Thermodynamics and Mass Transport in Multicomponent, Multiphase H$_2$O Systems of Planetary Interest

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Abstract

Heat and mass transport in low-temperature, low-pressure H$_2$O systems are important processes on Earth, and on a number of planets and moons in the Solar System. In most occurrences, these systems will contain other components, the so-called noncondensible gases, such as CO$_2$, CO, SO$_2$, CH$_4$, and N$_2$. The presence of the noncondensible components can greatly alter the thermodynamic properties of the phases and their flow properties as they move in and on the planets. We review various forms of phase diagrams that give information about pressure-temperature-volume-entropy-enthalpy-composition conditions in these complex systems. Fluid dynamic models must be coupled to the thermodynamics to accurately describe flow in gas-driven liquid and solid systems. The concepts are illustrated in detail by considering flow and flow instabilities such as geysering in modern geothermal systems on Earth, paleofluid systems on Mars, and cryogenic ice-gas systems on Mars and Enceladus. We emphasize that consideration of single-component end-member systems often leads to conclusions that exclude many qualitatively and quantitatively important phenomena.
INTRODUCTION: PLANETARY CONTEXT

A fundamental observation on terrestrial H\textsubscript{2}O geothermal systems, and even on cryogenic H\textsubscript{2}O systems, is that H\textsubscript{2}O is rarely the only component in the system. CO\textsubscript{2}, CO, N\textsubscript{2}, NH\textsubscript{3}, CH\textsubscript{4}, H\textsubscript{2}S, SO\textsubscript{2}, C\textsubscript{2}H\textsubscript{2} (acetylene), C\textsubscript{3}H\textsubscript{8} (propane), C\textsubscript{2}H\textsubscript{6} (ethane), and other gases appear in varying concentrations both in liquid and solid H\textsubscript{2}O systems. The systems are thus more typically multicomponent than single component. Freezing, melting, vaporization, condensation, sublimation, and deposition occur in these systems, so they are additionally multiphase. Any dynamic flow processes in such systems are inherently more complex than in single-component systems (Wallis 1969a,b,c,d). We illustrate these complexities here by focusing on flow from reservoirs in single- and multicomponent aqueous systems with both liquid and solid reservoirs.

Conditions conducive to multicomponent, multiphase flow occur on, and in, a wide variety of Solar System bodies, including Earth (Figure 1a,b), Mars, Jupiter, Neptune, Saturn, and comets, as well as numerous icy satellites, such as Enceladus (Figure 1c). We present thermodynamic data and methods for analyzing such systems at low temperatures and illustrate with a few examples how combining the thermodynamics with fluid dynamics models leads to complex fluid flow phenomena that differ from the single-component counterparts. The eruption of a pure H\textsubscript{2}O geyser (or one with only minute traces of other gases) is driven by processes related to the boiling conditions of H\textsubscript{2}O, e.g., Old Faithful geyser (Kieffer 1984, Ingebritsen & Rojstaszer 1993), although it is possible that even Old Faithful has significant noncondensible gases (Hutchinson et al. 1997). Eruptions of CO\textsubscript{2}-rich geysers are driven by conditions of gas exsolution rather than boiling of H\textsubscript{2}O (Lu 2004; Lu et al. 2005, 2006). Serious errors can be made by assuming that a partial pressure due to an H\textsubscript{2}O component is equal to the total pressure of a mixture. In engineering, it is well known that drilled wells into gas-rich liquid are much more difficult to manage and contain than those that contain only H\textsubscript{2}O liquid or solid ice. Ignoring gases in

![Image](image_url)
analysis of fracture flow can lead to erroneous conclusions about the nature of the flow or reservoir properties.

Our initial perspective from Earth is from studies of low-temperature geothermal systems (White 1967; Rinehart 1980a,b; Henley et al. 1984; Economides & Ungemach 1987). We include the even lower-temperature clathrate systems (Kvenvolden 1993). Clathrates are ices that contain foreign gas molecules in cages of $H_2O$ molecules. Both geothermal fluids and clathrates have significant amounts of non-$H_2O$ components—dissolved gases ranging from approximately 0.01% to several tens of percent (Giggenbach 1980, Henley & Ellis 1983, Sloan 1998). We especially focus on those systems that are below the boiling point of pure water in which dissolved gases play a major role in the fluid dynamics (Lu et al. 2005, 2006). Similar dynamics were involved in the explosive eruptions of Lake Nyos, Cameroon (Zhang & Kling 2006). In the frozen form, the formation of methane clathrates in glaciers (Miller 1961) and on the ocean floor (Sloan 1998, Max et al. 2006), and their degassing upon either heating or release from high pressure, involves multicomponent, multiphase processes.

Pressure ($P$), temperature ($T$), and composition ($x$) relations of these systems can be found in the fluid inclusion literature (Bodnar 2003). However, quantitative analysis of dynamics in geothermal and planetary systems requires knowledge of other valuables, such as specific entropy ($s$), enthalpy ($h$), and volume ($v$), as well as different choices of independent and dependent variables, and these are the focus of this review.

For planetary applications, we have focused on two bodies that are the current topics of intense exploration: Mars and Enceladus, a satellite of Saturn. On Mars, CO$_2$ and H$_2O$ in solid, gas, and possibly liquid and clathrate forms are the dominant volatile components in the crust and at the icy poles (Miller & Smythe 1970, Milton 1974, Longhi 2006). Methane (CH$_4$) has been observed in the atmosphere (Formisano et al. 2004) and is of interest because it could indicate either life or active volcanic processes. The behavior of subsurface ices versus latitude and season is of great interest for Mars, and the recent arguments for “seeps” of a fluid (Malin & Edgett 2000, Hartmann 2001) versus granular flow (Shinbrot et al. 2004) have made the studies of volatiles of current interest. It is also possible that there is a liquid water–CO$_2$ fluid at shallow depths, or a liquid water–CH$_4$ fluid (Lyons et al. 2005).

The discovery of a large plume emanating from the frigid south pole of Enceladus (Figure 1c) during the Cassini spacecraft mission to Saturn has raised the fundamental question, “What kind of reservoir produces these plumes?” Porco et al. (2006) used a single-component H$_2O$ model (“Cold Faithful”) to suggest that the reservoir is liquid water. The proposal that liquid water could be as close as 7 m to the surface and related models for a deeper “ocean” (Nimmo et al. 2007) have generated much speculation that Enceladus could host near-surface life and thus might be an astrobiological target in near-term Solar System exploration.

Kieffer et al. (2006) pointed out that the Cold Faithful model cannot account for the presence of at least two of the three noncondensible gases in the observed abundances (N$_2$ and CH$_4$); the third major gas, CO$_2$, could be in solution in liquid water, but only at depths greater than 20 km. They proposed instead a multicomponent model (dubbed “Frigid Faithful”) in which cold decomposing clathrates host all of these gases (as well as the other minor organic

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1The substance observed by the INMS instrument on the first Cassini encounter with Enceladus in 2006 has a molecular weight of 28. Initially it was attributed to N$_2$ (Waite et al. 2006). During later encounters in 2008, J.H. Waite (NASA/JPL/ SwRI news conference of 3/26/08, available at http://saturn.jpl.nasa.gov; unpublished as of the time of preparation of this review) proposed that it was CO, which also has a molecular weight of 28. Either molecule forms clathrates with roughly similar properties and thus the conclusions here are unaffected by this uncertainty.
constituents seen in the plume). This system forms a self-sealing advection machine that operates at a much lower temperature than required for liquid water (Gioia et al. 2007). Initially, the difference between the Cold Faithful and Frigid Faithful scenarios appears to be temperature, but more fundamentally, the difference is the behavior of single- versus multicomponent systems.

Although ammonia (NH$_3$) has not been detected on Enceladus, there has been much speculation that it has existed in the interior in the past, and possibly at present (Matson et al. 2007). Clathrate and ammonia hydrates have long been suspected to play key roles in the evolution and present state of Titan (Lunine & Stevenson 1985, 1987). We do not discuss this complex system in this review.

Analysis of multicomponent, multiphase systems is complicated, and systems are often simplified in composition to a single component. In this review, we discuss the thermodynamic phase diagrams that apply to a number of multicomponent, multiphase systems using various coordinate systems that are appropriate to the particular problems of fluid dynamics considered, with applications to Earth, Mars, and Enceladus. We focus on depressurizing processes as a fluid moves from a high-pressure reservoir to a lower-pressure environment, and we show how differing conclusions are reached from analysis of single- versus multicomponent systems. Our approach brings in some analyses that are common in engineering practice and explains these in the context of geologic and planetary problems. In many ways, this review complements, and does not overlap, that of Zhang & Kling (2006) by considering the complex thermodynamics of multiphase multicomponent systems, combining the thermodynamics with fluid dynamics models of flow in cracks, and extending the work to cryogenic conditions and to other planets and moons.

**THERMODYNAMIC PROCESSES AND APPROPRIATE PHASE DIAGRAMS FOR ANALYSIS**

When analyzing a complex, multicomponent, multiphase process, the first and most basic step is to understand the first and second laws of thermodynamics and then to map the behavior required by the first and second laws onto relevant phase diagrams to get an estimate of the behavior of the system. However, these two steps must be combined with calculation of another fundamental parameter, the sound speed, to constrain the behavior of a system. Sound speed is the velocity at which small disturbances in pressure or density are propagated through a material. The relation of flow velocities to the sound velocity determines the flow regime.

If flow velocities are significantly lower than the sound speed, flow is subsonic and, therefore, nearly incompressible. This assumption underlies much of traditional geophysical fluid dynamics in understanding oceans, atmospheres, and Earth’s interior. If flow velocities are greater than the sound speed, flow is supersonic, and compressibility and nonlinear effects, such as shock waves, must be considered in analyses. Physical phenomena and analytic approaches are very different in the two different flow regimes. We demonstrate that these effects are important in decompression of geothermal and volcanic systems on Earth and other planets. As we demonstrate here, the sound speed in multiphase systems can be very low and this allows supersonic flow regimes not encountered in single-component regimes to be possible.

When the fluid velocity equals the sound speed, the phenomenon of “choking” plays a major, and controlling, role in high-velocity fluid dynamics because choked conditions control the mass flux from depressurizing systems. Low sound speed means that the flow would choke at relatively low velocities and thus low mass fluxes. Choking phenomena are found in many terrestrial geothermal exploration and exploitation situations, and they control mass flux and, therefore, power production and economic potential.
**Thermodynamic Processes**

Standard thermodynamic variables used in many analyses are state variables such as pressure, temperature, density, entropy, and enthalpy. Fluid dynamic analyses require additionally some first partial derivatives of these variables, such as the sound speed. These derivatives have some fundamentally different properties in multiphase and multicomponent systems.

**First law, second law, and sound speed.** For an open system with fluids flowing in and out, the general form of the first law is as follows (Huang 1988a):

\[
\dot{Q}_{\text{syst}} = \dot{E}_{\text{syst}} + \dot{W}_{s} + \dot{m}_{\text{out}} \left( h + \frac{V^2}{2} + gz \right)_{\text{out}} - \dot{m}_{\text{in}} \left( h + \frac{V^2}{2} + gz \right)_{\text{in}},
\]

where \( \dot{Q}_{\text{syst}} \) is the rate of the heat gained by the system, \( \dot{E}_{\text{syst}} \) is the rate of change of stored energy within the system, \( \dot{W}_{s} \) is rate of work (power) done by the system (except flow work), \( \dot{m} \) is mass flow rate of the fluid, \( h \) is specific enthalpy, \( V \) is velocity of the fluid, and \( z \) is the elevation. The subscripts in and out represent the thermodynamic state of the fluid flowing in and out of the system, respectively. Below in this review, we use subscripts such as this, or 1, 2, 3, etc., to indicate the values of variables along flow paths without further definition where obvious. Enthalpy \( h \) is

\[
h = u + P\nu = u + \frac{P}{\rho},
\]

where \( u \) is specific internal energy, and \( \rho \) is density.

For a steady-state steady flow with no power done by the system, \( \dot{m}_{\text{out}} = \dot{m}_{\text{in}} = \dot{m}, \dot{E}_{\text{syst}} = 0, \) and \( W_{s} = 0. \) Considering a thermodynamic process from state 1 to 2 (Adkins 1983), Equation 1 becomes

\[
q = (h_{2} - h_{1}) + \frac{1}{2} (V_{2}^2 - V_{1}^2) + g(z_{2} - z_{1}),
\]

where \( q \) is the heat gained by the system per unit mass. In the cases we discuss here, the depressurizing process is very fast, and the heat transfer rate to or from the surrounding of the system is much smaller compared with other terms in Equation 3, so \( q = 0 \) can be assumed for the energy balance. In many decompression-driven flows on Earth and other planetary bodies, the potential energy term \( g(z_{2} - z_{1}) \) is also negligible in Equation 3. When heat transfer \( q \) and initial velocity \( V_{1} \) are also negligible, the exit velocity \( V_{2} \) in Equation 3 can be expressed as

\[
V_{2} = \sqrt{2(h_{1} - h_{2})}.
\]

The general form of the second law of thermodynamics for an open system (Huang 1988b) can be expressed mathematically as

\[
\left( \frac{dS_{\text{irr}}}{dt} \right)_{\text{irr}} = \frac{dS}{dt} + \sum_{\text{out}} \dot{m} s - \sum_{\text{in}} \dot{m} s - \sum Q_{k} / T_{k},
\]

where \( \left( \frac{dS_{\text{irr}}}{dt} \right)_{\text{irr}} \) is the rate of entropy production (the so-called path function) owing to internal irreversibility; \( \frac{dS}{dt} \) is the rate of the entropy change within the open system; \( \sum_{\text{out}} \dot{m} s \) and \( \sum_{\text{in}} \dot{m} s \) are total entropy contents of the outgoing and incoming streams, respectively; and \( Q_{k} \) is the heat transfer rate at temperature \( T_{k} \) (\( k \) is the index indicating the different heat sources and their temperatures).

The second law of thermodynamics requires \( \left( \frac{dS_{\text{irr}}}{dt} \right)_{\text{irr}} > 0 \) for any irreversible process (i.e., for all real processes). \( \left( \frac{dS}{dt} \right)_{\text{irr}} = 0 \) only for reversible ideal processes. Irreversibility can be caused by heat transfer driven by a temperature difference, free-expansion owing to a pressure difference.
(not quasi-static), and dissipation (Thompson 1972) in a viscous flow (viscous work going into deformation of a fluid particle). In steady-state conditions, \( \frac{dS}{dt} = 0 \).

If heat transfer is negligible or the process is adiabatic, Equation 5 becomes

\[
\left( \frac{dS}{dt} \right)_{irr} = \sum_{\text{out}} \dot{m} s - \sum_{\text{in}} \dot{m} s \geq 0.
\]  

(6a)

Note that, in Equation 6a, “\( > \)” corresponds to an irreversible process and “\( = \)” is for a reversible process. For one stream of fluid from state 1 to 2, Equation 6 can be further expressed as

\[ s_2 - s_1 \geq 0. \]  

(6b)

Although not usually thought of as a fundamental thermodynamic parameter in the context of P-x-T-s phase relations, the sound speed is an essential parameter for analysis of moving materials in planetary systems where pressure gradients can be great, and it is directly related to the static variables discussed above. Sound speed is a partial derivative of two fundamental static variables, pressure and density, and is related to the bulk modulus, \( K \) (which is a measure of incompressibility, and \( K = 1/\beta \), where \( \beta \) is the compressibility):

\[ c^2 = \frac{K}{\rho} = \left( \frac{\partial P}{\partial \rho} \right)_s. \]  

(7)

This derivative is taken for constant entropy conditions because sound wave propagation involves infinitesimally small and rapid amplitude changes assumed to be adiabatic and reversible, i.e., constant entropy. Although defined in terms of the static variables \( K \) and \( \rho \), the sound speed is a dynamic variable and plays an important role in the simple wave equation. Some finite amplitude processes, such as rapid decompression of a pressurized reservoir, are also well approximated by the adiabatic and reversible isentropic condition (Kieffer & Delany 1979, pp. 1612–15). We show in sections below how the sound speed varies in multicomponent, multiphase systems, and emphasize that it is a fundamental parameter that must be considered in modeling flow in these complex systems.

**Single-Component H\(_2\)O System: Phase Diagrams**

**Temperature-entropy diagrams.** Although pressure-temperature (P-T) diagrams are commonly used in Earth and planetary sciences, this representation of the phase relations does not show details of the two-phase region. Therefore, in many common flows where a flow undergoes a phase change, the P-T diagram is limited. The temperature-entropy (T-s) diagram is much more useful in analyzing the thermodynamic processes if the system is undergoing phase changes. These diagrams are commonly used in engineering and geothermal applications (thermodynamic analysis of power cycles, steam turbine thermal process design, flow in geothermal wells, and geothermal steam separation processes), and the phase diagrams (or their equivalent Mollier charts) are widely available for some substances. However, T-s diagrams typically do not include the low-temperature range and have had only limited application in planetary sciences. Although Kieffer (1982) generated T-s diagrams for SO\(_2\), S, and CO\(_2\) for very-low-temperature conditions, we could not find one for H\(_2\)O at low temperatures. We present one for temperatures down to 145 K in Figure 2.

Why are T-s diagrams useful? Because, as discussed above, many flow processes—to first order—are adiabatic and reversible, i.e., isentropic. An isentropic process is a vertical line on the T-s diagram, and thus many properties can be inferred directly from such a representation. The properties of each phase are represented and the properties of the mixture can be calculated from the proportions of the phases.
Figure 2  
(a, b) Diagrams of water system. Generated with Engineering Equation Solver, EES (Klein 2007). Thermodynamic properties from Harr et al. (1984). Correlations are valid up to a pressure of 10,000 bar. Properties of ice T < 273.15 K and pressures above the saturation vapor pressure of ice are based on Hyland & Wexler (1983) for temperatures from 173.15 K to 473.15 K. Data below −100°C (with vapor mass fraction shown by dashed curves) are extrapolated. In (b), A is the triple point, C is the critical point. AC is the vapor-pressure curve and AB is the sublimation-pressure curve. The melting-point temperature for ice Ih decreases with increasing pressure, AD. For pressure increases from triple point to 300 bar, the melting point slightly decreases approximately 2 K; however, when the pressure continues to increase to 2000 bar, the melting point decreases by approximately 18 K (Li et al. 2005, Luscher et al. 2004, Saitta & Datchi 2003, Longhi 2001, Chou et al. 1998). This is because water expands on freezing, causing the density of ice to be less than liquid water, which is different from most substances for which the solid density is greater than that of the liquid (Moore 1962). In (a), the data are extrapolated down to 145 K. Isobars, constant specific volume lines, isenthalpic lines, and x lines (mass fraction of saturated water vapor) in a two-phase region are all presented. The liquid-vapor (L + V) two-phase region corresponds to the vapor-pressure curve AC in (b). The solid-vapor (S + V) two-phase region corresponds to the sublimation-pressure curve AB in (b). The curve AD in (b) corresponds to many nearly horizontal lines in the solid-liquid region (S + L) in (a), with temperature very close to 273.16 K for pressures less than 300 bar. These lines are almost identical and look like a horizontal line in (a). Process 1-1′ is mentioned in the text.

Two typical isentropic decompression processes in the two-phase region are shown in Figure 3a (the high-temperature part of Figure 2). Process 1–1′ is decompression from a saturated liquid; process 2–2′ is decompression from a saturated vapor. If the reservoir condition (either 1 or 2) is known, then the mass fraction of steam (or liquid) can be determined by the lever rule, the enthalpy can be calculated, and an estimate of flow velocity can be calculated from Equation 4, assuming that the flow has not choked. Conversely, if the exit velocity and the vapor mass fraction (x1′) are known, state 1′ can be determined and hence the corresponding reservoir condition (state 1) can be inferred. Similar arguments apply to any initial state within the two-phase region instead of on the phase boundary.

For an adiabatic process, if the changes of kinetic energy and potential energy are negligible compared with the change of the enthalpy, the process is isenthalpic. In Figure 3a, the process 3–3′ is isenthalpic, a flow path typical of that in a geothermal well. One of the critical questions
in reservoir engineering is, “Can the enthalpy of the reservoir be inferred from measurements of the properties at the well head?”

Given the enthalpies of the saturated liquid and vapor of the outflow, \( h_f \) and \( h_g \), and the mass fraction of vapor in the outflow, \( x_f \), and the assumption that the process is isenthalpic, then the reservoir enthalpy, \( h_3 \), can be inferred from the lever rule:

\[
x_f = \frac{h_3 - h_f}{h_g - h_f}.
\]

\( (8) \)
In the liquid-alone region, these processes can only be shown at an exaggerated scale (Figure 3b). 0–1 is an isobaric process, 0–2 is isothermal, 0–3 is isenthalpic, and 0–4 is isentropic. On or near the surface of planets and moons where the surface pressure and temperature are very low, the depressurizing process will involve the low-temperature ice-vapor part of the phase diagram (Figure 3c, the enlarged low temperature region of Figure 2).

We can illustrate the usefulness of this representation for examining the plumes erupting from Enceladus. The plumes were reported to have a mass ratio of solid/vapor of 0.42, corresponding to a fraction vapor of \( x = 0.7 \) (70%) (Porco et al. 2006). What kind of reservoir and process produces these plumes? We illustrate the processes suggested for the single-component reservoir here, and then contrast these results with a multicomponent analysis below.

In a single-component \( \text{H}_2\text{O} \) system, two processes are available to produce the mixture in the plume: sublimation of ice with subsequent recondensation of some of the vapor, and boiling of liquid. Consider first the recondensation scenario path 1–1’ in Figure 2. The initial state chosen for our example is the sublimated vapor on the phase boundary (state 1 in Figure 2) corresponding to 225 K. We chose the final state to correspond to the relatively low temperature of 145 K. From the lever rule, a plume in equilibrium at this final state has a composition of that reported, \( x \approx 0.7 \).

Porco et al. (2006, p. 1398) were considering the masses of ice and vapor to be comparable, which would correspond to \( x \approx 0.5 \). It can be seen from Figure 2 that this is a more difficult composition to obtain from sublimation under plausible Enceladus conditions. If the kinetic limitations are such that the final temperature of reaction would be approximately 180–190 K, it is difficult to obtain \( x \approx 0.5 \), because the final state is more vapor rich \( x \approx 0.8 \). Note that this corresponds to the recalculated conditions mentioned in Footnote 2.

Instead, the behavior of a reservoir of boiling water at 273 K was considered as the most plausible candidate for producing the plume. Three potential reservoirs that correspond to the Cold Faithful model are illustrated in Figure 3c: (a) a liquid water reservoir just at triple point conditions (process 1–1’–1”’), (b) a liquid water reservoir 20° above the triple point (process 2–2’–2”), and (c) a 50%-50% mixed ice-liquid slurry at conditions very close to triple point (3’–3’’–3”). The final state is assumed to be 145 K. From this T-s diagram, it is easily seen that these conditions only produce approximately 10% vapor; a higher final temperature of 180–190 would produce even less vapor. As noted by Porco et al., a mixture forming from a liquid reservoir is mostly ice. If all ice was entrained, the plume should contain more ice than observed, and more than 90% of the ice must be left behind.

The two different conclusions (boiling water versus recondensation of sublimated vapor) are at the root of the current controversy over the subsurface conditions at Enceladus’s south pole. We discuss below how the presence of noncondensible gases also affects this conclusion.

T-v phase diagrams to illustrate nonequilibrium effects in condensing vapor flow. Nonequilibrium thermodynamic processes occur in condensing flow because supersaturation of the vapor is required for the nucleation of condensed phases. These effects become pronounced even at temperatures characteristic of terrestrial geothermal regions (e.g., \( \sim 200^\circ \text{C} \)) and may be especially prominent at the low temperatures of interest for planetary surface conditions (e.g., see Kieffer 1982 for a discussion of this in the context of \( \text{SO}_2 \) volcanism on Io; Ingersoll et al. 1985, 1989 for sublimation dynamics on Io; and Byrne & Ingersoll 2003 for a discussion of sublimation of Mars polar caps).

\(^2\)We picked the example to address the mass fraction reported by Porco et al. (2006). Kieffer et al. (2009) subsequently recalculated the mass fraction and show that it is significantly higher than this value (\( x > 0.8 \)).
Although the topic of nonequilibrium flows with condensation could be the subject of a separate review article because so many new computational and experimental techniques have shed light on this problem, the basic concepts can be illustrated with yet a different phase diagram: the temperature-volume (T-v) diagram introduced by Zel’dovich & Raizer (1966) and applied to SO$_2$ condensation in the context of Io by Kieffer (1982). This diagram is useful because expansions are well described by the specific volume of the system, and kinetic effects can be specified in terms of temperature or temperature differences.

We illustrate the phenomena for the specific case of decompression of H$_2$O from a typical geothermal reservoir at 200°C, 15.5 bars (Figure 4). Decompression from icy conditions follows as a subset of this case (discussed below starting at 190 K), and we then apply the analysis to nonequilibrium condensing flow in fractures on Enceladus.

An equilibrium expansion process is one end-member of possibilities in which the mixture composition is always the equilibrium composition at given conditions (curve A-F-B of Figure 4). Condensation of droplets must occur rapidly enough for equilibrium to be maintained. The expansion path lies so close to the saturation curve boundary that it is nearly indistinguishable, even in semilog coordinates.

If condensation does not occur (e.g., if there is insufficient supersaturation of the vapor, lack of nucleation sites, or insufficient time to form nucleation centers), then the fluid remains in the vapor phase and expands isentropically. The fluid can be treated as an ideal gas. For a given initial condition (T$_0$, P$_0$, v$_0$ at point A) and a given final temperature T, the specific volume v and pressure P along the isentropic metastable process can be determined using the perfect gas law equations for v(T) and P(T), giving the metastable vapor isentrope, path A-D-C.

There are significant differences between equilibrium and metastable expansion. For example, the pressure at 375 K is six times higher for a metastable expansion than for an equilibrium one, and
the corresponding volumes are different by a factor of 6. A real expansion process is usually a path between these two limiting processes, shown schematically by the path A-D-E-G in Figure 4, where we have arbitrarily illustrated a metastable vapor isentrope to 100°C supersaturation.

The enthalpy drop for the metastable expansion from A to D is 234 kJ kg\(^{-1}\), less than the 297 kJ kg\(^{-1}\) enthalpy drop of the equilibrium expansion from A to F. Conduit velocities, which are directly proportional to the enthalpy change, are correspondingly less (684 m s\(^{-1}\) versus 771 m s\(^{-1}\)).

These effects become more extreme as the temperature difference between initial and final state increases, as shown by the spread between curves A-D-C and A-F-B in Figure 4. The specific volume difference between the two processes at 348 K is approximately 1 order of magnitude, whereas it becomes 5 orders of magnitude at 223 K. This volume difference is mainly due to the difference in system pressures at a given temperature.

At the triple point, ice is the stable phase in equilibrium with vapor and water. Vapor expansion at a temperature below its freezing point can be different from the behavior in the liquid-vapor two-phase region. For the temperature range analogous to that on the south pole of Enceladus, curves I-J (blue curve) and I-B (blue dots) in Figure 4 show the metastable vapor expansion and the two-phase equilibrium expansion, respectively, from the initial state of saturated vapor at 190 K. At a condition with a very low temperature and pressure, the specific volume becomes very large and the spacing between molecules is so rarified that the vapor may not find solid nuclei to grow on.

On Enceladus, nonequilibrium conditions may be dominant because of the very low temperature. To illustrate the effects of nonequilibrium conditions on condensation in low-temperature flows, consider the formation of a micron-sized ice particle. Assuming the mass flux onto the surface of an ice particle is \(\rho_v \nu_{rms} (2\pi)^{-1/2}\) (Ingersoll 1989), the radius growth rate of a spherical particle in a condensing flow is

\[
\frac{dr}{dt} = \left(\frac{\rho_v}{\rho_{ice}}\right) \nu_{rms} (2\pi)^{-1/2},
\]

where the root mean square molecular velocity \(\nu_{rms} = (3RT/M)^{1/2}\), \(R\) is the universal gas constant = 8.314 J mol-K\(^{-1}\), \(T\) is temperature in Kelvin, \(M\) is molar mass of vapor in kg mol\(^{-1}\), and \(\rho_v\) and \(\rho_{ice}\) are the vapor and ice densities in kg m\(^{-3}\), respectively.

In a low-temperature vapor that is flowing fast and has a relatively short flow path, such as water vapor escaping from fractures on Enceladus, it is more likely that flow would follow a nonequilibrium process (I-J in Figure 4) than an equilibrium process. If an expanding vapor follows a nonequilibrium path, such as I-J, the vapor density at any given temperature is greater than that at equilibrium condition (about 1 order of magnitude at 175 K). Growth rates will therefore be higher, possibly by an order of magnitude, and conclusions based on growth rates in single-component systems may tend to underestimate possible growth rates. However, the presence of noncondensible gases in conduits, as advocated by Kieffer et al. (2006), will also influence growth rates, so many factors must be considered.

Sound speeds in multiphase systems: s-\(\rho\) phase diagrams. Finally, we consider a fourth phase diagram that illustrates yet another thermodynamic property: the sound speed. The sound speed of end-member phases can be quite high: 1435 m s\(^{-1}\) for liquid water and 470 m s\(^{-1}\) for steam. However, the sound speed of a mixed liquid-gas fluid can be as low as a meter or a few meters per second (Figure 5). The speed of sound in a multiphase system depends on whether heat and mass transfer are maintained in equilibrium as the small pressure pulses associated with the sound wave pass through the fluid. If equilibrium is not maintained, the sound speed drops by approximately
one order of magnitude (Figure 5a, top), whereas if it is maintained, the sound speed drops by nearly two orders of magnitude (Figure 5a, bottom). It can be as low as 1 m s\(^{-1}\) (magnitude varies with pressure).

The sound speed depends on the mass fraction of vapor in the liquid-vapor system. The fluid can be either a liquid with gas bubbles (boiling liquid) or a vapor with liquid droplets (aerosol or mist). What causes this phenomenon? The definition of sound speed has two terms (Equation 7): a direct proportionality to the compressibility, \(K\), and an inverse proportionality to the density, \(\rho\). In a boiling two-phase mixture, the density is nearly that of the liquid phase, but the compressibility is that of the gas phase—much lower than that of the liquid phase. These two effects dramatically diminish the sound speed (left side of Figures 5a). However, as the vapor mass fraction increases toward the aerosol state, the mixture density decreases and the effect is reversed (right side of Figure 5a).

Referring again to Equation 7, note that the sound speed (squared) is \((\delta P/\delta \rho)\)\(_c\), which suggests that changes of sound speed between liquid, gas, and (gas + liquid) phases (both boiling liquid and aerosol phases) can be visually seen on a plot of entropy versus density with contours of constant...
pressure (Figure 5b) (Kieffer & Delany 1979). This plot is analogous to a normal topographic map where contours of elevation \( z \) are plotted against two directions, \( x \) and \( y \): \( \delta z / \delta y \). Thus, when a \( s-\rho \) graph is read as a topo map and \( P \) is considered equivalent to \( z \), the topography of a \( s-\rho \) graph visually illustrates the large variations in sound speed that characterize the single and multiphase regions (Figure 5b). When traversed in a vertical direction at constant entropy, the spacing between isobars on such a plot reflects the magnitude of the sound speed—large spacing indicates small gradients reflecting low sound speeds, and tight spacing indicates large gradients and high sound speeds.

**Multicomponent, Multiphase Liquid-Gas Systems**

Unfortunately, it is difficult to make similar representations of these phase diagrams in multicomponent systems because solubility of the gas into the liquid or solid adds additional complexity. We use the commonly occurring systems, including \( \text{H}_2\text{O}-\text{CO}_2 \) and \( \text{H}_2\text{O}-\text{CH}_4 \), to illustrate how Henry's law and solubility curves are used in the study of multiphase and multicomponent flows.

If gas dissolves in a liquid in equilibrium, the molar concentration of a solute gas in a solution, \( X_{aq} \), is proportional to the partial pressure of that gas above the solution, \( P_g \):

\[
P_g = K_H X_{aq}.
\]

(10)

\( K_H \) is the Henry's law constant on the molar concentration scale, which can be determined by experiments, \( X_{aq} \):

\[
X_{aq} = \frac{n_{g,aq}}{n_{g,aq} + n_l},
\]

(11)

where \( n_{g,aq} \) is the number of moles of the gas in aqueous phase and \( n_l \) is the number of moles of liquid water.

Henry's law is accurate if concentrations or partial pressures are relatively low. Deviations from Henry's law become noticeable when concentrations and partial pressures are high, but first-order effects can be considered even in this case by using Henry's law. Detailed descriptions of the Henry's coefficient are given in Lu (2004).

**\( \text{H}_2\text{O}-\text{CO}_2 \) and \( \text{H}_2\text{O}-\text{CH}_4 \) systems.** The \( \text{H}_2\text{O}-\text{CO}_2 \) system is a typical aqueous system found in many geothermal systems on Earth, and it could be present on Mars (Lyons et al. 2005, Okubo & McEwen 2007, Than 2007) or other planetary bodies, such as Enceladus as discussed below.

Several experimental studies on the solubility of \( \text{CO}_2 \) in water were carried out by previous researchers (Ellis & Golding 1963, Malinin 1974; a review of work is in Lu 2004). Using Malinin’s correlation, Lu (2004) analyzed the thermodynamics of the \( \text{H}_2\text{O}-\text{CO}_2 \) system and generated solubility curves versus temperatures and total system pressures (Figure 6a,b). As is well known, and can be seen from these figures, at temperatures less than 160°C, the \( \text{CO}_2 \) solubility increases with decreasing temperature, but at temperatures above 160°C, the \( \text{CO}_2 \) solubility increases with increasing temperature.

Aqueous methane systems \( \text{H}_2\text{O}-\text{CH}_4 \) may exist on Mars (Lyons et al. 2005). The solubility of \( \text{CH}_4 \) is much less than that of \( \text{CO}_2 \) (Figure 6c). For example, at 50°C and 300 bar, the solubility of \( \text{CO}_2 \) is approximately 20 times that of \( \text{CH}_4 \). The lowest solubility region of \( \text{CH}_4 \) is at approximately 100°C, with a wide, flat curve range, whereas \( \text{CO}_2 \) has its lowest solubility at approximately 150°C, with a narrower, flat curve range.

Based on recent spectroscopic detections of \( \text{CH}_4 \) in the Martian atmosphere, Lyons et al. (2005) have reexamined the role of C-O-H fluids in the Martian crust. They concluded that there may be reservoirs of \( \text{H}_2\text{O}-\text{CH}_4 \) fluids at depths less than 9.5 km in the crust, with \( \text{H}_2\text{O}-\text{CO}_2 \)-rich fluids
Figure 6

(a) Solubility of CO$_2$ at different pressure and temperature conditions. (b) Solubility of CO$_2$ in a low-temperature and low-pressure region. (c) Solubility of CH$_4$ at different pressure and temperature conditions. See text for discussion of lettered points.

at greater depths. This suggests two possible scenarios for fluid migration in the Martian crust: (a) upward flow of H$_2$O-CO$_2$ mixtures from a deeper reservoir, and (b) upward flow of H$_2$O-CH$_4$ mixtures from shallow reservoirs. The existence of these reservoirs has strong implications for planetary degassing because the volatiles exsolve as the fluids ascend (Lyons et al. 2005). When H$_2$O-CH$_4$-rich fluids decompress and cool, they may encounter a two-phase region.

Slow ascent of the shallow fluids would allow degassing of a vapor-rich phase, providing methane to the atmosphere (Figure 6c). The illustrative process line A-B-C in this figure corresponds to the initial and final temperatures and lithostatic pressures of Lyons et al. (2005), with an initial concentration of CH$_4$ of 0.1 mole fraction. Upon ascent from the reservoir, the flow remains liquid with the gas in solution from A to B, ~8.5 km, and 320°C, but degassing occurs
at B as proposed by Lyons et al. (2005). From B to C, the flow is a liquid-gas two-phase mixture, unless flow separation occurs, for example, the liquid stagnates and the gas rises as a separate phase.

Upward flow from a \( \text{H}_2\text{O-} \text{CO}_2 \)-rich reservoir at a depth greater than 9.5 km could also produce two-phase flow as shown in Figure 6a, where the conditions for the process line A-B-C were again based on Lyons et al. (2005). Degassing occurs at point B at shallower and cooler conditions, \( \sim 6 \) km and \( 210^\circ \text{C} \), than for the \( \text{H}_2\text{O-} \text{CH}_4 \)-rich fluids.

Sound speed in multicomponent liquid-gas systems. Sound speeds in liquid-gas systems such as \( \text{H}_2\text{O-} \text{CO}_2 \) or \( \text{H}_2\text{O-} \text{CH}_4 \) are low because they have the increased compressibility of the gassy liquid, but the sound speeds do not drop as low as for those in liquid-vapor systems because there is no mass transfer between the two phases at the time scales of acoustic wave propagation. Therefore, to first order the \( \text{H}_2\text{O-} \text{air} \) system provides an illustration of the magnitude of the multiphase effect. These systems mimic the nonequilibrium \( \text{H}_2\text{O-} \text{steam} \) system shown in Figure 5a (top) (details in Kieffer 1977) and therefore we do not discuss this further here.

Multicomponent, Multiphase Solid-Gas Systems

At lower temperatures in multicomponent systems, the solid ice phase may contain dissolved gases. In general, these systems are called clathrates, from Latin and Greek roots meaning lattice. When the ice matrix is \( \text{H}_2\text{O} \) they are called gas hydrates; we use the terms interchangeably. With specific gases they are called, for example, methane hydrate, carbon dioxide hydrate, etc., if there are multiple gases, simply mixed hydrate or mixed clathrate.

Forty seven natural-gas hydrate locations are known on Earth, in permafrost and in ocean sediments (Sloan 1998), and they are potential natural gas resources. Gas hydrates can exist on other planetary bodies where pressure, temperature, and other conditions are favorable for their formation (Miller 1961, Kargel & Lunine 1998, Gautier & Hersant 2005, Hand et al. 2006). The possible existence of \( \text{CO}_2 \) clathrates on Mars has been proposed by many researchers (Miller & Smythe 1970, Longhi 2006, Kargel et al. 2000), and it has been suggested that methane clathrates may supply \( \text{CH}_4 \) to the Martian atmosphere (Prieto-Ballesteros et al. 2006).

The pressure-temperature decomposition (\( P_d-T_d \)) curves for clathrate stability and decomposition depend on the nature of the gas and gas mixture. The phases involved are hydrate (H), ice (I), and gas (G) (i.e., the decomposition reaction is H \( \rightarrow \) G + I). The decomposition curves (\( P_d-T_d \)) of the \( \text{N}_2 \), \( \text{CH}_4 \), and \( \text{CO}_2 \) gas hydrates, together with the data sources used to generate the curves, are shown in Figure 7a.

Energy balance for the decomposition of a clathrate reservoir. In the section on T-s diagrams, above, we considered the energy and mass balances for a single-component ice source for the plume of Enceladus. Consider a parallel analysis for decomposition of a clathrate reservoir to produce the plume. If a clathrate reservoir with temperature lower than 273 K is pierced by a fracture (or well), the clathrates will decompose (hydrate \( \rightarrow \) \( \text{H}_2\text{O} \) ice + gases) and material will leave the system.

To analyze this, consider the energy balances (Figure 7b) with flow through a control volume, CV. Denoting (\( h_{\text{out}} - h_{\text{in}} \)) as \( \Delta H_{\text{dis}} \), the enthalpy of dissociation of the clathrate hydrate (Yamamuro & Suga 1989, Kang et al. 2001), the energy balance of the system is

\[
Q_{\text{in}} + Q_{\text{source}} - Q_{\text{out}} = m_{\text{out,}d} \Delta H_{\text{dis}} + m_{\text{out,}i} I_{\text{sub}} + m_{\text{out},P} \frac{P_r}{P_i}.
\]
Figure 7
(a) Phase equilibrium (H = I + G) for N₂, CH₄, CO₂, and mixed gas clathrates at temperature below 273 K. The composition of the mixed gas clathrate is that of the plume emanating from Enceladus’ south pole in the first Cassini encounter (Waite 2006). (b) Schematic diagram of the derivation of energy balance of a clathrate reservoir with outgoing fluids due to decomposition.

The left side of Equation 12 is the net heat gained by the system, whereas the right side is the heat that is required to dissociate the clathrate hydrate and to accelerate the outgoing fluids, but includes a term for possible sublimation of ice as well. Assuming steady-state conditions, the left side of Equation 12 is equal to the right side.

The rate of heat leaving the system (Q_{out}) from the south pole of Enceladus is estimated to be 3 to 7 GW (Spencer et al. 2006). Based on the mole fractions of N₂, CH₄, and CO₂ (Waite et al. 2006) and the values of enthalpies of dissociation of pure N₂, CH₄, and CO₂ hydrates (Kang et al. 2001, Yamamuro & Suga 1989), the enthalpy of dissociation of the mixed hydrate \( \Delta H_{dis} \) is \( \Delta H_{dis} = 890 \text{ kJ kg}^{-1} \) of the gas mixture.

To estimate the magnitude of the terms on the right side, we use an approximate density \( \rho_r = 1000 \text{ kg m}^{-3} \). For an order-of-magnitude reservoir pressure we use \( P_r = 5 \text{ bar} \) (Kieffer et al. 2006). The molar ratio of the mixture of gases (N₂, CH₄, and CO₂) to H₂O vapor is approximately 1:10 (Waite et al. 2006), which is equivalent to the mass ratio of 1:7 for the given molar fractions detected. The total mass flow rate of H₂O in the plume is \( m_{out} \approx 100 \text{ kg s}^{-1} \) (Hansen et al. 2006), thus the mass flow rate of the gas mixture (N₂, CH₄, and CO₂) is \( m_{out,g} \approx 15 \text{ kg s}^{-1} \). The first two terms on the right side of Equation 12 are \( \sim 1 \times 10^{-2} \text{ GW} \) and \( 2 \times 10^{-4} \text{ GW} \), very small compared with the observed energy flux.

Taking the mass rate of the sublimated H₂O vapor, \( m_{out,v} \), as 350 kg s⁻¹, and the latent heat for the sublimation of ice \( L_{sub} = 2800 \text{ kJ kg}^{-1} \), we can estimate the third term as 0.84 GW. The three terms are \( \sim 1 \text{ GW} \), small compared with the radiated heat. This led Kieffer et al. (2006) to propose that the plume represents a small leak on a massive advection system in which large amounts of vapor are condensing on the walls releasing latent heat, which contributes an additional radiated energy component.
Sound speeds in multicomponent, multiphase solid-gas systems. We conclude our review of sound speeds in multicomponent, multiphase systems by summarizing the effects of particles entrained in gases on the sound speed. We do not attempt to cover densely packed solid-gas mixtures, such as granular materials (see Jaeger et al. 1996 for a review of the behavior of these complex substances), or the more subtle effects of embedded particles or bubbles in solid H$_2$O.

Two effects are important in determining the sound speed of gas-solid mixtures: mass loading of the gas by the particles and heat transfer from the particles to the gas. To first order, it is assumed that the particles move with the gas, the so-called pseudogas approximation (Wallis 1969b). For a perfect gas, Equation 7 gives the sound speed as

\[ c = \left( \frac{\gamma RT}{M} \right)^{\frac{1}{2}}, \]

(13)

where \( \gamma \) is the isentropic exponent for the gas, and M is the molecular weight. For a perfect gas, the sound speed is a direct function of temperature and \( \gamma \), and inversely proportional to molecular weight.

If the mass ratio of solids/gas is denoted by m, then the effect of the mass loading alone in the pseudogas approximation is to change R/M from that of the gas to R/M(1+m) (Wallis 1969b, equation 2.17), that is, mass loading mimics increasing molecular weight and decreases the sound speed. If heat transfer is important, then \( \gamma \), the ratio of heat capacities, is changed to

\[ \gamma = \frac{c_{p,\text{gas}} + mc_s}{c_{v,\text{gas}} + mc_s}, \]

(14)

where \( c_{p,\text{gas}} \) and \( c_{v,\text{gas}} \) are the heat capacities at constant pressure and constant volume for the gas, and \( c_s \) is the averaged heat capacity for the solid phase. For significant mass loading, \( \gamma \) tends toward unity. These effects are shown in Figure 8a, which compares the behavior of an H$_2$O-solid dusty

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Figure 8

(a) Dependence of sound speed on mass loading, temperature, and composition. (b) Temperature-entropy phase diagram for H$_2$O comparing the thermodynamic history of the H$_2$O during isentropic ascent of the fluid alone (m = 0 path) with isentropic ascent of a mixture containing weight ratio, m, of solids to vapor (reproduced from Kieffer 1984). L, liquid; V, vapor; S, solid.
gas with that of a heavy-molecular-weight gas SF₆. SF₆ could provide a good analog for dusty gas behavior for m > 5.

Particles entrained in a gas also affect the thermodynamics of an ascending gas phase, as is illustrated in Figure 8b (compare with Figure 3). If no heat is transferred from the particles to the gas phase, the gas expands adiabatically and isentropically as discussed in Thermodynamic Processes and Appropriate Phase Diagrams for Analysis, above (m = 0 path in Figure 8b). In many cases, the initial conditions are such that adiabatic expansion would cause the fluid to expand from the vapor or supercritical initial state into the two-phase field (e.g., m = 0, or m = 0.2 in Figure 8b). However, if sufficient particles transfer heat to the vapor, the expansion is no longer nearly adiabatic and the thermodynamic paths veer toward the vapor field. The amount of heat available for transfer to the gas depends on the mass loading (m). For high values of mass loading (m > 10), the expansion tends to be more isothermal than isentropic, and two-phase conditions are avoided.

Choked versus Unchoked Flow

When a fluid flows through a pressure gradient in pipes or fractures, the flow velocity might exceed the sound speed. Normally, for pure liquids such situations do not arise in geologic settings because the sound speeds are a kilometer to a few kilometers per second.

However, the situation is very different for liquid-gas or gas-solid systems. Fluids easily attain the low velocities (meters to a few hundred meters per second) in a number of situations, particularly in geothermal and volcanic settings. In pipe, fracture, or nozzle flow, when the fluid velocity reaches sonic velocity, the flow chokes and mass flux is limited. In such settings, full decompression to the ambient pressure may occur downstream of the choke point, which is often underground (e.g., in plumes). It has been suggested that Old Faithful geyser is choked (Kieffer 1989); Plinian volcanic eruptions and steam blasts are choked (Buresti & Casarosa 1989, Mastin 1995); and that choked flow played a role in triggering long-period seismic events at Redoubt Volcano, Alaska (Morrissey & Chouet 1997), and in eruptions on Mars (Wilson & Head 2007). In such cases, flow in the conduit only partially decompresses erupting material, and the remaining decompression to ambient pressure occurs downstream of the choke point in an underexpanded (overpressured) plume (Kieffer 1982).

Determination of choked conditions is crucial for understanding the relation of plumes to the reservoirs and conduits that feed them. Transition from subsonic conduit flow to supersonic plume flow is complicated and includes many nonlinear processes.

DYNAMICS AND NUMERICAL SIMULATIONS:
EXAMPLES OF GAS-LIQUID SYSTEMS

Thermodynamic analysis as reviewed above is very useful in defining relations between initial and final states and for estimating flow properties given certain thermodynamic paths. But dynamical models are required when dealing with materials in motion for determining various properties (velocity, pressure, temperature, and density, etc.) of the material as functions of space and time. The coupling of the thermodynamic equations of state with conservation laws for motion results in complex equations that almost always require numerical solution. Compared with the number of single-component models, there are relatively few multiphase, multicomponent models, and they always contain many embedded assumptions. Here and in the next section, we illustrate several specific examples for both gas-liquid flows and gas-solid systems.
Fluid flow in fractures may be steady or not. Steady fracture flow is indicated by the discharges of liquid hot springs, or vapor/wet vapor fumaroles. However, two-phase flows may be unsteady for at least two reasons. They may break down internally into various flow regimes (homogeneous, bubbly, slug, annular, mist, etc.), which we do not consider here. They may also break down because heat and mass discharges are not balanced, for example, the cyclic phenomenon of geysering, which is observed both naturally and industrially (Rinehart 1980a,b; Jiang et al. 1995). Understanding sources of cyclicity in fractures that feed plumes, and separating these effects from atmospheric processes that may contribute to plume unsteadiness, is important for interpreting plumes and their relation to the subsurface.

We use the words vapor and gas very specifically in this section: gas means a noncondensible constituent of the liquid, and vapor means the vapor phase, which may contain gas (e.g., CO₂) in addition to the condensable phase (e.g., the H₂O). Gas-rich liquids can bubble in response to pressure or temperature changes at fluid temperatures well below the boiling point of pure water. For example, in an H₂O-CO₂ system (Figure 6b), at 1 bar pressure pure water boils at 100°C, but aqueous CO₂ solutions will bubble (degas, fizz, flash) at only 70°C (point R) if the CO₂ concentration is greater than 500 ppm. At 8 bar, pure water boils at 170°C, but if the CO₂ concentration is more than 4000 ppm, the solution bubbles at only 90°C at the same pressure (point Q). Unlike pure H₂O systems, the composition of the bubble is determined by gas solubility and the latent heat associated with partial pressure of H₂O is negligible.

The exsolution of gases from gas-water aqueous systems can cause hazardous engineering situations and the gas plays a crucial role in the low-temperature geysers. To analyze this complex system and to describe the flow behavior, it is necessary to develop a multiphase, multicomponent flow model, with mass transfer between the phases being considered.

Partial formulations of the flow equations have been provided for pure water systems with phase change or water-air mixtures without mass transfer at the two-phase interface (e.g., Wallis 1969c). However, for systems with dissolved gases, a source term must be introduced into the governing equations to account for the mass exchange between the phases and components. This was provided recently for geysering flow (Lu 2004, 2006).

Conservation Equations

For one-dimensional, time-dependent flow in a vertical pipe, the mass conservation equations for the liquid and gas phases are

\[ \frac{\partial}{\partial t} \left[ \rho_L (1 - \alpha) \right] + \frac{\partial}{\partial z} \left[ \rho_L (1 - \alpha) v_L \right] = S_{LG} \]  

and

\[ \frac{\partial}{\partial t} \left( \rho_G \alpha \right) + \frac{\partial}{\partial z} \left( \rho_G \alpha v_G \right) = -S_{LG}, \]

where \( \rho \), \( \alpha \), and \( v \) are density, void fraction, and velocity, respectively; \( t \) is time; and \( S_{LG} \) is the total mass exchange rate (including CO₂ and water vapor) between liquid and gaseous phases. Expressions for the mass exchange \( S_{LG} \) can be found in Lu (2004) and Lu et al. (2006). The

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1We avoid using boiling to describe this phenomenon because boiling usually refers to a rapid vaporization of a pure liquid, which typically occurs when a liquid is heated to its boiling point. We introduce the equivalent words bubbling, fizzing, or flashing.
momentum conservation equation is

\[
\frac{\partial P}{\partial z} = (\frac{\partial P}{\partial z})_G + (\frac{\partial P}{\partial z})_A + (\frac{\partial P}{\partial z})_F,
\]

(17)

where \((\frac{\partial P}{\partial z})_G\), \((\frac{\partial P}{\partial z})_A\), and \((\frac{\partial P}{\partial z})_F\) are the three components of pressure gradients of gravitation, acceleration, and friction, respectively (Wallis 1969b).

These equations differ from the equations for boiling flow in a pipe discussed by Wallis with regard to the mass exchange between the phases and components. Additional equations required to close the model include (a) a drift flux model for coupling the velocities of the gas and liquid phases for bubbly and slug flow regimes, such as that proposed by Zuber & Findlay (1965) or Wallis (1969a,d); (b) a temperature profile along the flow path or energy equation for determining the temperature profile; (c) a pressure distribution along the flow path at initial state; and (d) equations for determining the thermophysical and fluid properties.

Model Implementation and Verification: Te Aroha Geyser, New Zealand

For verification of this formulation, Lu et al. (2004, 2006) carried out experimental and numerical studies for flow in a vertical geothermal well at Te Aroha, on the north island of New Zealand. The well is 70 m deep and 10 cm in diameter. The temperature at the bottom of the well is approximately 90°C and approximately 70°C on the top. The fluid in the well is water with high levels of dissolved CO\(_2\) (~3000 ppm). The well can be shut down, but when it is fully opened to the atmosphere, the flow is not steady, but cyclic, with a small geyser several meters high erupting approximately every 12 min.

For the verification, the inlet boundary at the bottom was assumed to have a constant flux. The outlet boundary condition at the wellhead is defined by atmospheric pressure, 1 bar at sea level on Earth, i.e., the flow was not choked. The initial pressure distribution along the well is determined from the momentum balance, assuming that pure water is flowing up the well.

The thermodynamic processes that occur as the fluid flows from the bottom of the well (point Q) to the top (point R) are shown by the path Q-R in Figure 6b. As the fluid rises up the well, the decompression causes the CO\(_2\) solution to become supersaturated and so the CO\(_2\) comes out of solution. This degassing process forms a cyclic two-phase flow.

Close agreement was obtained between the analytical and measured results with regard to the major variables, such as void fraction and pressure variations at different depths (Figure 9a,b) of the well, cycle period, water level variations at the top part of the well, and flash point (the start of degassing) variations at the lower part of the well (Lu et al. 2005, 2006). Sensitivity studies showed the range of conditions under which the flow would and would not be steady.

The study showed that the supersaturated CO\(_2\) solution, instead of superheated water, causes bubble generation and intermittent flashing, which induces geysering in the well. The sensitivity studies showed that a larger inflow rate does not make a positive contribution in generating geysering flow. On the contrary, too large an inflow rate may cause the CO\(_2\)-driven geysering to disappear and be replaced by a steady gas-liquid two-phase flow.

Geysering is a unique phenomenon of transient two-phase flow with intermittent discharge characteristics that happen only when some key parameters have particular values that match one another. In pure H\(_2\)O systems, boiling conditions determine the conditions; in multicomponent systems, gas exsolution determines them.
An Example of How Gravity Conditions Influence the Behavior of CO$_2$-H$_2$O Aqueous Flow: Earth versus Mars

There is strong evidence for fracture-controlled paleofluid flow on Mars (Okubo & McEwen 2007). How would Te Aroha behave if it were erupting on Mars, which has approximately one-third the gravitational field of Earth? Would it be geysering flow?

If the Martian atmospheric pressure was lower than $\sim$1 bar when the flow occurred, the proper analog would be discharging terrestrial geothermal wells. The wellhead pressures of open flowing geothermal wells are often tens of bars. In this case, the flow is choked at the exit plane and a flared, noisy supersonic plume forms downstream of the exit plane (Armstead 1983, p. 123, plate 9). The noise results from both edge noise and internal shock waves in the tulip-shaped plume. By analogy, we can assume that flow from a fracture on Mars would be choked if the atmosphere were at low pressure unless the flow itself erodes the conduit (Kieffer 1982).

To isolate the effect of gravity alone, we assume that in the past the atmosphere may have been at pressures of approximately 1 bar. The key parameters determining flow rate are then gravity and inflow rate. If the conduit is the same length as that of Te Aroha (70 m), the reservoir pressure is approximately one-third of that on Earth. After a transient initial phase of approximately 2000 s, the geysering behavior stops and the flow becomes a continuous gassy-liquid discharge (Figure 9a,b).

![Figure 9](image_url)

Figure 9
Numerical simulation and comparison of terrestrial and Martian gravity conditions on the behavior of CO$_2$-H$_2$O aqueous flow: (a) pressure variations and (b) void fractions. Numerical simulation of pressure variations and void fractions on Mars (scenario 2, see text): (c) pressure variations and (d) void fractions.
curves marked with Mars). The void fraction is, however, greater for the Martian analog because of the lower gravitation. On Earth, gravitational pressure suppresses bubble formation below a certain level (the flash point, the start of degassing) that is changing during a cycle (Lu et al. 2005, 2006). The reduced hydrostatic pressure on Mars results in (a) more CO\textsubscript{2} released from the solution at different depths in an upward flow, and (b) the same mass of gases in fluid occupying more volume than on Earth and hence a bigger value of void fraction as shown in Figure 9b. As a result, the intermittent discharge (geysering) on Earth has turned into a continuous two-phase discharge on Mars.

However, if the geyser were extended to 210 m depth so that the reservoir has the same hydrostatic pressure as Te Aroha, a different phenomenon is observed (Figure 9b,c). The geysering phenomenon remains under Martian conditions, but the period changes to 37 min instead of 12 min. The hydrostatic pressure matches the given CO\textsubscript{2} concentration and the inflow rate and hence causes geysering to happen again. The hydrostatic pressures at 60 m, 90 m, 120 m, and 150 m on Mars are almost equal to those on Earth at 20 m, 30 m, 40 m, 50 m, respectively; i.e., the rate of change of hydrostatic pressure is approximately one-third of that on Earth. The time for the whole changing process in each cycle (period) mainly depends on the rate of change of hydrostatic pressure. The lower rate of change in pressure results in a longer cycle period. We conclude that geysering flow is as likely to have occurred on Mars as on Earth.

DYNAMICS AND NUMERICAL SIMULATIONS: EXAMPLES OF GAS-ICE SYSTEMS (CLATHRATES)

Because sublimation of ice in the single-component H\textsubscript{2}O system under terrestrial and planetary conditions has been the subject of much literature (see, for example, Brown & Cruikshank 1997, Brown et al. 1988, and references therein), we concentrate here on reviewing the dynamics of multicomponent ice-gas systems, namely, clathrates. No comprehensive mathematical or numerical model has yet been formulated for simulating the clathrate reservoir degassing process under the low-pressure and low-temperature conditions of other planets. Models have been developed only in the past few years for terrestrial degassing of clathrates. They are typically 1D, or axisymmetric, models for simulating methane hydrate reservoir dissociation and predicting natural gas production either by heating or depressurizing reservoir hydrates (Ji et al. 2001, Goel et al. 2001, Moridis et al. 2004, Sun et al. 2005). All models are for temperatures greater than 273 K, where the dissociation of the methane hydrate causes the hydrate to decompose into methane gas and water. Effects that are considered in the models include reservoir temperature and pressure, zone permeability, heat transfer into the decomposing zone, kinetics of decomposition, thermal parameters of the materials, and flow regime.

The only reservoir on Earth for which there are data to validate such models is the Messo Yakhi field in Siberia (Makogon 1997), and refinements of the available data in planetary settings are not sufficiently abundant to allow verification for extrapolations. More importantly, the terrestrial clathrates decompose from hydrate into gas plus liquid water, whereas the planetary clathrates are so cold that decomposition would be into gas plus ice, for which there are no formulations. To examine clathrate decomposition under cold, low-pressure conditions, we modified the model of Ji et al. (2001) to apply to decomposition of the clathrate into ice and gas. We chose this model because of its simplicity and because it is easy to use for a parametric study when extended to low-temperature conditions, but we emphasize that many effects not considered in the model need to be included in future studies.
Consider natural gas production from methane hydrate due to depressurization of a porous permeable clathrate zone by injection of a production well into the zone (Figure 10a) (see details in Ji et al. 2001). The governing equations of mass, momentum, and energy, including heat transfer and the effects of throttling (isenthalpic process), were linearized by Ji et al. (2001) to give a set of self-similar solutions for temperature and pressure distributions in the reservoir. This results in a system of coupled algebraic equations for the location of the decomposition front expressed by
the distance of the decomposition front from the well, \( l(t) \), and the temperature (\( T_d \)) and pressure (\( P_d \)) at the front. The distance from the well \( l(t) \) is

\[
l(t) = \sqrt{\gamma t},
\]

(18)

where \( \gamma \) is a constant in \( \text{m}^2/\text{s} \).

For a given reservoir pressure and temperature and the pressure at the well, \( T_d, P_d \), and \( \gamma \) can be determined through an iterative scheme by simultaneously satisfying three equations: (a) equilibrium pressure and temperature relation on the decomposition front (i.e., \( T_d = P_d \) decomposition curve), (b) linearized energy equation at the decomposition front, and (c) the combined equation of momentum and mass balances at the decomposition front (Ji et al. 2001). From \( T_d, P_d \), and \( \gamma \), the pressure and temperature distributions in the reservoir are calculated from the self-similar solutions of the linearized momentum and energy equations by satisfying the corresponding boundary conditions.

For Enceladus, the question is, “Can this process produce the observed mass fluxes?” The volumetric production rate \( Q_v \) (degassing rate) and its time dependence are (Ji et al. 2001)

\[
Q_v(t) = \frac{k_1 P_d^2 - P_g^2}{\mu_g} \frac{1}{\text{erf} \alpha_1} \frac{1}{2\sqrt{\pi} \chi_1 t},
\]

(19)

which depends on the phase permeability of gas in zone 1 (dissociated hydrate zone) \( k_1 \), the pressure of the gas in the fracture \( P_g \) is the pressure of the gas in the well, the viscosity of the gas, \( \mu_g \). Two variables that appear here are mostly introduced for ease of calculation:

\[
\chi_1 = \frac{k_1 P_g}{\Phi_1 \mu_g}
\]

(20a)

and

\[
\alpha_1 = \frac{\sqrt{\gamma}}{\sqrt{4 \chi_1}},
\]

(20b)

one of which includes the porosity on the reservoir, \( \Phi_1 \). Sensitivity of the natural gas production from hydrate by depressurization to variations of reservoir parameters can be found in Ji et al. (2001). The mass flux \( Q_m(t) \) (degassing rate) of the gas mixture is then \( Q_m(t) = Q_v(t)/\rho_g \).

**Model Implementation: Plumes on Enceladus**

The general principles of clathrate degassing by depressurization for Enceladus were illustrated by Kieffer et al. (2006) using an extension of the Ji et al. (2001) model. The model was extended by Fortes (2007) and Halevy & Stewart (2008). The gas composition was modified to reflect the mixed gases of the plume, using a simplified mixing law. Decomposition into liquid + gas assumed by Ji et al. was changed to reflect decomposition into ice + gas. The degassing fluxes \( Q_m \) were calculated for two plausible reservoirs: one shallow and cool (5 km, 5 bar, 190 K) and one deeper and warmer (40 km, 41 bar, 250 K) (Figure 10b,c). The pressure in the fracture, \( P_g \), was assumed to be half of the reservoir pressure based on the assumption that when gas flows in complicated networks, pressure conditions are commonly determined by narrow constrictions where the flow chokes to sonic conditions of pressure, temperature, and flow velocity (Mach number = 1) (Kieffer 1989). Sensitivity studies, and the assumed role of entrained ice particles, were considered.

The time-variable flux for these, shown in Figure 10b,c, is of the order of that measured in the plume, \( 10^{-7} \) to \( 10^{-6} \) kg s\(^{-1}\) m\(^{-2}\). The rapid time variability implied by the process (opening and closing of small fractures) is similar to the time scale of variabilities observed by the instruments on Cassini (<1 month). Much refinement of models needs to be done as data provide more...
constraints on interior processes on Enceladus (Kieffer & Jakosky 2008), but results from these calculations suggest that degassing of clathrates on Enceladus can produce gases at roughly the rates observed.

**SUMMARY POINTS**

1. Mixed phases in a single-component system can have complicated properties, such as sound speed in boiling liquids or aerosols. These properties complicate fluid motions. The flow of H$_2$O as a pure liquid phase or a pure vapor phase alone in a conduit is much simpler than the flow of boiling or gassy fluid, which can choke at sonic velocity, and can develop flow instabilities such as geysering, under certain conditions of heat and mass transport. Serious errors can be made by assuming that a partial pressure due to an H$_2$O component is equal to the total pressure of a mixture.

2. Multiphase, multicomponent systems are inherently more complicated than multiphase, single-component systems. Counterintuitive phenomena may occur, such as gases being more soluble in H$_2$O ice (clathrate) than in H$_2$O liquid. Even phenomena that superficially appear to be similar can have significant differences when examined in detail. Geysering, for example, in a cool CO$_2$-driven system is induced by a periodic bubble generation that is caused not by the superheated water, as it is in single-component systems, but by the supersaturated CO$_2$ solution.

**FUTURE ISSUES**

1. The differences between multiphase, multicomponent systems and multiphase, single-component systems need to be kept in mind in quantitative interpretations of multicomponent systems; for example, in efforts to infer reservoir characteristics on the planets or moons from surface or plume observations. Resolution of the controversy about the nature of the reservoir feeding Enceladus’ plume depends on accounting for all of the gas components (CO$_2$, N$_2$, CH$_4$, plus trace simple organics) as well as the phases.

2. Creation of a thermodynamic database that would allow the exploration of the various thermodynamic processes discussed in the first part of this paper and the various dynamic processes discussed in the latter part is essential for understanding the processes in the colder planetary settings of Mars and of some moons. This includes the standard thermodynamic properties and their derivatives, the properties of metastable H$_2$O at temperatures below 0°C, the standard thermodynamic properties of clathrate phases, as well as data for clathrates in cold saline environments.

3. Extension and development of degassing models to colder planetary conditions is much needed, as are kinetic data.

4. Thinking and teaching about multicomponent systems is needed to educate future Earth and planetary scientists about the similarities and dissimilarities of multicomponent and single-component systems. The use of single-component approximation can lead to conclusions that are not only quantitatively wrong, but also qualitatively wrong. Degassing, depressurizing, and flow instabilities occur for fundamentally different reasons in the two systems.
DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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Errata

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