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Energetics of gas-driven limnic and volcanic eruptions

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Abstract

This paper lays the foundation for the rigorous treatment of the energetics of gas exsolution from a gas-containing liquid, which powers gas-driven volcanic and limnic eruptions. Various exsolution processes (reversible or irreversible, slow or rapid) are discussed, and the maximum amount of kinetic energy derivable from a reversible gas exsolution process is obtained. The concept of dynamic irreversibility is proposed for discussing the kinetic energy available from irreversible gas exsolution processes. The changes of thermodynamic properties during gas exsolution processes are derived. Density–pressure relations for gas–liquid mixtures are presented, including empirical relations for irreversible gas exsolution. The energetics of gas-driven eruptions through both fluid and rigid media, including the role of buoyancy and the role of magma chamber expansion work, are investigated. For reversible processes, the energetics can be used to discuss the dynamics of gas-driven eruptions, leading to maximum erupting velocities and maximum eruptible fractions. For irreversible processes, empirical relations and parameters must be employed. The exit velocities of the Lake Nyos eruption and the 18 May 1980 eruption of Mount St. Helens are modeled by incorporating possible irreversibility. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

A gas-driven eruption is powered by the exsolution of dissolved gas or gases in a liquid, such as volcanic eruptions driven by H₂O exsolution from magma (Self et al., 1979; Wilson et al., 1980) and limnic eruptions driven by CO₂ exsolution from water (Kling et al., 1987; Sigurdsson et al., 1987; Sigvaldason, 1989; Sabroux et al., 1990; Zhang, 1996). The violence of such an eruption is caused by the large amount of kinetic energy that is ultimately harvested from the thermal energy stored in the initially gas-saturated liquid. As a gas-saturated liquid is decompressed, it vesiculates and the bubbly liquid system expands. Under the right conditions, the volume expansion causes rapid upward acceleration, leading to an

explosive eruption. It is hence of great interest to investigate the general aspects of thermodynamics and energetics of gas exsolution from a liquid. Some volcanic eruptions are not gas-driven. For example, gas exsolution is often not critical in basaltic eruptions (MORB and Hawaiian type eruptions) because basaltic melts typically contain low H₂O and CO₂. These eruptions are not the subject of this paper.

Because gas-driven limnic and volcanic eruptions are rapid and large in scale compared to heat diffusion distance, heat loss from the bubbly liquid during an eruption is expected to be negligible and the process is roughly adiabatic. Therefore, this paper concentrates on the energetics of the adiabatic gas exsolution from a liquid, including: (1) the amount of kinetic energy derivable from the process; and (2) thermal effects, to lay the foundation for the rigorous treatment of the energetics of gas-driven eruptions. My treatment from the energetics point of view also leads to some simple

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Nomenclature

a	Activity of a component (subscript) in a phase (superscript)
C	Concentration in kg m^{-3} . $C = \rho$ if there is only one component in the phase
\bar{C}	Molar isobaric heat capacity
D	Diffusivity
f	The ratio of mass of the entrained liquid to that of the original erupting gas–liquid
g	Acceleration due to Earth's gravity
H & \bar{H}	Enthalpy and partial molar enthalpy
I_d	Dynamic irreversibility defined in Eq. (2b)
KE	Kinetic energy
\bar{KE}	Kinetic energy per unit mass
k_1 & k_2	Constants defined in Eq. (21). k_1 is dimensionless
k_3 & k_4	Constants defined in Eq. (23). k_3 is dimensionless
k_5 & k_6	Dimensionless constants defined in Eq. (27)
n	Number of moles
P	Pressure
PE	Potential energy
\bar{PE}	Potential energy per unit mass
R	Gas constant in $\text{J kg}^{-1} \text{K}^{-1}$. R is $461.5 \text{ J kg}^{-1} \text{K}^{-1}$ for H_2O , and $188.9 \text{ J kg}^{-1} \text{K}^{-1}$ for CO_2
R_d	Dynamic reversibility defined in Eq. (2a)
S & \bar{S}	Entropy and partial molar entropy
T	Temperature
U	Internal energy
u	Erupting velocity
V	Volume
W	Work done by the system
X	Mole fraction of a component
α	Isobaric thermal expansivity
δ	The mass fraction of the gas phase
ϵ	A coefficient defined in Eq. (16)
κ	Heat (or thermal) diffusivity
λ	Ostwald solubility coefficient of a gas in a liquid
ρ	Density, or density of the gas–liquid mixture if without super or subscript
Z	$\equiv P^g V / (RT)$; it characterizes the nonideality of the gas ($Z = 1$ for an ideal gas)

Subscript

A	Component A (volatile). A1 and A2 are used to refer to two volatile components
B	Component B (nonvolatile)
max	Maximum
0	Initial state
s	At saturation
t	Total amount in the liquid and gas phases

Superscript

g	Gas phase
l	Liquid phase
0	Pure standard state

equations describing the dynamics of eruptions. These dynamic equations are similar to the equations in and are alternatives to earlier work in modeling eruption dynamics (e.g. Sparks, 1978; Wilson et al., 1980; Jaupart and Tait, 1990).

In this paper, the kinds of gas exsolution processes will be discussed first and the concept of dynamic reversibility is introduced. Then the changes of thermodynamic properties during an eruption are derived. Then the equations of state for gas–liquid mixtures are obtained for several cases, including the case for two volatile components. Using these results, the energetics of both types of gas-driven eruptions (CO_2 -driven limnic eruptions and H_2O -driven volcanic eruptions) are investigated. Finally, disequilibrium between the gas and liquid phases are modeled and applied to Lake Nyos eruption and the 1980 Mount St. Helens eruption.

2. Thermodynamics of gas exsolution from a liquid

2.1. Kinds of gas exsolution processes

Gas exsolution from a liquid can be accomplished in many ways. One way is through formation of bubbles that ascend relatively slowly to the surface and escape from the liquid without carrying liquid droplets. This will be referred to as degassing, as in fumaroles and in beer and soft drinks. This slow degassing process is not considered here. Following Zhang et al. (1997), an eruption is defined as the ejection of a significant amount of liquid from the system. Even though there is always some relative motion between the liquid and gas phases, the focus in this paper is on the uniform exsolution of a gas from a liquid without significant flow of one phase relative to the other. That is, on a scale larger than individual gas bubbles or liquid drops but smaller than the diameter of the erupting conduit, the gas–liquid mixture is regarded as uniform, either a bubbly liquid (in which the liquid phase is continuous and bubbles are not), or a drop-laden or dusty gas (in which the gas phase is continuous). This characteristic will be referred to as uniform gas exsolution.

A uniform gas exsolution process can be rapid or slow, reversible or irreversible. From a thermodynamic

point of view, slowness or rapidness of a process is irrelevant, only the reversibility or irreversibility is important. However, from a dynamic point of view, whether the process is slow or rapid is very important because the amount of kinetic energy obtained from a uniform gas exsolution process is crucial to understanding explosive eruptions. Slow processes, whether reversible or not, do not generate kinetic energy that is important to gas-driven eruptions.

In an explosive eruption due to gas exsolution from a liquid, the pressure increases with depth as $dP = \rho(g + a) dh$ where P is the pressure, ρ the density of the gas–liquid mixture, g the acceleration due to Earth's gravity, a the upward acceleration of the erupting mass, and h the depth. That is, the total system pressure consists of two parts: (1) the static pressure owing to the outside pressure (such as atmospheric) and the overlying weight of the column; and (2) the acceleration pressure (similar to the dynamic pressure, e.g. White, 1991) owing to the acceleration of the gas–liquid mixture. The acceleration pressure increases the kinetic energy of the system. In a slow process, either the acceleration pressure is negligible or the viscosity is very high. In a rapid process, the acceleration pressure is significant. That is, only when the total system pressure is greater than the static surrounding pressure, is kinetic energy produced. The greater the difference, the greater the kinetic energy. The following examples illustrate several cases of rapid or slow, and reversible or irreversible processes:

(1) A classical reversible process is a slow exsolution process in which the static surrounding pressure is always roughly the same as the system pressure and the system itself is always at equilibrium. For gas exsolution from a liquid, if the static surrounding pressure decreases very slowly due to slow ascent of the bubbly magma, gas bubbles would grow slowly and the gas and liquid phases in the system would be in equilibrium (no concentration gradient of the volatile component in the liquid away from bubble walls). The result is a classical reversible process, producing no kinetic energy. A reversible adiabatic process is isentropic.

(2) The general conditions for a reversible adiabatic gas exsolution process ($dS = 0$) are: (a) the system pressure equals the static surrounding pressure plus

the acceleration pressure; (b) the gas and liquid phases are in bulk equilibrium (not just surface equilibrium); and (c) viscous dissipation is negligible. Hence, one may conceive a rapid gas exsolution process that is roughly reversible. For a rapid decrease of the static surrounding pressure in a gas–liquid system, if the number density of bubbles is high or the diffusivity of the gas component in the liquid is large (such as CO₂ in water), diffusion may be able to maintain bulk equilibrium between the gas and liquid phases (i.e. no concentration gradients from bubble wall to the interior of the liquid). If furthermore the liquid viscosity does not impede bubble growth and flow ascent, the gas exsolution process would be reversible. Such a reversible rapid exsolution process due to rapid decrease in the surrounding pressure will be referred to as a dynamic reversible process, to distinguish it from the slow reversible process above. A dynamic reversible process generates a significant amount of kinetic energy.

(3) A very slow exsolution process is not necessarily reversible. For example, exsolution of H₂O from a hydrous rhyolitic glass at relatively low temperatures (such as 550°C) is slow (that is, bubble growth is slow) and irreversible. If a piece of hydrous rhyolitic glass containing 2.0% H₂O is heated to 550°C at 1 bar (equivalent to decompressed to 1 bar at 550°C), bubbles nucleate and grow slowly and the glassy liquid deforms slowly to accommodate bubble growth. The slowness is due to the high viscosity of the liquid ($\sim 10^{10}$ Pa s) and small diffusivity of the gas component in the liquid. This process is irreversible because bubble growth occurs in a strong concentration gradient and because there is viscous flow. This process will be referred to as “dynamically completely irreversible” since it is irreversible and since no kinetic energy is generated. If the process is adiabatic, entropy of the system increases. Even though the determination of entropy increase is not straightforward for this process, the enthalpy change for an adiabatic and dynamically completely irreversible process can be determined as follows. Starting from the initial equilibrium state (P_0 , T_0 , V_0 , liquid, no gas phase), accomplish the process in two steps: step 1 is to release the system pressure adiabatically from P_0 to P without any exsolution (due to slow diffusion) so that the system changes to (P , T_1 , V_1 , liquid, no gas phase). For step 1, $dH = (\partial H / \partial P)_S dP = V dP$, where

H is the enthalpy. Step 2 is for the system to adiabatically and slowly (hence complete dynamic irreversibility) expand through slow bubble formation and growth to its final state (P , T , V , bubbly liquid). For step 2, $dH = d(U + PV) = \delta Q + \delta W + P dV + V dP = (P - P_{\text{sur}}) dV + V dP = 0$ because $\delta Q = 0$, $\delta W = -P_{\text{sur}} dV$, $P = P_{\text{sur}}$ and $dP = 0$. Therefore, the second step of this adiabatic process is enthalpic, which can be used to determine the final temperature of the system. The total enthalpy change in the process is the same as the enthalpy change in the first step:

$$\Delta H = V_0^l (P - P_0), \quad (1)$$

where V_0^l is the initial liquid volume (see Nomenclature for notations).

(4) All gas-driven eruptions are expected to be irreversible to some degree owing to the presence of concentration gradients and viscous dissipation but not dynamically completely irreversible. As the static surrounding pressure decreases, bubbles grow rapidly but typically not rapid enough to maintain bulk equilibrium between the liquid and gas phases. The rapid growth of bubbles leads to volume expansion and density decrease, resulting in rapid upward motion (an eruption) of the gas–liquid mixture and an increase in both kinetic and potential energies. The kinetic energy obtained from such a process is between that of cases (2) and (3) above. That is, other conditions being equal, the maximum amount of kinetic energy is derived from a dynamically reversible process.

From the above discussion of different types of processes, I propose to define dynamic reversibility (R_d) and irreversibility (I_d) as follows:

$$R_d = KE / KE_{\text{max}}, \quad (2a)$$

$$I_d \equiv 1 - R_d = 1 - KE / KE_{\text{max}}, \quad (2b)$$

where $0 \leq R_d \leq 1$, KE is the kinetic energy derived from a given process, and KE_{max} is the maximum kinetic energy derivable from the reversible process from the same initial state to the same final pressure. For case (1) above (a slow reversible process), the dynamic reversibility is undefined because both KE and KE_{max} are zero. For case (2) above (a dynamic reversible process), $R_d = 1$ and $I_d = 0$. For case (3) above (a dynamically completely irreversible process),

$R_d = 0$ and $I_d = 1$. For case (4) above (a general dynamic irreversible process), I_d is between 0 and 1. The above definition of dynamic irreversibility quantifies the relation between dynamic irreversibility and kinetic energy generated in a gas-driven eruption.

2.2. General thermodynamic considerations

Consider a binary system in which A is the volatile component and B is assumed to be perfectly non-volatile. That is, the gas phase is purely A. There are two phases in the system: gas and liquid. The temperature is assumed to be uniform in the system but it may vary as a function of time. That is, the gas and liquid phases are assumed to be in thermal equilibrium since bubbles in liquid (or drops in gas) are small and since the Lewis number $Le = D/\kappa \ll 1$ where D is the chemical diffusivity of the gas component in the liquid and κ is the diffusivity of heat. The variation of the liquid density with volatile concentration, temperature and pressure is ignored when considering the density of the bubbly liquid.

Consider a gas-saturated liquid solution plus an equilibrium gas phase at an initial state $(T_0, P_0, n_{A,0}^l, n_{B,0}^l, n_{A,0}^g)$ where $n_{A,0}^l$ is the initial number of moles of A in the liquid (subscript 0 means initial; subscript A or B means component A or B; superscript l or g means the liquid or gas phase; and superscript 0 will be used to indicate the pure standard state). The initial concentration of A in the liquid is expressed as $C_{A,0}^l$ in kg m^{-3} . The concentration can also be expressed as molar fraction $X_{A,0}^l$. The final state is $(T, P, n_A^l, n_{B,0}^l, n_A^g)$ with $n_{A,0}^l + n_{A,0}^g = n_A^l + n_A^g = n_{A,t}$. Using entropy as an example, the change in a thermodynamic property can be found as follows:

$$\begin{aligned} \Delta S &= S(T, P, n_A^g, n_A^l, n_{B,0}^l) - S(T_0, P_0, n_{A,0}^g, n_{A,0}^l, n_{B,0}^l) \\ &= n_A^g \bar{S}_A^g(T, P) + n_A^l \bar{S}_A^l(T, P, X_A^l) + n_{B,0}^l \bar{S}_B^l(T, P, X_B^l) \\ &\quad - n_{A,0}^g \bar{S}_A^g(T_0, P_0) - n_{A,0}^l \bar{S}_A^l(T_0, P_0, X_{A,0}^l) \\ &\quad - n_{B,0}^l \bar{S}_B^l(T_0, P_0, X_{B,0}^l) \end{aligned}$$

$$\begin{aligned} &= n_A^g [\bar{S}_A^g(T, P) - \bar{S}_A^l(T, P, X_A^l)] - n_{A,0}^g [\bar{S}_A^g(T_0, P_0) \\ &\quad - \bar{S}_A^l(T_0, P_0, X_{A,0}^l)] + n_{A,t} [\bar{S}_A^l(T, P, X_A^l) \\ &\quad - \bar{S}_A^l(T_0, P_0, X_{A,0}^l)] + n_{B,0}^l [\bar{S}_B^l(T, P, X_B^l) \\ &\quad - \bar{S}_B^l(T_0, P_0, X_{B,0}^l)]. \end{aligned} \quad (3)$$

The terms $n_A^g [\bar{S}_A^g(T, P) - \bar{S}_A^l(T, P, X_A^l)]$ and $n_{A,0}^g [\bar{S}_A^g(T_0, P_0) - \bar{S}_A^l(T_0, P_0, X_{A,0}^l)]$ represent the entropy change owing to the exsolution of component A from the liquid under isothermal, isobaric, and equilibrium conditions. Therefore, they can be written in terms of exsolution (vaporization) enthalpy. For example,

$$\bar{S}_A^g(T, P) - \bar{S}_A^l(T, P, X_A^l) = \frac{\bar{H}_A^g(T, P) - \bar{H}_A^l(T, P, X_A^l)}{T}. \quad (4)$$

Since the gas phase is assumed to be pure A, P is the same as the partial pressure of A and X_A^l is a function of T and P . Hence the above difference in the partial molar entropy is a function of T and P only. If the gas is ideal (hence enthalpy of the gas is independent of pressure) and the liquid phase is an ideal mixture (hence no mixing enthalpy), Eq. (4) can be simplified as:

$$\begin{aligned} \bar{S}_A^g(T, P) - \bar{S}_A^l(T, P, X_A^l) &\approx \frac{\bar{H}_A^{g,0}(T) - \bar{H}_A^{l,0}(T, P)}{T} \\ &= \frac{\Delta \bar{H}_{\text{ex}}^0(T, P)}{T}, \end{aligned} \quad (5)$$

where $\Delta \bar{H}_{\text{ex}}^0$ is the standard-state molar enthalpy of exsolution (or evaporation) of component A. Note that mixing entropy does not enter into Eq. (5), nor does the pressure dependence of gas entropy. Hence, the dependence of the exsolution entropy and enthalpy on pressure is due to: (1) the pressure dependence of the molar enthalpy of the gas phase, which is weak (e.g. at 800°C , enthalpy of H_2O fluid decreases by $8.4 \text{ J mol}^{-1} \text{ bar}^{-1}$ at $P < 500 \text{ bar}$, Burnham et al., 1969); and (2) the pressure and compositional dependence of the partial molar enthalpy of the dissolved gas component in the liquid, which is also expected to be weak. Therefore, the exsolution enthalpy is not expected to depend strongly on pressure, especially at low

pressures. The specific case for the exsolution enthalpy of water (a multi-species component) from silicate melts, and its pressure dependence, will be discussed elsewhere.

The terms $\bar{S}_A^l(T, P, X_A^l) - \bar{S}_A^l(T_0, P_0, X_{A,0}^l)$ and $\bar{S}_B^l(T, P, X_B^l) - \bar{S}_B^l(T_0, P_0, X_{B,0}^l)$ in Eq. (3) represent the entropy variation in the liquid phase as a function of temperature, pressure and composition. They can be simplified as follows:

$$\begin{aligned} \bar{S}_B^l(T, P, X_B^l) - \bar{S}_B^l(T_0, P_0, X_{B,0}^l) &= [\bar{S}_B^l(T, P, X_B^l) - \bar{S}_B^l(T, P_0, X_B^l)] + [\bar{S}_B^l(T, P_0, X_B^l) \\ &\quad - \bar{S}_B^l(T, P_0, X_{B,0}^l)] + [\bar{S}_B^l(T, P_0, X_{B,0}^l) \\ &\quad - \bar{S}_B^l(T_0, P_0, X_{B,0}^l)] \\ &= (P_0 - P)\alpha_B^l \bar{V}_B^l + \bar{C}_{B,0}^l \ln \frac{T}{T_0} + R \ln \frac{a_{B,0}^l}{a_B^l}, \end{aligned} \quad (6)$$

where α is the isobaric thermal expansivity, \bar{C} is the molar isobaric heat capacity, a the activity (the dependence of the activity on temperature has been ignored), and R the gas constant in $\text{J mol}^{-1} \text{K}^{-1}$. Replacing Eqs. (5) and (6) into Eq. (3), the expression for S is:

$$\begin{aligned} \Delta S \approx & \left[n_A^g \frac{\Delta \bar{H}_{\text{ex}}^0(T, P)}{T} - n_{A,0}^g \frac{\Delta \bar{H}_{\text{ex}}^0(T_0, P_0)}{T_0} \right] \\ & + (n_{A,t} \bar{C}_A^l + n_{B,0}^g \bar{C}_B^l) \ln \frac{T}{T_0} \\ & + \left(n_{A,t} R \ln \frac{a_{A,t}^l}{a_A^l} + n_{B,0}^l R \ln \frac{a_{B,0}^l}{a_B^l} \right) + (P_0 - P) \\ & \times (n_{A,t} \alpha_A^l \bar{V}_A^l + n_{B,0}^l \alpha_{B,0}^l \bar{V}_B^l). \end{aligned} \quad (7)$$

The last term in Eq. (7) is often negligible (i.e. the effect of thermal expansion and compression of the liquid is often negligible). The mixing terms involving the logarithm of activity ratios can be rewritten as $\Delta G_{\text{mix}}/T$ (that is nonzero even for ideal mixtures) where G is the Gibbs free energy, not $\Delta H_{\text{mix}}/T$ (that is zero for ideal mixtures) as in Sahagian and Proussevitch (1996). The differential form of the above

equation is:

$$\begin{aligned} dS = & d\left(\frac{n_A^g \Delta \bar{H}_{\text{ex}}}{T} \right) + \frac{n_{A,t} \bar{C}_A^l + n_{B,0}^l \bar{C}_B^l}{T} dT \\ & + \left[n_{A,t} \left(\frac{\partial \bar{S}_A^l}{\partial X_A^l} \right)_{P,T} - n_{B,0}^l \left(\frac{\partial \bar{S}_B^l}{\partial X_B^l} \right)_{P,T} \right] dX_A^l \\ & - (n_{A,t} \alpha_A^l \bar{V}_A^l + n_{B,0}^l \alpha_B^l \bar{V}_B^l) dP. \end{aligned} \quad (8)$$

For a reversible adiabatic process, $dS = 0$, i.e. the right-hand side of Eqs. (7) and (8) is zero, which can be used to calculate the final T from T_0 , P_0 , and P .

Following the same procedure, ΔH can be found:

$$\begin{aligned} \Delta H \approx & n_A^g \Delta \bar{H}_{\text{ex}}(T, P) - n_{A,0}^g \Delta \bar{H}_{\text{ex}}(T_0, P_0) + (n_{A,t} \bar{C}_A^l \\ & + n_{B,0}^g \bar{C}_B^l)(T - T_0) + V_0^l(1 - \alpha_0^l T_0)(P - P_0). \end{aligned} \quad (9)$$

The differential form is:

$$\begin{aligned} dH \approx & d[n_A^g \Delta \bar{H}_{\text{ex}}(T, P)] + [n_{A,t} \bar{C}_A^l + n_{B,0}^g \bar{C}_B^l] dT \\ & + V_0^l(1 - \alpha_0^l T_0) dP. \end{aligned} \quad (10)$$

The change in the internal energy of the system can be found to be:

$$\Delta U = \Delta H - (PV - P_0 V_0). \quad (11)$$

The work done by the system is:

$$W = \int P_{\text{sur}} dV, \quad (12)$$

where P_{sur} is the surrounding pressure (not necessarily the same as the system pressure). For an adiabatic process, $W = -\Delta U$. The work done by the system is related to the kinetic energy.

Expressions (7), (9), (11) and (12) for ΔS , ΔH , ΔU , and W are general expressions and independent of the type of processes (whether the processes are reversible or not). They depend on both T and P . For a specific process, there is a relation between T and P . Hence given the final P , the values of T , ΔS , ΔH , ΔU , and W can be calculated if the molar exsolution enthalpy, heat capacity, mixing entropy and the solubility relation are known.

Table 1 summarizes equations for calculating

Table 1

Thermodynamics of adiabatic gas exsolution from a solution. Initial saturation state: (T_0 , P_0 , C_0); final equilibrium state: (T , P , C); no initial gas phase. Given P , find V (or $V = V - V_0$) and T (or $T = T - T_0$), S , H , U , and W

1. Regardless of the process (reversible or irreversible):

$$V = \frac{M^l}{\rho^l} + \frac{(n_A^g + n_B^g)RT}{P}$$

$$\Delta V = V_0(\lambda_0 \frac{P_0}{P} \frac{T}{T_0} - \lambda) \text{ by ignoring component B in the vapor}$$

$$\Delta V \approx \lambda V_0(\frac{P_0}{P} - 1) \text{ if } \lambda \text{ is constant and } T/T_0 \approx 1$$

$$\Delta S = (\sum_i n_{i,0}^l C_{P,i}^l) \ln \frac{T}{T_0} + \sum_i n_i^g \frac{\Delta \bar{H}_{ex,i}^0(T, P)}{T} + R \sum_i n_{i,0}^l \ln \frac{a_{i,0}^l}{a_i^l} + (P_0 - P) \sum_i n_{i,0}^l \alpha_{P,i}^l \bar{V}_i^l,$$

$$\Delta H = C_{P,0}^l(T - T_0) + \sum_i n_i^g \Delta \bar{H}_{ex,i}^0(T, P) + V_0^l(1 - \alpha_0^l T_0)(P - P_0).$$

$$\Delta U = \Delta H - (PV - P_0 V_0) = -W = -P_{sur} dV.$$

2. Reversible process (either slow or rapid):

T is solved from: $\Delta S = 0$.

$$W_{rev} \approx \lambda P_0 V_0 \ln \frac{P_0}{P} \text{ assuming } \lambda \text{ is constant in the temperature and pressure range}$$

$$W_{rev} \approx \lambda_0 P_0 V_0 \ln \frac{P_0}{P} - (k_2 P_0)^{1/2} V_0 [1 - (P/P_0)^{1/2}]$$

$$\text{for } \lambda = k_1 + (k_2/P)^{1/2}.$$

3. Dynamically completely irreversible process ($R_d = 0$):

$$T \text{ is solved from: } \Delta T = -n_A^g \Delta \bar{H}_{ex}^0(T, P)/C_{P,0}^l.$$

$$W = P \Delta V \approx V_0(\lambda_0 P_0 T/T_0 - \lambda P).$$

$$\Delta S > 0.$$

Subscripts indicate component A, B, or i ; superscripts indicate the phase (l, liquid; g, gas). Work done by the system is W . Subscript 0 indicates the initial state. Superscript 0 indicates the standard state. The heat capacity of the whole liquid solution is C_P^l . $\Delta \bar{H}_{ex}$ is the molar exsolution enthalpy (19.3 kJ mol⁻¹ for CO₂ exsolution from water). Activity of a component is a . Thermal expansion coef-

the thermodynamic properties of the final state and the total work done by the system. Given initial conditions, a process (providing a relation between final T and P), and final P , the general procedure for calculating the final T and changes in thermodynamic properties is as follows. Give a unit mass of a gas–liquid mixture (such as one kg). Guess

a final temperature. Then calculate solubility coefficient, and the molar exsolution enthalpy of A. The concentration of A in the liquid is then calculated from the solubility coefficient. Next the total amount of A in the gas phase can be calculated from a mass balance. Then ΔS and ΔH can be calculated. For a reversible adiabatic process, vary T so that $\Delta S = 0$ and the resultant state is the final state. For a completely dynamically irreversible process, vary T so that $\Delta H = V_0^l(P - P_0)$ (Eq. (1)), which is equivalent to:

$$n_A^g \Delta \bar{H}_{ex}(T, P) - n_{A,0}^g \Delta \bar{H}_{ex}(T_0, P_0) + (n_{A,t}^l \bar{C}_A^l + n_{B,0}^g \bar{C}_B^l) \times (T - T_0) \approx 0, \quad (13)$$

according to Eq. (9). Knowing the final T , all other thermodynamic properties of the final state can be calculated. Some worked numerical examples for calculation of temperature and thermodynamic functions are given below.

Worked example 1, limnic eruption of Lake Nyos.

Assume that the bottom water (208 m depth) was initially saturated with CO₂. Therefore $P_0 = 2.13$ MPa, $P_{out} = 0.09$ MPa, $T_0 = 296$ K. Assume $\Delta \bar{H}_{ex}^{CO_2} = 19.3$ kJ mol⁻¹, $C_{P,0}^l = 4.184$ kJ kg⁻¹ K⁻¹, $\alpha_{P,0}^l = 0.00023$ K⁻¹, and $n_{A,0}^g = 0$. Evaporation of water is ignored. If the process is reversible, the final T is 291.7 K with $\Delta T = -4.3$ K. The total work done by the system ($-\Delta U$) is 5.7 kJ kg⁻¹. This work includes the expansion work and the work done to increase the kinetic energy of the system (which could reach 4.1 kJ kg⁻¹; Zhang, 1996). To examine the relative importance of each term in Eq. (7), the first term (brackets) on the right-hand side of Eq. (7) is -61.1, the second term 47.4, the third mixing term 13.2, and the last term 0.47 J kg⁻¹ K⁻¹. Hence the last term is not important but the mixing terms are significant. If the process is completely dynamically irreversible, using Eq. (13), the final T would be 292.7 K with $\Delta T = -3.3$ K. The total work done by the system would be 1.6 kJ kg⁻¹ and there would be no kinetic energy. The entropy of the system increases by 14.0 J kg⁻¹ K⁻¹.

Worked example 2, CO₂ exsolution from water in Experiment #89 of Zhang et al. (1997). $P_0 = 496$ kPa, $P_{out} = 11$ kPa, and $T_0 = 295.35$ K. If the process is reversible, the final T is found to be 294.24 using

Eq. (7) with $\Delta T = -1.1$ K. The work done by the system is 1.7 kJ kg^{-1} and kinetic energy is generated. If the process is completely dynamically irreversible, the final T is 294.54 K using Eq. (13). The work done by the system is 0.4 kJ kg^{-1} and no kinetic energy is generated. The entropy increases by $4.3 \text{ J kg}^{-1} \text{ K}^{-1}$.

2.3. Equation of state for a gas–liquid mixture during reversible exsolution

The equation of state of a gas–liquid mixture, i.e. the dependence of ρ (the density of a gas–liquid mixture) on P (the system pressure) and T (that depend on P), is essential for the calculation of volume work done by a gas–liquid system through gas exsolution. The temperature effect on ρ is small (the effect is $\leq 20\%$ on the gas density and smaller on ρ) and complicated. Hence the effect is ignored. The general relation is derived below for a gas–liquid mixture for both reversible and irreversible exsolution. Assume that initially, the mass fraction of the gas phase is δ_0 and the system pressure is P_0 at which the gas in the liquid is at saturation. A gas phase exsolves as P is reduced. At P , the mass fraction of the gas phase is δ and that of the liquid is $1 - \delta$. From Wilson et al. (1980):

$$\frac{1}{\rho} = \frac{\delta}{\rho^g} + \frac{1 - \delta}{\rho^l}, \quad (14)$$

where ρ , ρ^g and ρ^l are the densities of the gas–liquid mixture, the gas and the liquid. The density of the liquid is assumed to be constant (ignoring T or P effect). Wilson et al. (1980) used constant mass fraction of the gas δ (δ at fragmentation) to model the dynamics of explosive eruptions. In the following discussion, δ is allowed to increase from the continuous exsolution of the gas from the liquid.

2.3.1. Equation of state for a gas–liquid mixture when the gas phase contains only one component, whether or not equilibrium is reached between the gas and liquid phases

The density of the one-component gas is:

$$\rho^g = P^g / (ZRT), \quad (15)$$

where R is the gas constant in $\text{J kg}^{-1} \text{ K}^{-1}$

($188.9 \text{ J kg}^{-1} \text{ K}^{-1}$ for CO_2 and $461.5 \text{ J kg}^{-1} \text{ K}^{-1}$ for H_2O), T is in K, and Z ($\equiv P^g V / (RT)$) characterizes the nonideality of the gas ($Z = 1$ for an ideal gas). For H_2O vapor at $\geq 800^\circ\text{C}$ and ≤ 3 kbar, $|Z - 1| < 0.15$ (Burnham et al., 1969). For CO_2 gas at 20°C and ≤ 25 bar, $|Z - 1| \leq 0.15$ (Angus et al., 1976). Hence the ideal gas assumption will be used in these cases. For CO_2 at 800 – 1500°C and ≤ 3 kbar, Z can be significantly greater than 1 and, to a first-order approximation, can be expressed as:

$$Z \approx 1 + \epsilon P, \quad (16)$$

where $\epsilon \approx 0.3 \text{ kbar}^{-1}$ at 1100 K and 0.25 kbar^{-1} at 1600 K (Stern and Pitzer, 1994).

The general expression for δ is:

$$\delta = \delta_0 + \frac{C_{A,0}^l}{\rho_0^l} - (1 - \delta + \delta_0) \frac{C_A^l}{\rho^l}, \quad (17)$$

where C_A^l is the concentration of the gas component A in the liquid (in kg m^{-3}). Combining Eqs. (14) and (17) to eliminate d leads to:

$$\begin{aligned} \frac{\rho_0^l}{\rho} &= \frac{\rho_0^l}{\rho^l} \left(\frac{1 - C_{A,0}^l / \rho_0^l}{1 - C_A^l / \rho^l} - \delta_0 \right) \\ &+ \frac{\rho_0^l}{\rho^g} \left(\delta_0 + \frac{C_{A,0}^l / \rho_0^l - C_A^l / \rho^l}{1 - C_A^l / \rho^l} \right). \end{aligned} \quad (18)$$

Using the approximations that the liquid density is constant, and $1 - C_{A,0}^l / \rho_0^l \approx 1$, then:

$$\begin{aligned} \frac{\rho^l}{\rho} &= 1 - \delta_0 + \frac{\delta_0 \rho^l + C_{A,0}^l}{\rho^g} - \frac{C_A^l}{\rho^g} \\ &= 1 + \delta_0 \left(\frac{\rho^l}{\rho^g} - 1 \right) + \lambda_0 \frac{Z P_0}{Z_0 P^g} - \frac{C_A^l}{\rho^g}. \end{aligned} \quad (19)$$

The above equation is the most general equation of state for a gas–liquid mixture and applies whether or not equilibrium between the gas and liquid phases is reached. Therefore, the above equation also applies to irreversible processes. Because Eq. (19) does not explicitly relate ρ to P , other constraints (such as equilibrium between the gas and liquid, see below; the case for irreversible processes will be discussed in a later section) must be used to relate ρ to P .

2.3.2. Equilibrium between the gas and liquid phases

If chemical equilibrium between the liquid and gas

phases is always maintained, then:

$$C_A^l/C_A^g = C_A^l/P^g = \lambda, \quad (20)$$

where λ is the Ostwald solubility coefficient that may depend on both temperature and pressure.

For H_2O gas (assumed to be ideal) in silicate liquid, λ depends on pressure as:

$$\lambda = k_1 + (k_2/P^g)^{1/2}, \quad (21)$$

where k_1 and k_2 are the two constants. For H_2O gas in rhyolitic melt at 850°C , using data of Blank et al. (1993), Silver et al. (1990), Kadik et al. (1972) and Khitarov and Kadik (1973), $k_1 = 0.085$ and $k_2 = 10^{7.2}$ Pa.

For CO_2 gas in liquid water at ≤ 25 bar, using data of Weiss (1974), Wiebe and Gaddy (1940), Weast (1983) and Dean (1985), $\lambda = 1$ at 18°C , and the temperature dependence is roughly:

$$\lambda = e^{3.12 - 4042/T + 911269/T^2} \quad (22)$$

at 0 – 50°C and ≤ 20 bar.

For the nonideal CO_2 in silicate melt, λ depends on CO_2 gas pressure as:

$$\lambda = k_3 + k_4 P^g, \quad (23)$$

where k_3 and k_4 are the two constants. For CO_2 in basaltic melt at $\sim 1300^\circ\text{C}$, $k_3 = 0.00244$ and $k_4 = 1.933 \times 10^{-11} \text{ Pa}^{-1}$ from experimental data of Pan et al. (1991), Pawley et al. (1992) and Dixon et al. (1995).

2.3.3. Equation of state for a gas–liquid mixture when the gas phase contains only one component and when equilibrium is reached between the gas and liquid phases

If chemical equilibrium between the liquid and gas phases is always maintained, the equation of state for the gas–liquid mixture can be found by combining Eqs. (19) and (20):

$$\frac{\rho^l}{\rho} = 1 - \delta_0 + \delta_0 \frac{\rho^l ZRT}{P^g} + \lambda_0 \frac{Z}{P^g} \frac{P_0^g}{Z_0} - \lambda, \quad (24)$$

where the effect of T on the gas-phase density is ignored (i.e. $T/T_0 \approx 1$). Eq. (24) is a general equation of state for a gas–liquid mixture for a reversible

process if equilibrium is reached and if there is only one component in the gas phase. For generality, the above and below expressions are given in terms of gas-phase pressure. The gas-phase pressure is the system pressure for dusty or drop-laden gas flows (after fragmentation). For most bubbly flows (before fragmentation), the gas-phase pressure can also be taken as the liquid and system pressure (but see Prousevitch et al., 1993, for possible differences between gas phase pressure and liquid pressure owing to dynamic pressure, surface tension pressure, etc.). Section 4 discusses cases in which the gas pressure may differ from the liquid pressure.

2.3.4. Three special cases for the equation of state for a gas–liquid mixture when the gas phase contains only one component and when equilibrium is reached between the gas and liquid phases

One special case of Eq. (24) is for ideal gas and for $\delta_0 = 0$:

$$\frac{\rho_0^l}{\rho} \approx 1 - \lambda + \lambda_0 \frac{P_0}{P^g}. \quad (25)$$

The above equation is applicable to, for example, CO_2 or CH_4 in water at relatively low pressures. A second special case is for H_2O in silicate melts with $Z = 1$ and λ given by Eq. (21):

$$\frac{\rho^l}{\rho} = 1 - \delta_0 - k_1 + \delta_0 \frac{\rho^l RT}{P^g} + \lambda_0 \frac{1}{P^g} \frac{P_0^g}{Z_0} - \left(\frac{k_2}{P^g} \right)^{1/2}. \quad (26)$$

A third special case is for CO_2 in silicate melts at high pressures with Z given by Eq. (16) and λ given by Eq. (23):

$$\frac{\rho^l}{\rho} = k_5 + k_6 \frac{P_0^g}{P^g} - k_4 P^g, \quad (27)$$

where $k_5 = 1 - \delta_0 - k_3 + k_6 \epsilon P_0^g$, and $k_6 = \lambda_0/Z_0 + \delta_0 \rho^l RT/P_0^g$ are two dimensionless constants.

2.3.5. Equation of state for a gas–liquid mixture when the gas phase contains two components and when equilibrium is reached between the gas and liquid phases

Natural silicate melts often contain two major volatiles, CO_2 and H_2O . Following the procedures above, the EOS for the reversible exsolution of two

gases from a liquid is:

$$\frac{\rho_0^1}{\rho} = 1 + \frac{\frac{\lambda_{A1,0}P_{A1,0}}{Z_{A1,0}R_{A1}} + \frac{\lambda_{A2,0}P_{A2,0}}{Z_{A2,0}R_{A2}} - \frac{\lambda_{A1}P_{A1}}{Z_{A1}R_{A1}} - \frac{\lambda_{A2}P_{A2}}{Z_{A2}R_{A2}}}{P_{A1}/(Z_{A1}R_{A1}) + P_{A2}/(Z_{A2}R_{A2})}, \quad (28)$$

where the first subscript of λ , Z and P indicates the gas component A1 or A2, and the optional second subscript 0 indicates the initial state. P_{A1} and P_{A2} in Eq. (28) are related by:

$$\frac{\lambda_{A1,0}Z_{A1}P_{A1,0}}{Z_{A1,0}P_{A1}} - \lambda_{A1} = \frac{\lambda_{A2,0}Z_{A2}P_{A2,0}}{Z_{A2,0}P_{A2}} - \lambda_{A2}. \quad (29)$$

If initially there are bubbles in the magma, the saturation pressure (P_s) at which bubbles would completely dissolve into the magma can be found from the initial volume or mass fraction of the gas phase. The equation of state are then similar to Eq. (28) but the initial properties P_0 , λ_0 and Z_0 must be replaced by the saturation properties P_s , λ_s and Z_s .

These equations of states will be used in the next section to calculate the energetics of gas-driven eruptions.

3. Energetics of gas-driven eruptions

3.1. General considerations

The expansion work against the acceleration pressure increases the kinetic energy of the erupting mass. The increase of kinetic energy per unit erupted mass ($\overline{KE} = u^2/2$) due to the acceleration pressure as the pressure decreases from P_1 to P_2 is:

$$\overline{KE} = \int_{1/\rho \text{ at } P=P_1}^{1/\rho \text{ at } P=P_2} P_{acc} d(1/\rho) + \bar{W}_{extra}, \quad (30a)$$

where P_{acc} is the acceleration pressure, $1/\rho$ is the volume per unit mass, and \bar{W}_{extra} is the work done to the unit mass by the rest of the system or by the surroundings. \bar{W}_{extra} may include: (1) the effect of friction (negative term); (2) work done by magma expansion in the magma chamber to the erupting mass (positive term); (3) the effect of entrainment of shallow water, magma, or wall rock (negative term);

and (4) the role of buoyancy for eruption through a fluid medium (positive term). The acceleration pressure can be expressed as: $P_{acc} = P - P_{static} = P - (P_{out} + P_{wt})$, where P , P_{static} , P_{out} , and P_{wt} are, respectively, the system pressure, the static pressure, the outside pressure (such as the atmospheric pressure), and the pressure due to the overlying weight of the erupting column. Because $\int P d(1/\rho)$ is the total expansion work done by the unit mass (\bar{W}), and $\int P_{wt} d(1/\rho)$ is work done per unit mass to increase its own potential energy ($\overline{PE} = gh$ where h is the height from depth 1 to depth 2), Eq. (30a) can also be written as:

$$\overline{KE} = \int_{1/\rho \text{ at } P=P_1}^{1/\rho \text{ at } P=P_2} (P - P_{out} - P_{wt}) d(1/\rho) + \bar{W}_{extra}, \quad (30b)$$

or

$$\overline{KE} = \bar{W} - \int_{1/\rho_1}^{1/\rho_2} P_{out} d(1/\rho) - \overline{PE} + \bar{W}_{extra}, \quad (30c)$$

or

$$\overline{KE} = \int_{1/\rho_1}^{1/\rho_2} (P - P_{out}) d(1/\rho) - \overline{PE} + \bar{W}_{extra}. \quad (30d)$$

Because the maximum amount of total expansion work is done in a reversible process, the maximum amount of kinetic energy is obtained when: (1) the process is reversible; and (2) the system pressure is much greater than the static pressure.

Integration of $\int (P - P_{out}) d(1/\rho)$ in Eq. (30d) by parts leads to:

$$\int_{1/\rho_1}^{1/\rho_2} (P - P_{out}) d(1/\rho) = \frac{P_2 - P_{out}}{\rho_2} - \frac{P_1 - P_{out}}{\rho_1} - \int_{P_1}^{P_2} \frac{dP}{\rho}. \quad (31)$$

Replacing Eq. (31) into Eq. (30d) leads to:

$$\overline{KE} + \overline{PE} + \int_{P_1}^{P_2} \frac{dP}{\rho} - \bar{W}_{extra} - \frac{P_2 - P_{out}}{\rho_2} + \frac{P_1 - P_{out}}{\rho_1} = 0. \quad (32)$$

The velocity (or kinetic energy) of a gas-driven eruptions at the exit (i.e. $P_2 = P_{out}$) can be obtained

from:

$$\overline{KE}_{\text{exit}} + \overline{PE}_{\text{exit}} + \int_{P_1}^{P_{\text{out}}} \frac{dP}{\rho} - \bar{W}_{\text{extra}} + \frac{P_1 - P_{\text{out}}}{\rho_1} = 0. \quad (33)$$

3.2. Differences between eruptions through a fluid medium and those through a rigid medium

A gas-driven eruption may be discharged either through a fluid medium, such as a limnic eruption through water and an eruption through a lava lake, or through a rigid medium, such as most volcanic eruptions through rocks. There are several differences for eruptions through a fluid medium and those through a rigid medium:

(1) The relation between the local system pressure and the local hydrostatic or lithostatic pressure. The local system pressure in the “conduit” for an eruption through a fluid medium is expected to be roughly the same as the hydrostatic pressure (Zhang, 1996). Therefore, for an eruption through a fluid conduit, although there is no definite chamber, the local system pressure is known a priori to be roughly equal to the hydrostatic pressure and the source pressure stays the same (P_0). However, for an eruption through a rigid medium, the local system pressure in the magma chamber and in the erupting column does not necessarily equal the lithostatic pressure (Jaupart and Tait, 1990) because rocks may withstand significant stress and do not deform instantaneously at the time scale of a violent eruption. To a first-order approximation, the chamber volume does not vary with time. As eruption goes on, the mass, density and pressure in the magma chamber decreases. The pressure decrease in the magma chamber affects the eruption dynamics and may eventually lead to the collapse of the overlying rocks into the chamber and the formation of a caldera.

(2) The role of buoyancy and chamber processes. For eruptions through a fluid medium, buoyancy plays a role so that lifting a parcel of liquid (mass m) from a lake bottom to the lake surface (without exsolution) requires little work, roughly $mgh(\Delta\rho)/\rho$ where h is the height increase, ρ the average density of water, ρ the density difference between the bottom water and the surface water ($\Delta\rho/\rho$ is typically of order 0.001, a small number). For eruptions through a rigid medium, the gas exsolution in the magma chamber contributes

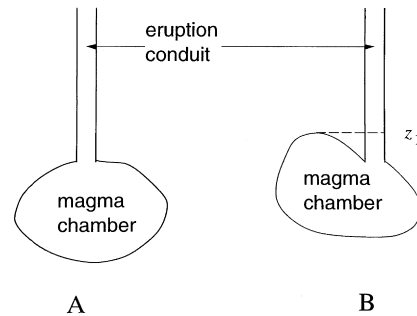


Fig. 1. Magma chamber shape and possible buoyancy effect: (a) no buoyancy effect; and (b) there is a buoyancy effect. The melt in the chamber above the entrance level of the eruption conduit pushes the melt up into the conduit to the height z_1 .

to the energy of the erupting column. However, buoyancy does not play a direct role unless the magma chamber is shaped in such a way for buoyancy to play a role (Fig. 1) because rocks may withstand significant stress and do not deform continuously at the time scale of a violent eruption. The elastic stress distribution in the rocks may conspire to produce either positive or negative buoyancy, the sign of which depends on the detailed geology of the system (L. Wilson, personal communication).

(3) The role of entrainment. For eruptions through a fluid medium, the effect of entraining shallow water or shallow magma may reduce the erupting velocity significantly. For eruptions through a rigid medium, there may be entrainment of wall rocks but the effect may be small. To rigorously treat shallow water entrainment in a limnic eruption, the concentration of CO_2 in the entrained water, and much other detailed information, must be known. Without considering such details, a simple treatment of the effect of shallow water entrainment is to assume that the entrained shallow water only adds mass to the erupting column but does not affect the equilibrium between the gas and liquid phases due to the imperfect mixing between entrained water and original high- CO_2 water. If so, the kinetic energy per unit original mass is the same but the velocity decreases as:

$$u = [2\overline{KE}/(1 + f)]^{1/2}, \quad (34)$$

where f is the ratio of the entrained mass to the original mass.

(4) Material properties. The diffusivity of CO_2 in

water is ≥ 200 times greater than that of H_2O in rhyolitic magma (Zhang et al., 1991). Therefore, limnic eruptions are expected to be more dynamically reversible. The viscosity of hydrous rhyolitic magma (Hess and Dingwell, 1996) is ~ 8 orders of magnitude greater than that of water. Therefore, buoyant rise of bubbles in liquid, which tends to decrease the eruptibility, plays a larger role in limnic eruptions.

3.3. Dynamics of reversible gas-driven eruptions through a fluid medium

Because buoyancy plays an important role in gas-driven eruptions through a fluid medium, the surrounding does work to raise the liquid. When the initial liquid is bubble-free, the initial liquid is neutrally buoyant and buoyancy work matches the potential energy. That is, $\bar{W}_{\text{extra}} \approx \bar{P}E_{\text{exit}}$ in Eq. (33) for eruptions through a fluid medium (limnic eruptions and eruptions through a lava lake). Therefore, for a gas-driven eruption through a fluid medium that can deform rapidly to maintain steady state and hydrostatic pressure in the conduit, recognizing that the initial saturation pressure is $P_{\text{out}} + \rho_0 gh$ and that the pressure at the initial depth does not change with time, $(P_1 - P_{\text{out}})/\rho_1 = (P_0 - P_{\text{out}})/\rho_0 = \rho_0 gh/\rho_0 = gh = \bar{P}E_{\text{exit}}$, Eq. (33) reduces to the Bernoulli equation:

$$\bar{K}E_{\text{exit}} + \bar{P}E_{\text{exit}} + \int_{P_0}^{P_{\text{out}}} \frac{dP}{\rho} = 0. \quad (35)$$

For CO_2 -driven limnic eruptions, assuming: (1) nucleation sites are abundant in lake water and CO_2 bubbles start to nucleate with only small supersaturation, leading to reversible exsolution; and (2) CO_2 gas is ideal, Eq. (25) is applicable with $\lambda \lambda_0$. Carrying out the integration in Eq. (35) using Eq. (25) leads to (Zhang, 1996)

$$\frac{1}{2}u^2 \approx \lambda \frac{P_0}{\rho_0} \left(\ln \frac{P_0}{P} - 1 + \frac{P}{P_0} \right), \quad (36)$$

where u is the ascent velocity and becomes the exit velocity at $P = P_{\text{out}}$. Because the process is assumed to be reversible and shallow fluid entrainment is ignored, u calculated from Eq. (36) is the maximum ascent velocity. The above equation has been used to investigate the dynamics of CO_2 -driven water eruption from Lake Nyos and Lake Monoun and to show that such eruptions can be violent (Zhang, 1996). For

example, the eruption of CO_2 -saturated water may reach an exit velocity of 52 m s^{-1} if starting from 100 m saturation depth, 86 m s^{-1} if starting from 200 m depth. If the mass of the entrained shallow water is about the same as the mass of the erupting water from bottom, and if shallow water entrainment is treated in a simple way as in Eq. (34), the exit velocity would be 37 m s^{-1} if the eruption starts from 100 m saturation depth, 61 m s^{-1} if it starts from 200 m depth.

A limnic eruption can be terminated when insufficiently saturated water is drawn into the eruption conduit. Once such conditions arise, the initial momentum of the batch of water is not enough for it to rise to a shallow enough depth for bubbles to grow (equivalent to too small a trigger). Without buoyancy induced by bubble growth, the batch of water, being slightly denser than the surrounding water, will stop rising and sink. The eruption thus will not continue. That is, a limnic eruption is not expected to completely degas the whole lake.

For H_2O -driven basaltic eruptions through a lava lake, ignoring shallow magma entrainment and using Eq. (26), integration of Eq. (35) leads to:

$$\begin{aligned} \frac{1}{2}u^2 \approx & \frac{P_0}{\rho_0} \left(\lambda_0 \ln \frac{P_0}{P} - k_1 + k_1 \frac{P}{P_0} - 2\sqrt{\frac{k_2}{P_0}} \right. \\ & \left. + 2\sqrt{\frac{k_2}{P}} \frac{P}{P_0} \right). \end{aligned} \quad (37)$$

If a batch of basaltic melt containing 0.5% of total H_2O is injected into a lava lake 100 m deep (26.5 bar), the injected melt would be at saturation. Upon rising, bubbles form and grow in the batch, causing it to rise more rapidly. The maximum exit velocity is $\sim 100 \text{ m s}^{-1}$. Entrainment of shallow magma and irreversibility would reduce this exit velocity.

3.4. Dynamics of reversible gas-driven eruptions through a rigid medium

For gas-driven eruptions through a rigid medium (most violent volcanic eruptions because the wall rocks can withstand stress and cannot relax in the time scale of a violent eruption), buoyancy does not help the eruption. However, the expansion work done

by the bubbly magma inside the chamber, minus the expansion work against the outside pressure, is supplied to the erupting column. To evaluate this extra work on the erupting column, consider a thin disk-shaped magma chamber so that the magma chamber can be characterized by a single pressure P_1 . Initially, the magma chamber pressure (the saturation pressure) is P_0 . The pressure in the magma chamber (and conduit) can be different from the lithospheric pressure. The fall of rock pieces into the chamber does not change significantly the volume of the chamber since the new magma chamber includes the space left by the falling rock. Elastic deformation of the lithosphere does not change the volume of the chamber significantly. Hence, before the total collapse of the overlying rocks to form a caldera, which probably restores the magma chamber pressure to lithostatic pressure and seals the conduit, the chamber volume may be regarded as constant. Therefore, $M_1/\rho_1 = M_0/\rho_0$ where M_1 and ρ_1 are the mass and density of the bubbly magma in the chamber. As the eruption proceeds and magma is removed, bubbly magma in the chamber expands to fill space, and pressure and density in the magma chamber decreases.

Assume that the eruption process is quasi-steady so that the variation of the mass and flow velocity in the conduit is negligible (or when the conduit volume is negligible compared to either the erupted volume or the magma chamber volume). The extra work done by the expansion of the magma in the chamber minus the work against the outside pressure is supplied to the erupted magma. (Kinetic energy variation inside the magma chamber is ignored since the process is assumed to be quasi-steady.) Hence for the eruption of mass dM , magma chamber mass changes from M_1 to $M_1 - dM$ and its pressure changes from P_1 to $P_1 - dP$. The work done by the magma chamber to a unit erupted mass is:

$$\begin{aligned}\bar{W}_{\text{extra}} &= \frac{M_1}{dM} \int_{1/\rho_1 \text{ at } P_1}^{1/\rho_1 \text{ at } P_1 - dP} (P - P_{\text{out}}) d\frac{1}{\rho} \\ &= \frac{M_1}{dM} \int_{P_1}^{P_1 - dP} (P - P_{\text{out}}) \frac{d(1/\rho)}{dP} dP.\end{aligned}\quad (38)$$

Since $M_1/\rho_1 = M_0/\rho_0$, $M_1/dM = \rho_1/d\rho$. Since dP_1 is infinitesimally small, the integration equals $(P_1 - P_{\text{out}}) \times [d(1/\rho)/dP]_{P=P_1}(-dP) = -(P_1 - P_{\text{out}}) d(1/\rho)_{P=P_1}$.

Hence,

$$\bar{W}_{\text{extra}} = -\rho_1(P_1 - P_{\text{out}}) \frac{d(1/\rho)}{d\rho} \Big|_{\rho=\rho_1} = \frac{P_1 - P_{\text{out}}}{\rho_1}.\quad (39)$$

Therefore, for any given chamber pressure of P_1 , Eq. (33) again reduces to the Bernoulli equation:

$$\overline{\text{KE}}_{\text{exit}} + \overline{\text{PE}}_{\text{exit}} + \int_{P_1}^{P_{\text{out}}} \frac{dP}{\rho} = 0.\quad (40)$$

If friction is important, its effect can be added (e.g. Eq. (1) in Wilson et al., 1980). Note that even though eruptions through a fluid medium and those from a rigid medium are both described by the Bernoulli equation, the lower limit of the integration is different. In Eq. (35) for an eruption through a fluid medium, the lower limit of integration is a constant P_0 ; whereas in Eq. (40) for an eruption through a rigid medium, the lower limit is the instantaneous magma chamber pressure P_1 that decreases with time. A gas-driven explosive eruption can stop if either (1) P_1 is so small that $\overline{\text{KE}}_{\text{exit}}$ solved from Eq. (40) is equal to or less than zero or (2) the difference between the lithostatic pressure and the magma chamber pressure is large enough to lead to the collapse of rocks into the chamber, resulting in a caldera. Hence the above equation can be used to calculate the maximum fraction of magma that can be erupted for a given gas–magma system using reversible equation of state.

4. Some models for treating irreversibility

In estimating the exit velocity using the Bernoulli equation ignoring fluid/rock entrainment and friction with the conduit, the density of the bubbly liquid as a function of the system pressure must be known so that the integration can be carried out. For a reversible process, the gas and liquid phases are always in equilibrium and the gas pressure is the same as the uniform liquid pressure. Hence ρ can be calculated. However, irreversibility can arise because of: (1) chemical disequilibrium between the gas and liquid phases due to finite diffusivity of the gas component in the liquid (e.g. water concentration in erupted pumice does not correspond to equilibrium at 1 bar pressure; J. Blank, personal communication); and (2) the pressure difference between the gas and the

liquid due to dynamic pressure that depends on viscosity (Proussevitch et al., 1993). Hence the relation between ρ and P is complicated and future numerical calculations or experiments may elucidate the best approach. Below, I suggest several empirical models for estimating the relation between density and pressure.

4.1. Model 1

In the first class of models, chemical disequilibrium between the gas and liquid phases is considered but the pressure difference between the gas phase and the system is ignored. Assume that the initial state is always at equilibrium saturation and that the gas pressure is always the system pressure (ignoring surface and dynamic effects). Hence gas phase density is the same as treated before. However, because of disequilibrium between the gas and liquid phases, the liquid may contain more gas component than the equilibrium concentration. That is, the gas phase contains less gas mass than at equilibrium ($\delta \leq \delta_{eq}$). Hence the density of the bubbly liquid lies between that of the equilibrium bubbly liquid and that of pure liquid. Therefore, one way to write the equation of state for irreversible gas exsolution is:

$$\frac{\rho_0^l}{\rho} = \frac{\gamma_1}{\rho_{eq}} \rho_0^l + \frac{1 - \gamma_1}{\rho^l} \rho_0^l, \quad \text{where } 0 \leq \gamma \leq 1, \quad (41)$$

where γ_1 is a constant and ρ_{eq} is the density of the mixture at equilibrium (Eqs. (24)–(28)).

If there is only one volatile component, using ρ_{eq} from Eq. (24) with $\delta_0 = 0$, Eq. (41) becomes:

$$\frac{\rho_0^l}{\rho} = 1 - \gamma_1 \lambda + \gamma_1 \lambda_0 \frac{P_0}{P} \frac{Z}{Z_0}. \quad (42)$$

When $\gamma_1 = 1$, the above equation reduces to Eq. (24) with $\delta_0 = 0$. Eq. (42) can be rewritten in the form of actual average gas concentration in the liquid (C^l) which is not the equilibrium concentration $C_{eq}^l = \lambda P / (ZRT)$. When $C_A^l \neq C_{A,eq}^l$, comparison of Eq. (19) (with $\delta_0 = 0$) and Eq. (42) leads to:

$$C^l = \gamma_1 C_{eq}^l + (1 - \gamma_1) C_0^l. \quad (43)$$

That is, model 1a means that the actual average gas

concentration in the liquid is linear to the equilibrium concentration.

Model 1a is a one-parameter linear model. A nonlinear model containing two parameters for a one-component gas can be written in the form of

$$C^l = \gamma_1 C_{eq}^l + (1 - \gamma_1) C_0^l + \gamma_2 (C_{eq}^l - C_{eq,out}^l) \times (1 - C_{eq}^l / C_0^l), \quad (44)$$

where $C_{eq,out}^l$ is the equilibrium concentration of the gas component in the liquid at the final exit pressure (P_{out}), and γ_2 is another constant that is between $-\min(\gamma_1, 1 - \gamma_1) / (1 - C_{eq,out}^l / C_0^l)$ and $\gamma_1 / (1 - C_{eq,out}^l / C_0^l)$. The condition for γ_2 is to insure that: (1) C^l decreases monotonically as C_{eq}^l decreases with eruption (that is, the gas concentration in the liquid must decrease with time monotonically); and (2) C^l is always C_{eq}^l (i.e. the gas concentration in the liquid is always saturated or supersaturated). Model 1b reduces to model 1a when $\gamma_2 = 0$. In model 1b, C^l is a parabolic function of C_{eq}^l and the parabolic curve passes through two points: the initial point ($C_{eq}^l = C_0^l$, $C^l = C_0^l$) and the final point ($C_{eq}^l = C_{eq,out}^l$, $C^l = C_{out}^l$). Using Eq. (44), the equation of state becomes:

$$\frac{\rho_0^l}{\rho} = 1 - \gamma \lambda + \gamma \lambda_0 \frac{P_0}{P} \frac{Z}{Z_0} - \phi \left(\lambda - \lambda_{out} \frac{Z P_{out}}{Z_{out} P} \right) \times \left(1 - \frac{Z_0 P}{Z P_0} \right). \quad (45)$$

4.2. Model 2

In the second class of models, the gas pressure may deviate from the system pressure ($P^g \neq P$) owing to surface and dynamic pressure, but the gas concentration in the liquid is always in equilibrium with the gas pressure. Similar to the above development, model 2a can be defined as:

$$\frac{1}{P^g} = \frac{\phi_1}{P} + \frac{(1 - \phi_1)}{P_0}, \quad \text{where } 0 \leq \phi_1 \leq 1. \quad (46)$$

The equation of state becomes:

$$\frac{\rho_0^l}{\rho} \approx 1 - \lambda + \lambda_0 \frac{Z^g P_0}{Z_0 P^g}. \quad (47)$$

One may also define a complicated two-parameter model.

4.3. A combination model

More general models can be constructed by incorporating both the pressure difference and chemical disequilibrium between the gas and liquid phases. For example, incorporating both models 1a and 2a, the equation of state can be written from Eq. (19) (with $\delta_0 = 0$) as:

$$\frac{\rho^1}{\rho} = 1 - \gamma_1 \lambda + \gamma_1 \lambda_0 \frac{Z^g P_0}{Z_0 P^g}, \quad (48)$$

where P^g is given by Eq. (46).

4.4. Applications to Lake Nyos eruption

Zhang (1998) examined bubble growth rates using experimental data and whether the gas and liquid phases can be in equilibrium during limnic eruptions. He suggested that equilibrium is possible if number density of bubbles is much greater than 10^{10} m^{-3} . Since heterogeneous bubble nucleation density in lake water is expected to be high, it is possible that equilibrium between the gas and liquid phases is maintained. However, if equilibrium is not maintained, the effect of disequilibrium on the eruption dynamics can be modeled as follows. For limnic eruptions, since liquid viscosity is low, gas pressure is not expected to deviate significantly from the liquid pressure and irreversibility is most likely owing to chemical disequilibrium between the gas and liquid phases. Hence model (1a) or (1b) can be used. For example, using model (1a) with $\gamma_1 = 0.8$ during Lake Nyos eruption (meaning that as the water exits lake surface, it still contains an average CO_2 concentration corresponding to 5 bar), the exit velocity can be calculated from:

$$\frac{1}{2} u^2 \approx \gamma_1 \lambda \frac{P_0}{\rho_0} \left(\ln \frac{P_0}{P} - 1 + \frac{P}{P_0} \right), \quad (49)$$

to be 79 m s^{-1} (instead of 89 m s^{-1} for reversible eruption). The dynamic reversibility is $R_d = \gamma_1 = 0.8$. If furthermore entrainment of shallow water is treated simply using Eq. (34) with $f = 1$ (i.e. mass of entrained shallow water is about the same as the mass of the erupting bottom water), the exit velocity

would be 56 m s^{-1} , enough to rise to $\sim 160 \text{ m}$ above lake surface. Since there is no direct observation on the exit velocity, except for an estimate of minimum column height of 120 m based on the distribution of dead animals (Sigvaldason, 1989), all the above scenarios are possible.

4.5. Applications to Mount St. Helens

For explosive volcanic eruptions, there may be both pressure difference and chemical disequilibrium between the gas and liquid phases. The 18 May 1980 eruption of Mount St. Helens may be modeled as follows. Use or assume the following pre-eruptive conditions: $T_0 = 1200 \text{ K}$, $P_0 = 2.2 \text{ kbar}$, $P_{\text{H}_2\text{O},0} = 1.32 \text{ kbar}$, $P_{\text{CO}_2,0} = 0.88 \text{ kbar}$, initial H_2O_l content of 4.6% (Rutherford et al., 1985), $P_{\text{out}} = 0.7 \text{ bar}$, the initial depth of 8.3 km (from the initial pressure and a density of 2700 kg m^{-3}), and no initial bubbles in the magma and hence $P_s = P_0$. λ for H_2O_l in the dacitic melt is taken to be $0.085 + (10^{7.4} \text{ Pa}/P)$ so that at $P_{\text{H}_2\text{O},0} = 1.32 \text{ kbar}$, the equilibrium H_2O_l in the melt is 4.6%. λ for CO_2 in the dacitic melt is taken to be the same as that in basaltic melt. The nonideality of CO_2 is accounted for by using $Z = 1 + 0.29P$ at 1200 K where P is in kbar (Sternner and Pitzer, 1994). The small and complicated nonideality of H_2O is ignored. If friction is ignored and the process is assumed to be reversible, the calculated maximum initial exit velocity would be 542 m s^{-1} . The bubbly magma velocity in the conduit is 210 m s^{-1} at fragmentation if fragmentation is assumed to occur at 74% vesicularity. Hence calculating exit velocity by assuming that the bubbly magma velocity is zero at fragmentation may significantly underestimate the exit velocity. If friction is ignored but the exsolution process is irreversible, using a combination model with $\gamma_1 = 0.75$ (meaning that the erupted pumice still contains 0.9% H_2O_l) and $\phi_1 = 0.5$ (meaning that the gas pressure at the exit is 1.4 bars), the calculated initial exit velocity is 325 m s^{-1} and the dynamic reversibility is 0.4. Direct observations of the exit velocities are variable. The observed minimum choked exit velocity is $100\text{--}110 \text{ m s}^{-1}$ (Kieffer, 1981) and the velocity increased to 325 m s^{-1} at or after the exit (Kieffer, 1981). Another report of the observed velocity for a lateral eruption cloud is 150 m s^{-1} from photographic and seismic-station

evidence (Friedman et al., 1981; Voight, 1981). Hence, the eruption process was irreversible. The velocity 325 m s^{-1} is close to the estimated velocity incorporating irreversibility with $\gamma_1 = 0.75$ and $\phi_1 = 0.5$. Other combinations of γ_1 and ϕ_1 can also produce an exit velocity of $\sim 325 \text{ m s}^{-1}$. If friction is significant, the γ_1 and ϕ_1 values can be greater. The smaller observed velocity (150 m s^{-1}) would require either significant friction or smaller γ_1 and ϕ_1 .

5. Conclusions

In this paper, the thermodynamics of reversible and irreversible gas exsolution from a liquid is investigated to lay the foundation for the rigorous treatment of the energetics of gas-driven eruptions. Rapid and slow exsolution processes are also discussed from the point of view of eruption dynamics. Even though the roles of buoyancy and magma chamber process differ for gas-driven volcanic eruptions and limnic eruptions, the equations describing the dynamics are similar (Bernoulli equation at quasi-steady state). The relations between density of gas–liquid mixture and pressure are critical in modeling the dynamics. Such relations have been presented for CO_2 –water, H_2O –magma, and CO_2 –magma systems. For reversible eruption process, since the liquid and gas phases are always at equilibrium, the equation of state is a simple thermodynamic problem and the eruption dynamics can be modeled relatively easily. For irreversible eruptions, the concept of dynamic reversibility (actual kinetic energy divided by maximum derivable kinetic energy) or irreversibility is introduced and used in discussing the dynamics of eruptions. Since the exact equation of state in an irreversible process depends on the kinetics of bubble nucleation and growth, detailed experimentation for bubble nucleation and numerical calculation for bubble growth are necessary to understand the equation of state for gas–liquid mixtures during an eruption. Lacking such a complete understanding, empirical parametric methods are employed in this paper to estimate the equation of state and eruption dynamics. The parametric study shows that disequilibrium between the gas and liquid phases may significantly reduce the eruption velocity in

both limnic and volcanic eruptions. Such empirical approaches can also model the observed exit velocity of the 18 May 1980 eruption of Mount St. Helens.

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