

Supplementary Information

Energetics of water in the Solar System

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Fig S1. Thermodynamic model visualization: Description of thermodynamic model control volumes

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Fig S3. Equation of state specific Gibbs free energy validation: Comparison of Gibbs free energy predictions with different, experimentally validated water property databases

Fig S4. Equation of state least work of separation validation: Comparison of the least work of separation with different, experimentally validated water property databases

Fig S5. Equation of state least work of heating validation: Comparison of the least work of heating with different water property databases over temperature.

Fig S6. Equation of state least work of heating validation: Relative error between equations of state over temperature and humidity.

Fig S7. Water harvesting from air and pure water vapor mixtures: Comparison of the least work considering only water vapor versus water vapor in an air mixture.

Fig S8. Extended model of NaCl brine separation: Least work of a binary NaCl brine mixtures up to 4m concentration

Fig S9. Extended model for Mg (ClO₄)₂ brine separation: Least work of a binary Mg (ClO₄)₂ brine mixtures up to 1m concentration

Fig S10. Extended model for Mg (SO₄)₂ brine separation: Least work of a binary Mg (SO₄)₂ brine mixtures up to 2m concentration

Fig S11. Reduced order model for ice energetics: A polynomial on temperature curve fit using the data points computed for the manuscript

Table S1. Water-Ice ranges of conditions: Ranges of input conditions that were used for water-ice sources.

Table S2. Liquid water ranges of conditions: Ranges of input conditions that were used for liquid water sources.

Table S3. Water vapor ranges of conditions: Ranges of input conditions that were used for water vapor sources.

Table S4. Brine solution comparison: Comparison of known salts found in brine sources.

Table S5. Compressibility factor validation: A comparison of calculated and measured compressibility factors of water at low temperatures.

Data S1: Least work modeling results

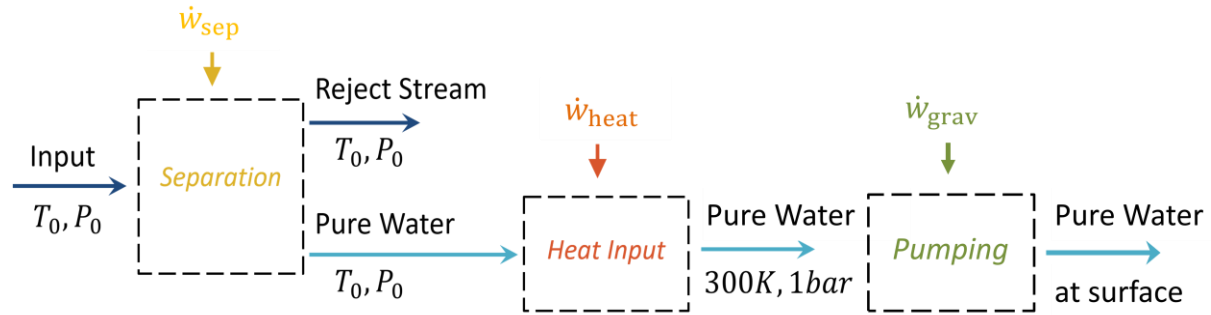


Fig. S1. Thermodynamic model visualization

The least work can be modeled as a staged, fully reversible process. The input and reject streams represent the feed and brine. These are evaluated the natural temperature of the source. The pure water from the input mixture is separated, isothermally using the minimum separation work described by S1. It is then brought to the Earth standard conditions, via the work due to heating. A third stage can be similarly added when gravitational potential is applicable.

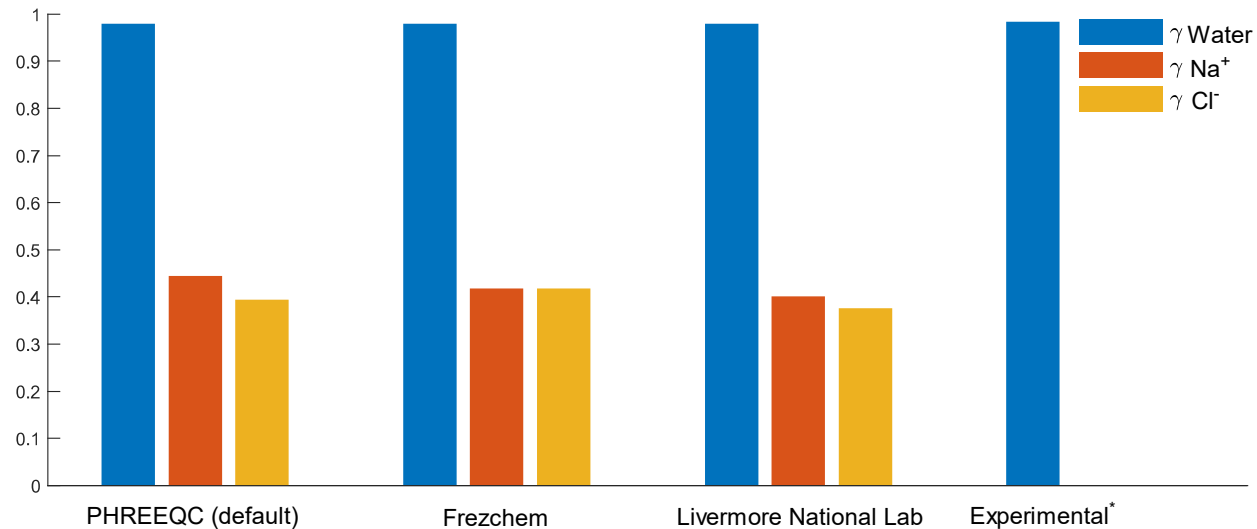


Fig. S2. PHREEQC model validation

A comparison of activity coefficient values to validate the thermochemical property models in PHREEQC is shown^{1,2}. The activity of water, Na⁺, and Cl⁻ are compared to prior literature for the thermochemical databases used in this study. The comparison was done at 300K and 0.596M (seawater salinity). The PHREEQC (default) and Livermore National Lab (LLNL) databases are publicly available at USGS. The Frezchem database is provided by Professor David Catling and Dr. Jon Toner³⁻⁵. Experimental values are provided at M = 0.6 from Chirife and Resnik (1984)⁶.

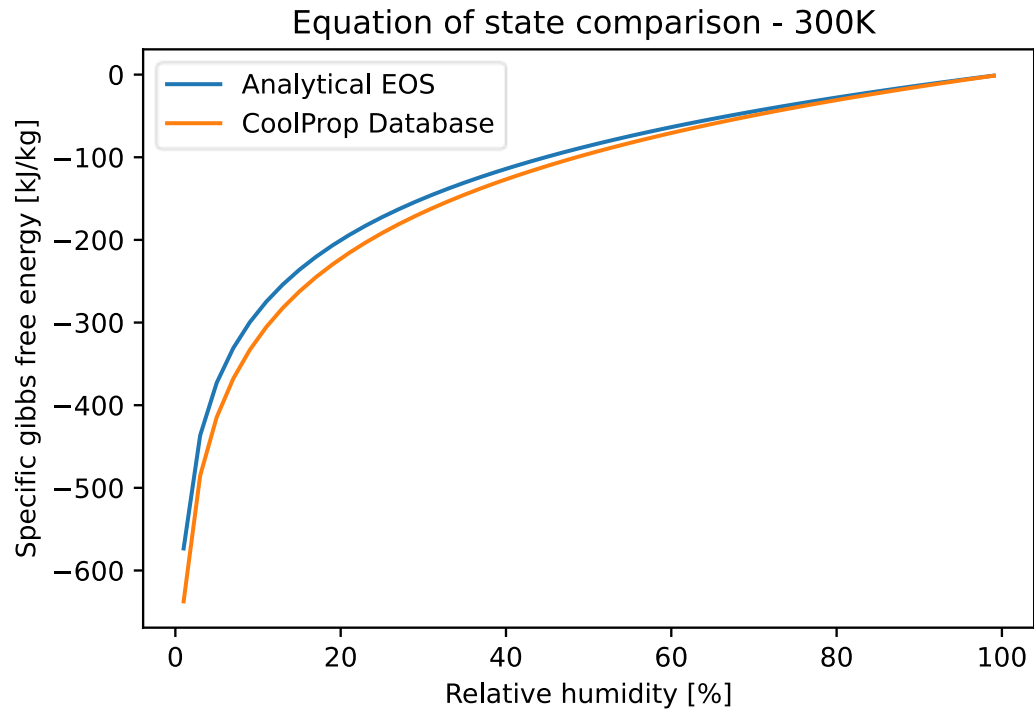


Fig. S3. Equation of state specific Gibbs free energy validation. The analytical EOS represents the property calculations based on the compressibility factor correlations, presented in methods. The CoolProp database of properties is validated against ASHRAE standards ⁷.

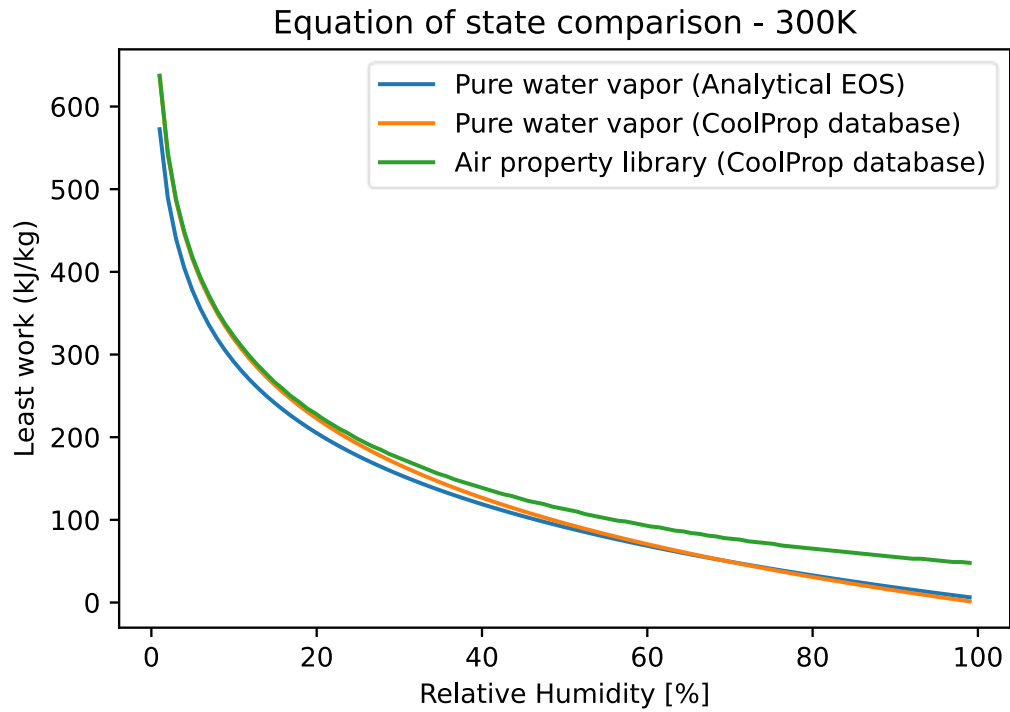


Fig. S4. Equation of state least work of separation validation. The calculation assumes an isothermal process at the thermodynamic dead state temperature (300K) to isolate the separation energy. The analytical equation of state (blue) and CoolProp property database (orange) are used for pure water vapor. The CoolProp database for humid air properties (green) is additionally used for comparison ⁷.

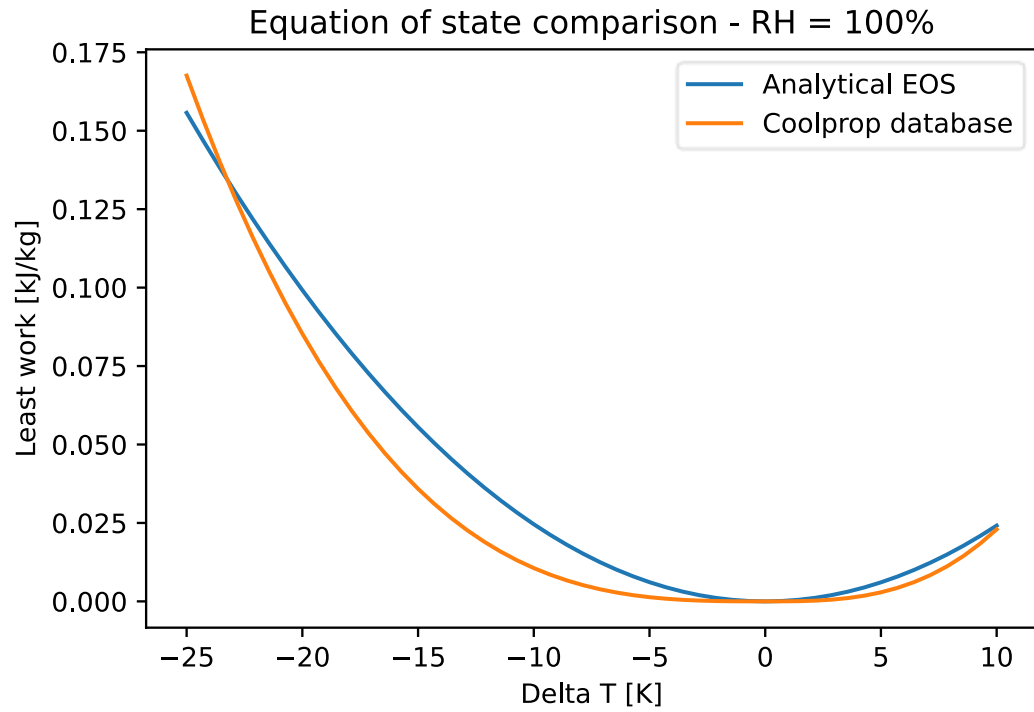


Fig. S5. Equation of state least work of heating validation. The calculation assumes an isobaric process at saturation (RH = 100%). The analytical equation of state (blue) and CoolProp database (orange) are used for pure water vapor ⁷. Regardless of the equation of state, the least work approaches zero at the thermodynamic dead state.

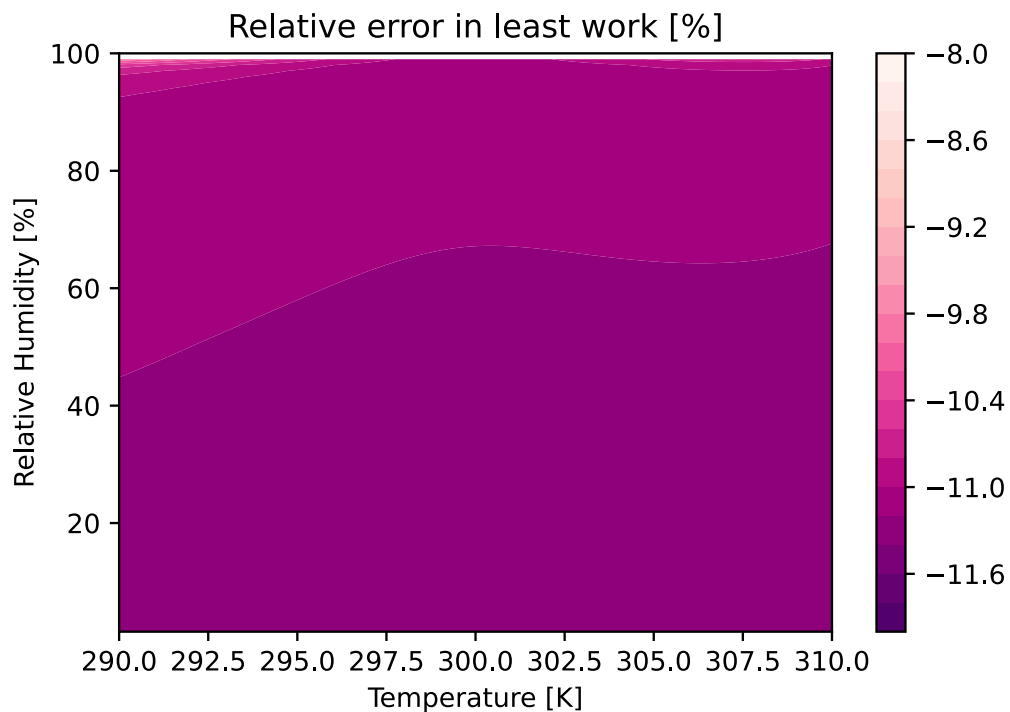


Fig. S6. Equation of state least work of heating validation. The calculation considers the total least work at ambient conditions that are well defined by the CoolProp database ⁷. The relative error is calculated by $err = 100 \left(\frac{W_{analytical} - W_{CoolProp}}{W_{analytical}} \right)$. The majority of the error may be attributed to the compressibility factor correlations since a 1st order Taylor series expansion in pressure was used. As shown by Wexler (1977) this error is reduced to less than 1% at temperatures below 273K ⁸, and therefore the range of this plot show the conditions of maximum model error.

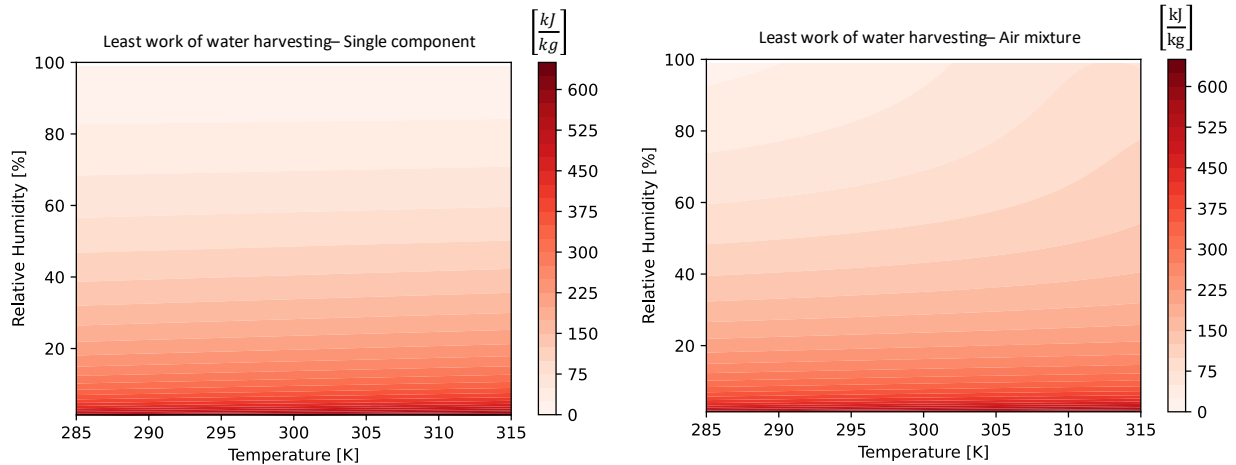


Fig. S7. Water harvesting from air and pure water vapor mixtures. This considers the full parametric sweep for water harvesting using the CoolProp database as the equation of state ⁷. The single-component version (left) assumes Dalton’s law and ignores other components in the mixture. The air version (right) assumes water is in a standard air mixture and accounts for energy interactions between mixture components. Nearly inert water vapor mixtures, like air, can behave as an ideal gas at low humidity. Water vapor on other planets is often found at low vapor pressures and concentrations. This suggests that the least work at low temperatures and humidity behaves similarly when computed with full mixture properties and water vapor partial properties.

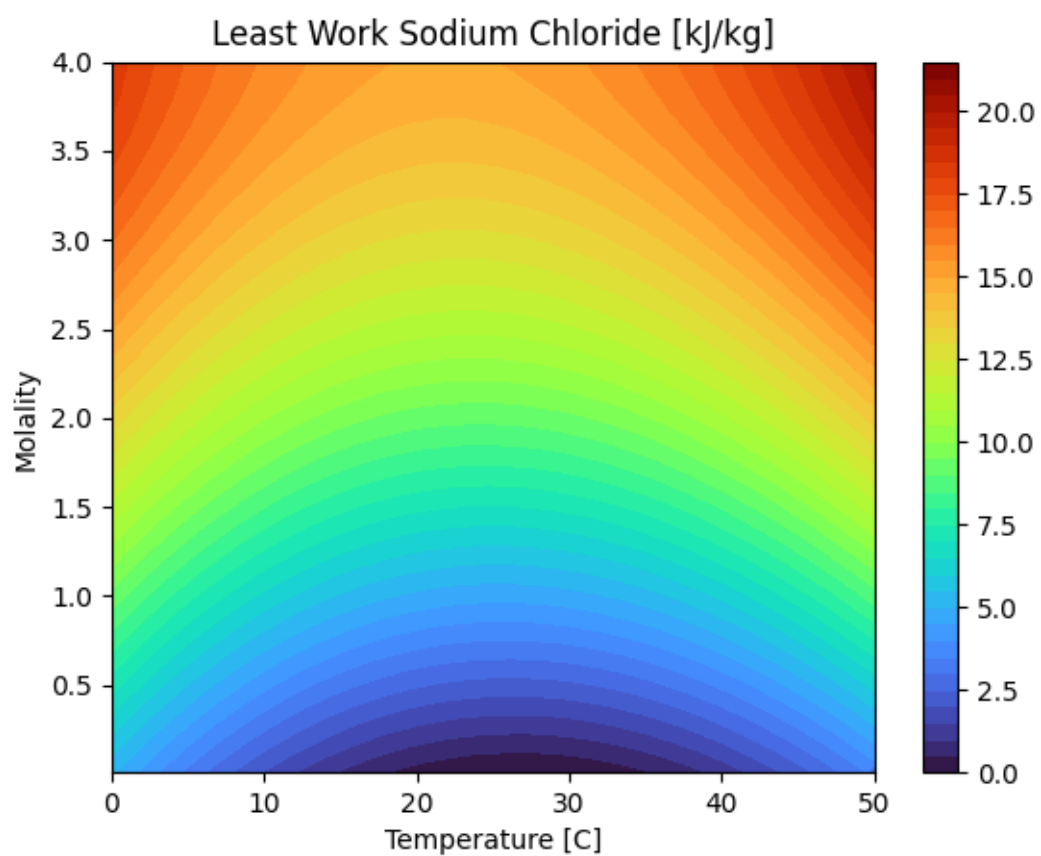


Fig. S8. Extended model of NaCl brine separation. Axes bounds represent the range of model validity. NaCl properties resemble water solutions on Earth and fall in between the upper and lower bounds shown in the manuscript Fig 1A. For reference, most solutions on Earth are less than 1m.

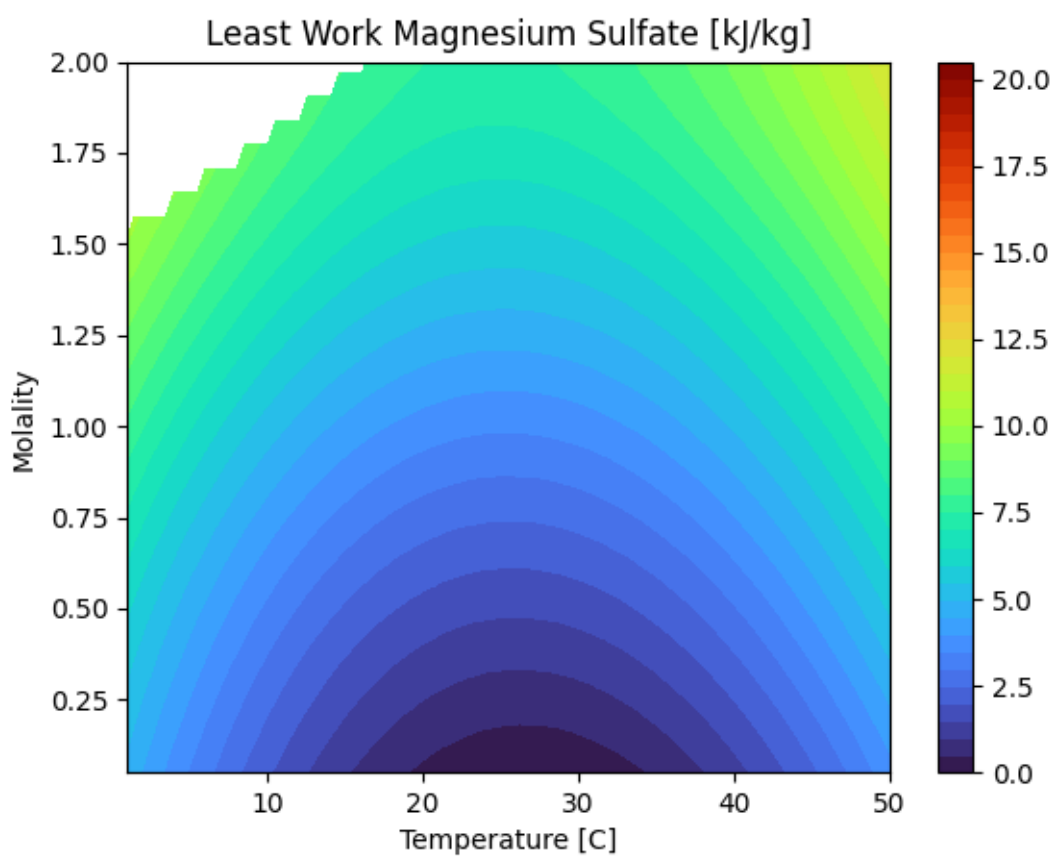


Fig. S9. Extended model for Mg (SO₄)₂ brine separation. Axes bounds represent the range of model validity. White space signifies supersaturation. Mg(SO₄)₂ solutions fall in between the upper and lower bounds shown in the manuscript Fig 1A.

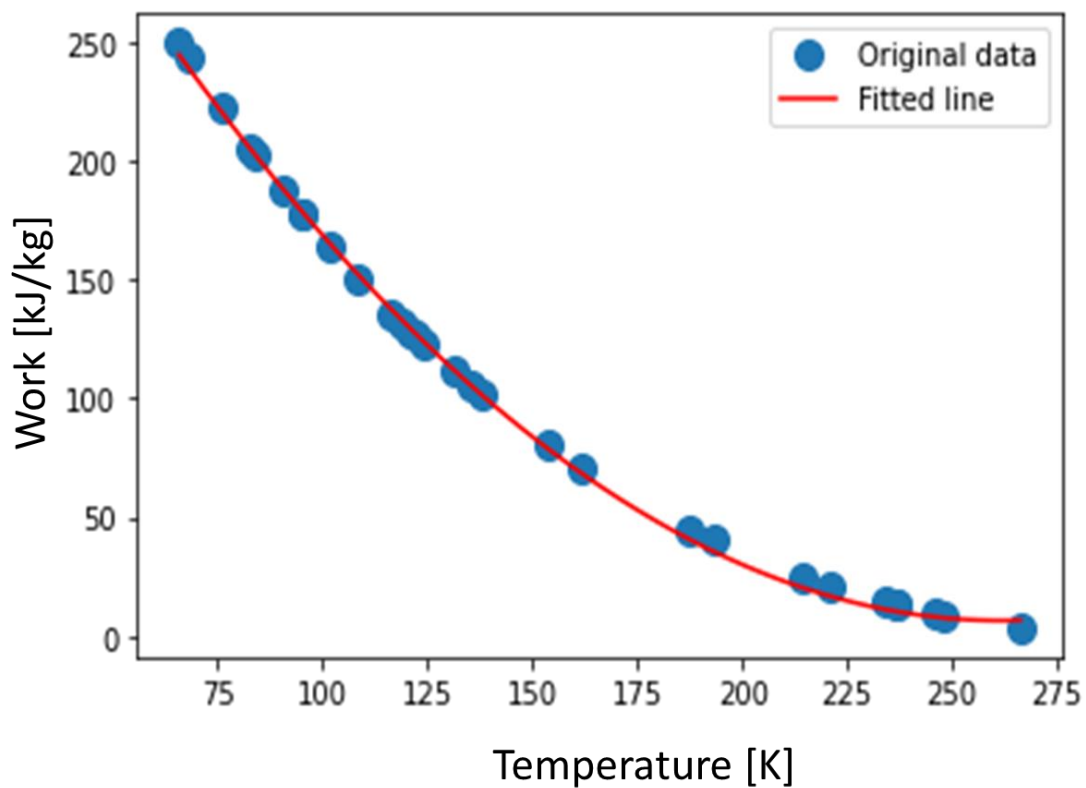


Fig. S10. Reduced order model for ice energetics. The least work (kJ/kg) model is fit to a 2nd degree polynomial on temperature (K): $W = 0.0062T^2 - 3.2436 T + 430.8821$. Coefficients must be accurate to 4 decimal places. The original data refers to the calculations made for the manuscript Figure 2.

Table S1. Water-Ice ranges of conditions. The explicit trials that are used for calculation can be found in Data S1.

Planetary Body	Temperature [K]	Depth [km]
Mercury	90 – 155	0
Earth	184 – 273	0
Moon	95 – 110	0
Mars	184 – 237	0
Europa	116 – 122	0
Ganymede	130 – 138	0
Enceladus	65 – 125	0
Tethys	75 – 85	0
Uranus	100 – 250	200-300
Jupiter	230 – 250	20-50

Table S2. Liquid water ranges of conditions. The explicit trials that are used for calculation can be found in Data S1.

Planetary Body	Temperature [K]	Depth [km]	Concentration [M]	Species Present
Earth	273 – 310	0	0.5 – 0.65	Na, Cl
Mars	271 – 285	0 – 0.75	0.4 – 1.2	Na, Mg, SO ₄
Europa	272 – 325	10 – 30	0.9 – 1	Mg, SO ₄
Ganymede	0 – 278	800	0.1 – 0.8	Na, Cl, HCO ₃ , CO ₂ , K
Enceladus	273 – 300	35	2.5 – 12	Na, Cl, Mg, K, Ca, ClO ₄

Table S3. Water vapor ranges of conditions. The explicit trials that are used for calculation can be found in Data S1.

Planetary Body	Temperature [K]	Depth [km]	Vapor Pressure** [kPa]
Venus	430 – 740	5 – 50	0.006 – 0.5
Earth	273 – 325	0	0.2 - 13
Mars*	250 – 337	0	0.00005 – 0.0002

* Due to the extreme low pressures, water is able to stay in the vapor state at low temperatures.

**Vapor pressure is used to represent mixing fraction and ambient pressure due to the ideal gas relationship

Table S4. Brine solution comparison. All simulations, except for ZnSO_4 , use the FREZCHEM thermochemistry database provided by Professor David Catling. Since FREZCHEM does not include Zinc, it is simulated using the LLNL database. Each trial is simulated at 0.5 molality and 300 K. Trends are validated with prior literature on NaCl and ZnSO_4 studies of least work and compared to the least work trends of five other relevant binary electrolyte solutions: KCl, MgCl_2 , CaCl_2 , Na_2SO_4 , and MgSO_4 . This comparison can be found in Figure 11 of Mistry, Hunter, Lienhard (2013) ⁹.

Binary electrolyte solution	Least work $\left[\frac{\text{kJ}}{\text{kg}}\right]$
NaCl	2.42
NaClO_4	2.35
$\text{Mg}(\text{ClO}_4)_2$	4.02
$\text{Ca}(\text{ClO}_4)_2$	3.97
ZnSO_4	1.55

Table. S5. Compressibility factor validation. The calculation of the compressibility factor for sub-freezing temperatures is compared to the compressibility factor presented in Wexler (1997) ⁸. The maximum percent difference between the two is 0.01%

Temperature [K]	Compressibility factor Z [-]	
	This work	Wexler, 1977
273.16	0.999624	0.999624
273.15	0.999624	0.999624
263.15	0.999807	0.999907
253.15	0.999907	0.999958
243.15	0.999959	0.999982
232.15	0.999982	0.999993
213.15	0.999999	0.999999
193.15	0.999999	1.00000
173.15	0.999999	1.00000

Data S1. (Separate file)

A component-wise breakdown of the results shown in Fig. 3 and the graphical abstract.

Additional References

1. Charlton, S. R. & Parkhurst, D. L. Modules based on the geochemical model PHREEQC for use in scripting and programming languages. *Computers and Geosciences* **37**, 1653–1663 (2011).
2. Parkhurst, D. & Appelo, C. *Description of Input and Examples for PHREEQC Version 3-A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*. <http://www.hydrochemistry.eu>.
3. Toner, J. D. & Catling, D. C. Water activities of NaClO₄, Ca(ClO₄)₂, and Mg(ClO₄)₂ brines from experimental heat capacities: Water activity >0.6 below 200 K. *Geochimica et Cosmochimica Acta* **181**, 164–174 (2016).
4. Toner, J. D., Catling, D. C. & Light, B. The formation of supercooled brines, viscous liquids, and low-temperature perchlorate glasses in aqueous solutions relevant to Mars. *Icarus* **233**, 36–47 (2014).
5. Toner, J. D., Catling, D. C. & Light, B. Soluble salts at the Phoenix Lander site, Mars: A reanalysis of the Wet Chemistry Laboratory data. *Geochimica et Cosmochimica Acta* **136**, 142–168 (2014).
6. Chirife, J. & Resnik, S. L. Unsaturated Solutions of Sodium Chloride as Reference Sources of Water Activity at Various Temperatures. *Journal of Food Science* **49**, 1486–1488 (1984).
7. Bell, I. H., Wronski, J., Quoilin, S. & Lemort, V. Pure and pseudo-pure fluid thermophysical property evaluation and the open-source thermophysical property library coolprop. *Industrial and Engineering Chemistry Research* **53**, 2498–2508 (2014).
8. Wexler, A. VAPOR PRESSURE FORMULATION FOR ICE. *J Res Natl Bur Stand Sect A Phys Chem* **81A**, 5–20 (1977).
9. Mistry, K. H., Hunter, H. A. & Lienhard V, J. H. Effect of composition and nonideal solution behavior on desalination calculations for mixed electrolyte solutions with comparison to seawater. *Desalination* **318**, 34–47 (2013).