

On laboratory simulation and the temperature dependence of the evaporation rate of brine on Mars

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[1] We have determined the evaporation rate of brine under simulated martian conditions at temperatures from 0°C to -26.0°C as part of our efforts to better understand the stability of water on Mars. Correcting for the effect of water build-up in the atmosphere and the lower gravity on Mars relative to Earth we observed a factor of almost 30 decrease in evaporation, from 0.88 mm/h at ~0°C to 0.04 mm/h at -25.0°C. The results are in excellent agreement with the predictions of Ingersoll's (1970) theoretical treatment, lending support to the theory and our procedures. Thus brine formation will increase the stability of water on Mars not only by extending the liquid temperature range, but also by considerably decreasing the evaporation rate. **Citation:** Sears, D. W. G., and J. D. Chittenden (2005), On laboratory simulation and the temperature dependence of the evaporation rate of brine on Mars, *Geophys. Res. Lett.*, 32, L23203, doi:10.1029/2005GL024154.

1. Introduction

[2] The stability of water on the martian surface is of considerable interest in understanding the geological, climatological and biological evolution and current state of the planet. Until recently, it was considered unlikely that liquid water could currently exist on the surface [Ingersoll, 1970]. However, the quantitative calculation of evaporation rates is not based on rigorous theory – but instead model estimates are derived from equations for analogous processes, such as convection and momentum exchange [Holman, 1990] – while until very recently the only experimental studies were either at mostly high pressures and required extrapolation to Mars pressures [Hecht, 2002] or were in poor agreement with theory or other experiments [Kuznetz and Gan, 2002]. Recently, Sears and Moore [2005] reported a detailed series of measurements at 7 mbar, 0°C, in a CO₂ atmosphere which, when corrected for the gravity difference between Earth and Mars, yielded an experimental estimate of the evaporation rate of water on Mars at 7 mbar and 0°C of 0.73 ± 0.14 mm/h, in excellent agreement with the Ingersoll estimate. Many factors affect the true evaporation rate of water on Mars, the most important being the presence and intensity of winds, the amount of insolation, and the presence of dissolved salts in the water. Here we are concerned with the effect of considerable amounts of dissolved salts on the evaporation rate of water on Mars.

[3] Brines on Earth range in composition from weak 0.50M solutions of the open sea to solutions at the eutectic for landlocked bodies of water and one might expect a

similar situation on Mars. Similarly, the composition of the brines will vary and might include the various chloride-rich solutions commonly observed on the present Earth and sulfate-rich solution once common on both Earth and Mars. The identity of the ions dictates the eutectic temperature (for instance, NaCl, CaCl₂, and MgSO₄ have eutectic temperatures of -21.2, -49.8 and -3.6°C, respectively) but has little influence on evaporation rate of the solutions. Simulation experiments suggest that a large number of ions could be present in waters on Mars [Bullock *et al.*, 2004]. We have measured the evaporation rate of water from solutions of NaCl and CaCl₂ under simulated Mars conditions in order to better understand the increased stability of water caused by the presence of solutes and the consequent suppression of the freezing point.

2. Experimental

[4] We used an experimental apparatus and set-up similar to that of Sears and Moore [2005] (Figure 1). Minor modifications consisted of a doubling (to ~50 meters) of the length of the heating cables and cooling coils so they could run the entire length of the chamber. As before, a dry ice-methanol mixture is pumped with a gravity fed 1.5 HP pump through the cooling coils. This method ensures that the walls of the chamber, the atmosphere and the test solution were all maintained at the same temperature. We have moved slightly the nine chromel-alumel thermocouples and the hygrometers; having five thermocouples on the walls, two in the atmosphere over the sample, one in the coolant reservoir and one on the water surface, and one hygrometer 20 cm above the water surface and one at the top of the chamber. ConvecTorr and Pirani gauges are used to measure the pressure. A seven-watt lamp could be momentarily turned on to view the water during the experiment via closed-circuit TV.

[5] A typical experiment involved evacuating the chamber to 0.09 mbar or lower, filling with dry gaseous CO₂ to atmospheric pressure and cooling the entire system to the desired temperature between 1.7°C and -25.2°C. A 100 mL beaker containing a eutectic NaCl or CaCl₂ was then placed on an Ainsworth analytical balance and a thermocouple was placed on the surface of the liquid. The chamber was then evacuated to 7 mbar at which point the logging of mass, pressure, temperature, and humidity began. The pressure was maintained between 6.5 and 8 mbar. Two digital television cameras viewed the beaker and enabled the balance to be read.

[6] Our data have been adjusted to allow for the difference in gravity between Earth and Mars since gravity will affect the buoyancy of water vapor in the CO₂ atmosphere.

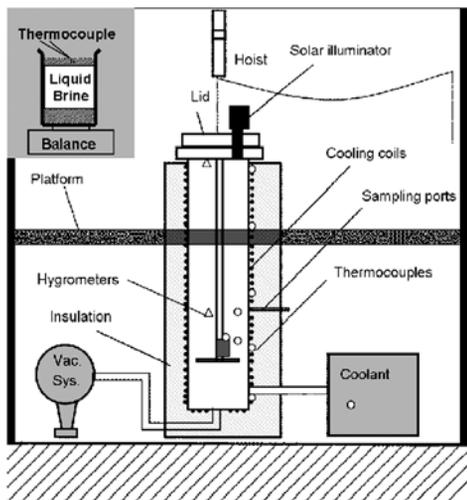


Figure 1. Schematic diagram of the apparatus used for the present work with the sample-balance set-up shown in the inset. A stainless steel chamber 61 cm high and 208 cm in diameter is surrounded by 50 m of heating cable and cooling coils. The experimental volume can be evacuated and filled with a CO₂ atmosphere and the conditions monitored with thermocouples, pressure gauges and hygrometers. The test solution sits on a balance that is placed on a platform that can be lowered into the chamber by an overhead hoist. The experimental set-up and the test solution are observed throughout the experiment by closed-circuit television.

We can correct for this by noting that buoyancy depends on the cube root of gravity (see below). Thus all else being equal, we can write.

$$E_{\text{Mars}}^{\text{Earth}} = \left(\frac{g_{\text{Mars}}}{g_{\text{Earth}}} \right)^{1/3} = \left(\frac{3.75}{9.81} \right)^{1/3} = 0.726 \quad (1)$$

Where E is the evaporation rate and g is the acceleration due to gravity (m/s^2). Our experimental evaporation rates have been multiplied by this factor.

3. Results

[7] Figure 2 shows three examples of our data. Typically we observe a decrease in mass over a one-hour period of about ~ 0.5 g at -20°C , 1.5 g at -10°C and 2.5 g at 0°C , and there is a slight decrease in the evaporation rate with time as water vapor accumulates in the atmosphere above the sample, which is less significant at lower temperatures and insignificant below about -15°C when the evaporation rate was very low. Thus, at the lower temperatures the mass loss curve is essentially linear. Correction for non-linearity in mass loss was made by fitting a second order curve to the data and taking the derivative of the line $t = 0$, before water vapor started to accumulate in the chamber.

[8] The evaporation rates determined in the present study, corrected for water pile-up and the gravity difference between Earth and Mars, are listed in Table 1. Evaporation rates varied from about 0.89 mm/h at 1.7°C to 0.27 mm/h at -10.9°C and 0.04 mm/h -25.2°C . It is difficult to rigorously calculate the experimental uncertainty on a given

result, but from the scatter about the trend line for evaporation rate vs. temperature we suggest that 2σ uncertainties are about 1°C for temperature and 10% for the evaporation rate. Mass-loss can be measured accurately at any temperature and the uncertainties depend on the overall control of the temperature, which is better at lower temperatures when less H₂O builds up in the atmosphere and experiments are longer.

4. Discussion

4.1. Evaporation Rate

[9] In the absence of advection (movement of air masses by wind) the movement of the water molecules away from the surface of the water is due to diffusion and buoyancy, the lighter water molecules rising above the heavier CO₂ molecules. Using relations based on analogous processes, an expression first applied to this problem by *Ingersoll* [1970] (modified to convert the units of evaporation rate, E , from $\text{g cm}^{-2}\text{s}^{-1}$ to mm h^{-1} and to account for the density of the brine) is:

$$E = 0.612 \Delta\eta \rho D [(\Delta\rho/\rho)g/\nu^2]^{1/3} / \rho_s \quad (2)$$

Where $\Delta\eta$ is the concentration difference between the surface and the atmosphere, ρ_{atm} is the atmospheric density, D is the mechanical diffusivity, g is the gravitational constant, ν is the kinematic viscosity, ρ_s is the density of the brine solution. $\Delta\rho/\rho$ can be defined as

$$\Delta\rho/\rho = \frac{VP(\text{H}_2\text{O})_{\text{Soln}} \times [m(\text{CO}_2) - m(\text{H}_2\text{O})]}{\{m(\text{CO}_2) \times P_{\text{atmos}} - [m(\text{CO}_2) - m(\text{H}_2\text{O})] \times VP(\text{H}_2\text{O})_{\text{Soln}}\}} \quad (3)$$

where $m(\text{CO}_2)$ is the molecular weight of CO₂, $m(\text{H}_2\text{O})$ is the molecular weight of water, $VP(\text{H}_2\text{O})_{\text{Soln}}$ is the saturation vapor pressure of water over the solution, and P_{atm} is the total atmospheric pressure. $\Delta\eta$ can be defined as

$$\Delta\eta = VP(\text{H}_2\text{O})_{\text{Soln}} \times m(\text{CO}_2)/P_{\text{atmos}} \times m(\text{H}_2\text{O}) \quad (4)$$

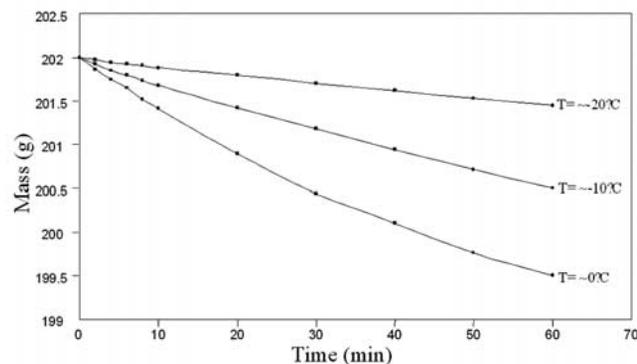


Figure 2. Representative data from experiments run at three temperatures normalized to the same starting mass. The curvature of the line, caused by the decrease in evaporation rate due to the build-up of water vapor in the atmosphere, decreases with decreasing temperature. Evaporation rates at the beginning of the run, when the atmosphere was perfectly dry, is determined by calculated by fitting a second order curve and determining the slope at $t = 0$.

Table 1. Experimental Determinations for the Evaporation Rate of Water in a Dry CO₂ Atmosphere at 7 mbar Compared With the Calculated Evaporation Rate for Water on Mars^a

T _{Sample} , °C	Evaporation Rate, mm/h
-25.2 ^b	0.04
-21.4 ^b	0.12
-21.2 ^b	0.09
-19.8 ^c	0.06
-18.5 ^b	0.11
-17.4 ^b	0.21
-14.8 ^c	0.17
-14 ^c	0.19
-10.9 ^c	0.27
-9.2 ^c	0.29
-8.6 ^c	0.35
-7.6 ^c	0.35
-7.3 ^c	0.38
-5.8 ^c	0.63
-5.7 ^c	0.48
-5.7 ^c	0.4
-5.4 ^c	0.41
-5.1 ^c	0.35
-5.0 ^c	0.38
-4.6 ^c	0.46
-4.4 ^c	0.52
-4.3 ^c	0.52
-4.1 ^c	0.47
-4.1 ^c	0.59
-3.6 ^c	0.46
-3.4 ^c	0.54
-3.4 ^c	0.75
-3.2 ^c	0.6
-2.1 ^c	0.62
-1.4 ^c	0.74
-1.2 ^c	0.62
-0.9 ^c	0.71
-0.6 ^c	0.61
-0.6 ^c	0.72
0.1 ^c	1.13
0.8 ^c	1.09
1.7 ^c	0.89

^aCorrected for the difference in gravity between Earth and Mars by multiplying the experimental data by 0.726 (see text for explanation). One-sigma experimental uncertainties on temperatures are 1°C and on evaporation rate are 10%.

^b29.8% CaCl₂ solution.

^c23.3% NaCl solution.

where $m(\text{CO}_2)$ is the molecular weight of CO₂. It is through the vapor pressure of water that the main temperature dependence of evaporation rate appears. Fitting the data given by CRC [1986] to an equation by the method of least squares, we find:

$$\log \text{VP}(\text{H}_2\text{O}) = \frac{-2342}{T} + 9.3583 \quad (5)$$

Where

$$\text{VP}(\text{H}_2\text{O})_{\text{Soln}} = \gamma N \text{VP}(\text{H}_2\text{O})$$

In which γ is the activity coefficient for the water in the solution and N is the mole fraction of solution that is water. γ is somewhat less than one, but for the present analysis we will assume a value of unity.

[10] Figure 3 shows the predicted evaporation rates (for NaCl₂ above -20°C and CaCl₂ below -20°C) superimposed on our experimental data. The agreement between these calculated values and the experimental values is very

good and lends credibility to both the theory and our experimental approach. The agreement between theory and experiment also indicates that while every term in expression (2) is temperature-dependent to some degree, the only important term is the vapor pressure, which largely dictates the shape of the theoretical curve.

4.2. Implications of the Present Results

[11] Clearly the presence of dissolved salts can greatly increase the stability of liquid water on Mars by depressing the freezing point and thereby extending the P-T field for the liquid phase. Haberle *et al.* [2001] have pointed out that while pure water could exist over 29% of the planet for 37 sols each year, while a NaCl eutectic solution could remain liquid over most of the planet at some time of the year and up to 100 sols in some regions. The formation of eutectic solutions of CaCl₂, with its much lower eutectic temperature, would greatly increase the extent and duration of liquid on Mars.

[12] However, just as significant as the extended P-T stability field for brines is the much lower evaporation rates. At the eutectic temperature of NaCl brine, evaporation rates are ~30 times less than pure water; at the eutectic temperatures of CaCl₂ evaporation rates are slightly lower. The evaporation of such highly concentrated brine solutions on Earth is always associated with conspicuous deposits of evaporites which have not, to our knowledge, been observed on Mars, perhaps because the parent liquids were at these very low temperatures and seepage into the surface was faster than evaporation. In fact, it might be that the concentrated brines with incredibly low freezing points may be more significant for understanding the widespread oc-

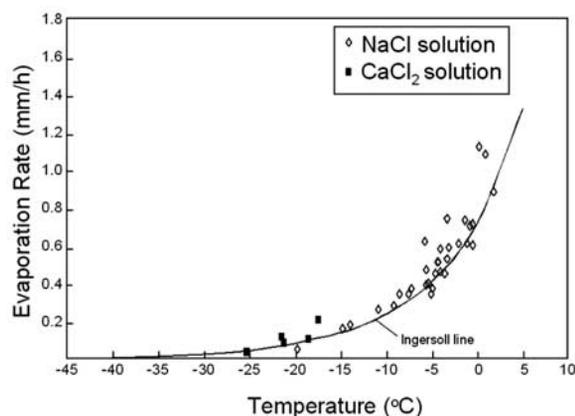


Figure 3. The present data for the evaporation rate of water on Mars from solutions of 23.3% NaCl (open diamonds, most of the data above -10°C) and 29.8% CaCl₂ (filled squares, most of the data below -10°C) as a function of temperature. The data have been corrected for the effect of Earth's greater gravity and for the effect of build-up of water vapor in the apparatus during the experiment. The solid curve represents the prediction of a model-dependent theoretical treatment described in the text. The excellent agreement between the calculated value and the experimental value lends credibility to both. The presence of solute in water on Mars increases its stability not only by suppressing the freezing point, but also by decreasing evaporation rates by factors of up to 30.

currence of chloride, bromide, and sulfate than previously assumed. Alternatively, of course, the martian evaporites could be buried under layers of windblown dust.

[13] Of course, many other factors also affect the stability of liquid water on Mars, such as winds, air temperature, pressure variations, insolation, and the influence of coverings of snow, ice and dust. Our understanding to date is that none of these are as important as the temperature effects reported here. These topics will be discussed elsewhere.

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