly to amphiboles. Nephelinites from Volcano Mountain, Yukon Territory, have chemical characteristics that suggest they formed from an amphibole source-rock (Francis & Ludden 1995) or from source rocks that isochemically recrys-

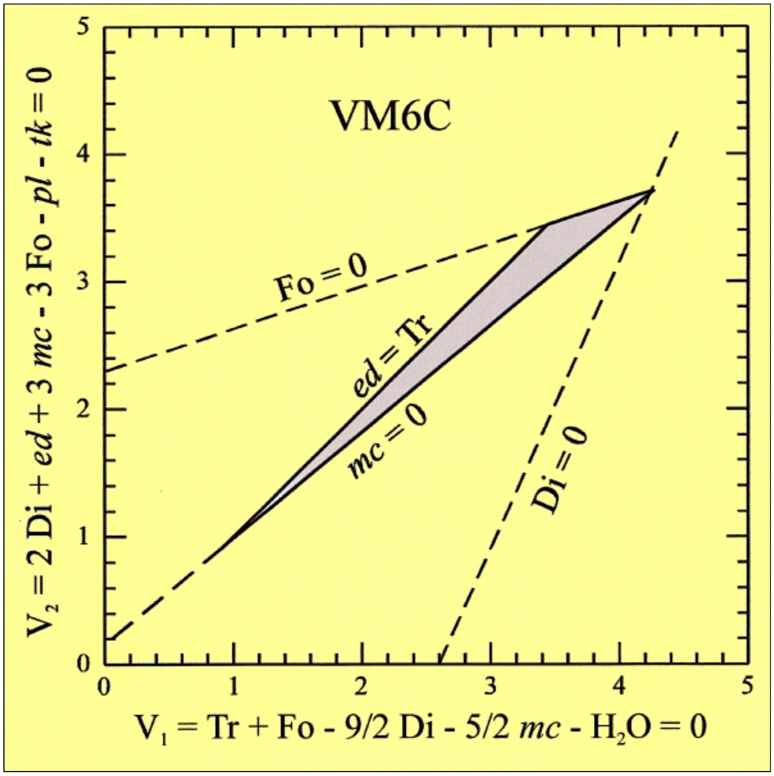


FIG. 10. A Thompson space diagram (Thompson 1982a, b, Nicholls *et al.* 1991) for a nephelinite from Volcano Mountain, Yukon Territory. The rock composition can be recalculated as mixtures of olivine, clinopyroxene, and amphibole that fall in the gray area. The point where lines representing Di = 0, Fo = 0, and *mc* = 0 meet has the coordinates in Thompson space where the rock composition can be recast as an amphibole.

tallized from amphibole-rich assemblages. That these nephelinites could exist as pure amphibole is illustrated on Figure 10. In addition, there is experimental evidence that basaltic melts can crystallize as amphibole. Yoder & Tilley (1962, p. 442) reported an experimental run on a high-aluminum basalt at 1150°C and 0.5 GPa H_2O pressure that quenched to rare magnetite and amphibole. Consequently, there is both analytical and experimental evidence that basaltic melts with the compositions of amphiboles exist and that they can crystallize to amphiboles at pressures expected in the crust.

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APPENDIX A. COUNTER EXAMPLES TO THE OTHER DEFINITIONS OF EQUILIBRIUM

Equilibrium systems do not change, no matter how long they are observed

As a counter example to this definition of equilibrium, consider a glass of water and ice in an environment at room temperature. The temperature in the glass is 0°C. In fact, the glass contains an assemblage of phases that defines a point on the thermodynamic temperature scale. Yet, obviously the system is changing with time as the ice melts. Purists will protest that the temperature is not really 0°C, but slightly greater than that. However, as a representation of reality, the mathematical representation of reality is adequate. A temperature scale based on phase assemblages out of equilibrium would be inconvenient at best and unusable normally. Consequently, for the practical purpose of the temperature scale, a mixture of ice and water is an equilibrium system, and the appropriate and adequate expression is:

$$\mu^{\mathrm{Ice}}{}_{\mathrm{H_2O}} - \mu^{\mathrm{Water}}{}_{\mathrm{H_2O}} = 0 \qquad (5)$$

an example of the First Statement.

At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction

Again, the mixture of ice and water example provides a counter example. The rate of melting is faster then freezing, yet, as shown above, the system can be represented as an equilibrium system.

When infinitesimally perturbed, equilibrium systems return to their original equilibrium state

Consider a large volume of water and ice into which a drop of hot water is added. The temperature quickly returns to 0°C, but the small amount of ice that melted to cool the drop does not freeze again. Unless the equilibrium state is defined by temperature alone, then the system of ice and water does not return to its original state when infinitesimally perturbed.

A *minimum in the value of a thermodynamic potential occurs at equilibrium*

A counter example to this condition is more difficult to contrive than the others. Consider a solid solution that can have a varying degree of order, for example, an ilmenite–hematite solid solution. Ghiorso (1990) derived an expression for the chemical potential of the hematite component:

$$\mu_{Hm} = \overline{G} - y\left(\partial\overline{G}\big/\partial y\right)_s - s\left(\partial\overline{G}\big/\partial s\right)_y \qquad (6)$$

where y is the mole fraction of Fe_2O_3 in solid solution, and s describes the degree of order of Fe and Ti on the metal sites of the structure. Disordered $FeTiO_3$ is characterized by s equal to zero, whereas fully ordered $FeTiO_3$ has a value of s equal to one. $\overline{G}$ is the Gibbs potential for the solution. In general, s is evaluated by setting the partial derivative of $\overline{G}$ with respect to s equal to zero (see, for example, Sack 1980). This exercise is equivalent to minimizing the Gibbs potential for the solid solution with respect to diffusion. However, it may happen that a solid solution encounters an environment where it will react with another phase under conditions where rates of internal diffusion in the solid solution are too slow to alter the state of order (*e.g.*, Liang 2000). Under such conditions, the chemical potential of Fe_2O_3 still exists (Eq. 6) and could be used to describe an equilibrium change in a geochemical system with an expression of the form of Equation (1). In such a system, the Gibbs potential for the system will not be a minimum because the Gibbs potential for the solid solution will not be a minimum.

Equilibrium systems are at constant temperature

A counter example to this statement can be visualized by recourse to that magical construct, an adiabatic semipermeable membrane. Suppose a solution on one side of the wall and a vapor consisting of the pure solvent on the other. The wall is assumed permeable to the solvent but impermeable to the solute. As an example, suppose that the solvent is water and the solution is ideal. The chemical potential of H_2O in the solution is:

$$\mu^{\mathrm{Water}}{}_{\mathrm{H_2O}} = -68317 - 16.712T_W + RT_W \ln x. \qquad (7)$$

R is the gas constant, and T_W is the temperature of the solution. The chemical potential of H_2O as steam, assuming ideal gas behavior, is:

$$\mu^{\mathrm{Steam}}{}_{\mathrm{H_2O}} = -5795 - 45.11T_S + RT_S \ln p. \qquad (8)$$

T_S is the temperature of the vapor. If the chemical potentials in Equations (7) and (8) are set equal, an equation in four unknowns results, T_W, T_S, x, and p. It remains to show that the equation can be satisfied by values of the unknowns that are physically realizable:

$$\begin{aligned} &0 < T_W < \infty \\ &T_W < T_S < \infty \\ &0 < p < \infty \\ &0 < x < 1 \end{aligned} \qquad (9)$$

Figure A1 shows a diagram drawn for a set of parameters that satisfy Equations (7) and (8), and the inequalities in (9).

In Part V of his paper, Verhoogen discussed the possible role of osmotic pressure in igneous processes. Goranson (1937) discussed the osmotic pressure in volcanic processes using $NaAlSi_3O_8$–H_2O as a model. Both Goranson (1937) and Verhoogen (1949) suggested that the walls of a magma chamber could act as a semipermeable membrane open to the gas phase but closed to the silicate melt. However, unless the walls of magma chambers are also insulating, there can be a difference in temperatures across the chamber wall. Consequently, both temperature and pressure differences may obtain, and the composition of the gas phase outside the chamber may be different than if osmotic conditions did not obtain. The equations in this section describe differences in osmotic temperature and are analogous to the equations that describe differences in osmotic pressure. A generalized discussion of osmotic conditions that include pressure, temperature and compositional effects has not been formulated, at least to my knowledge.

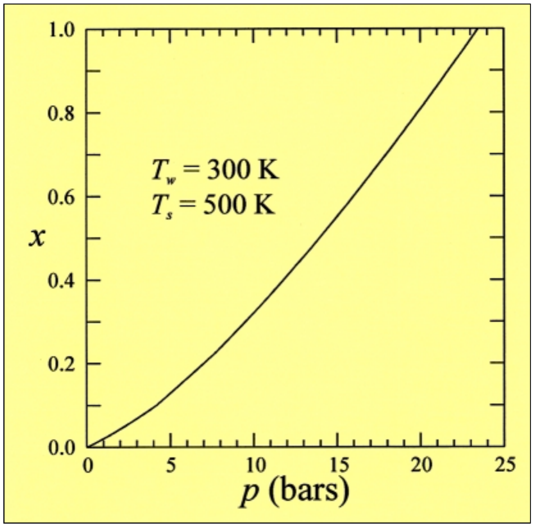

FIG. A1. Diagram showing the equilibrium conditions between an ideal aqueous solution and H_2O vapor through an impermeable membrane. Pressure, p, is plotted on the horizontal axis, and the mole fraction of H_2O in the solution, x, is plotted on the vertical axis. The solution and vapor are at different temperatures.

APPENDIX B. CALCULATING THE EFFECT OF A SECOND COMPONENT ON THE SOLUBILITY OF A FIRST

One assumes equilibrium between melt and vapor, and asks how the saturation of a particular component changes with the change in concentration of another component. In particular, one wishes to calculate the effect of HF (component 2) on the solubility of H_2O (component 1).

At equilibrium, one has:

$$\mu_1{}^{gas} = \mu_{H_2O}{}^{melt} \tag{10}$$

Finding the differential of each side of equation 10 gives:

$$-s_1^{gas} dT + v_1^{gas} dP = -\bar{s}_{H_2O}^{melt} dT + \bar{v}_{H_2O}^{melt} dP + \sum_{i=1}^{N} \mu_{H_2O,j}^{melt} \, dn_i \Big/ \sum_{i=1}^{N} n_i \tag{11}$$

where $\mu_{H_2O,j}^{melt}$ is the modified derivative:

$$\left(\partial \mu_{H_2O}^{melt} \big/ \partial n_i \right)_{P,T,n_j}^{melt} \sum_{i=1}^{N} n_i \, .$$

If HF and H_2O are the only two components that leave or enter the melt, equation 11 simplifies to:

$$-s_1^{gas} dT + v_1^{gas} dP = -\bar{s}_{H_2O}^{melt} dT + \bar{v}_{H_2O}^{melt} dP + \mu_{H_2O,H_2O}^{melt} dn_{H_2O} \Big/ \sum_{i=1}^{N} n_i + \mu_{H_2O,HF}^{melt} dn_{HF} \Big/ \sum_{i=1}^{N} n_i \tag{12}$$

The final step in the derivation is to convert terms with dn_i into terms with y_i and dy_i. The mole fraction of component i, y_i, is defined as $y_i = n_i \Big/ \sum_{i=1}^{N} n_k$. The derivatives with respect to n_i and n_j are:

$$\left(\partial y_i \big/ \partial n_i \right)_{P,T,n_k} = (1 - y_i) \Big/ \sum_{i=1}^{N} n_k$$

$$\left(\partial y_i \big/ \partial n_j \right)_{P,T,n_k} = -y_i \Big/ \sum_{i=1}^{N} n_k \tag{13}$$

Equation 14 contains four variables as differentials, P, T, n_{H_2O} and n_{HF}. The mutual variations in two variables can be calculated by holding the other two variables constant. For example, the variation of the pressure of saturation with change in concentration of HF at constant T and moles of H_2O is given by:

$$\left(\partial \ln(1 - y_{HF}) \big/ \partial P \right)_{T,n_k,n_{H_2O}} = \left(\bar{v}_{H_2O} - v_i^{gas} \right) \big/ \mu_{H_2O,HF}^{melt} \tag{14}$$

The relations in equation 14 are used to arrive at equation 15.

At constant P and T, one can calculate the change in concentration of H_2O at saturation with change in HF concentration. The result is:

$$\left(\partial y_{H_2O} \big/ \partial y_{HF} \right)_{P,T,n_k} = -\left[(1 - y_{H_2O}) \big/ (1 - y_{HF}) \right] \left(\mu_{H_2O,HF}^{melt} \big/ \mu_{H_2O,H_2O}^{melt} \right) \tag{15}$$

If there is a known relationship between the gain and loss of H_2O and the gain or loss of HF, then this relationship eliminates one of the dn_i, and one of the other variables can be left in the equation. For example, if $dn_{H_2O} = -dn_{HF}$, then:

$$\left(\partial \ln(1 - y_{H_2O}) \big/ \partial P \right)_{T,n_k,dn_{H_2O}=-dn_{HF}} = \left(\bar{v}_{H_2O} - v^{gas} \right) \big/ \left(\mu_{H_2O,H_2O}^{melt} - \mu_{H_2O,HF}^{melt} \right) \tag{16}$$