



WATER STRUCTURE AND SCIENCE

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Water Phase Diagram

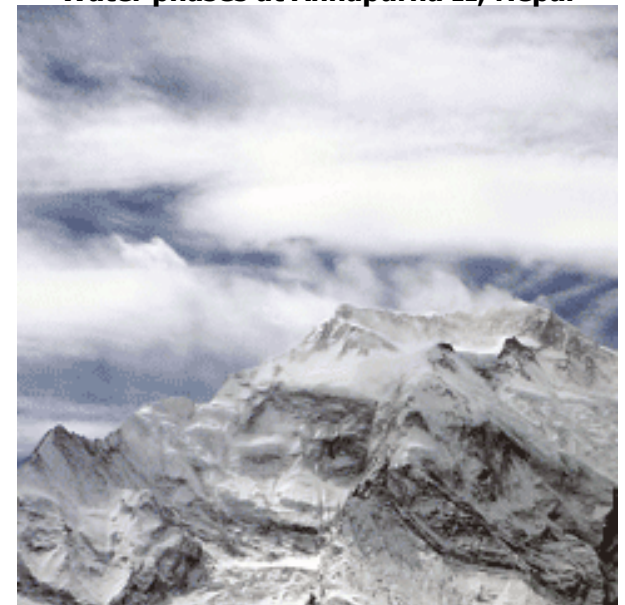
The properties of the all the known different phases of water are described.

- ▼ Phase diagrams
- ▼ The phase diagram of water
- ▼ Triple points
- ◀ Water density
- ◀ Supercooled water
- ◀ Supercritical water
- ◀ The ice phases

'Corresponding to the abnormal behavior of the liquid at low pressures, and probably connected to it, the solid also shows abnormal behavior...'

Percy Bridgman, 1911 [2472]

Water phases at Annapurna II, Nepal



Phase diagrams

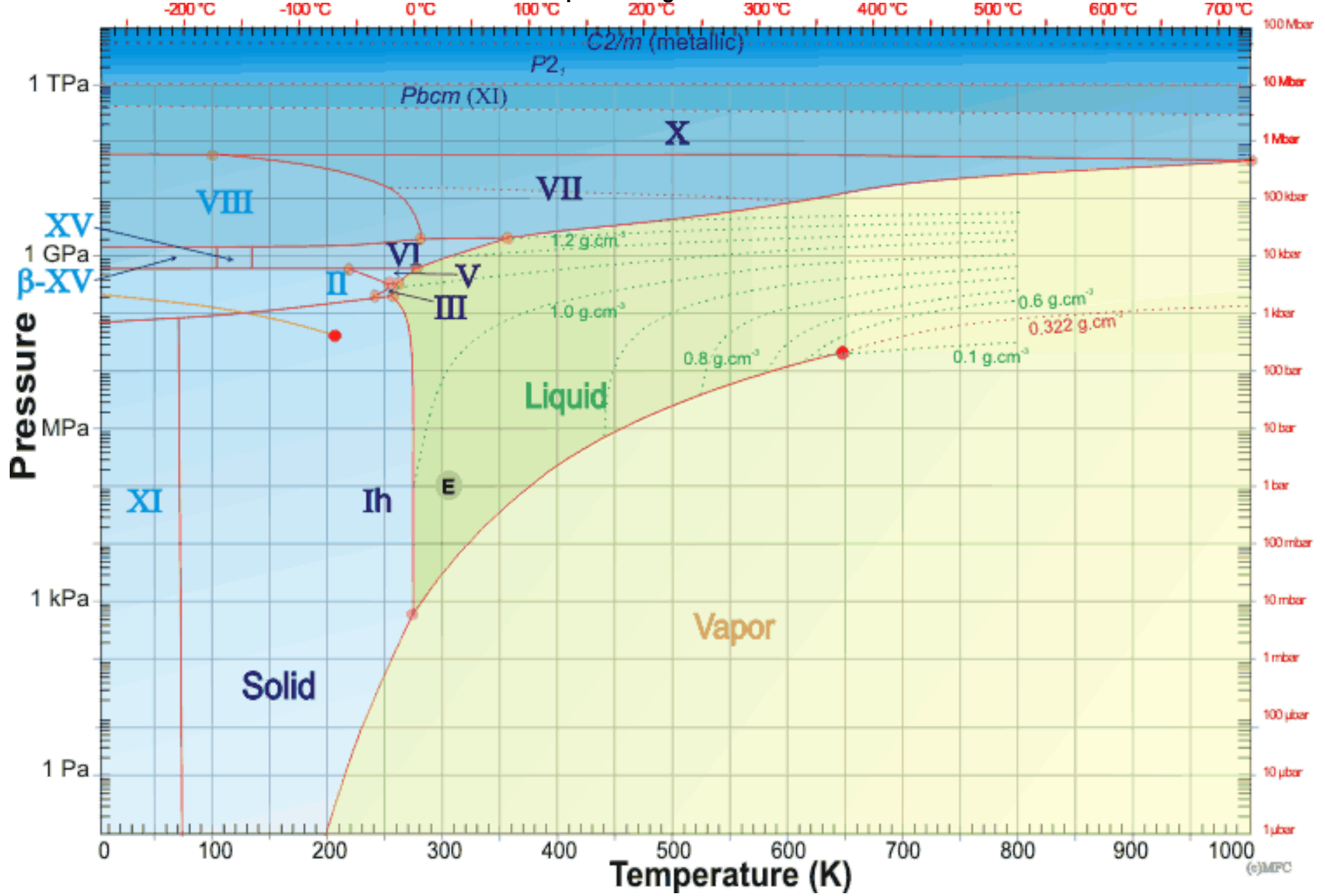
Phase diagrams show the preferred physical states of matter at different temperatures and pressure. Within each phase, the material is uniform with respect to its chemical composition and physical state. At typical temperatures and pressures on Earth (marked by an 'E' below) water is a liquid, but it becomes solid (that is, ice) if its temperature is lowered below 0 °C and gaseous (that is, water vapor) if its temperature is raised above 100 °C, at the same pressure. Each line (phase line)^d on a phase diagram represents a phase boundary and gives the conditions when two phases may stably coexist in any relative proportions (having the same Gibbs free energy). Here, a slight change in temperature or pressure may cause the phases to abruptly change from one physical state to the other. Where three phase lines join, there is a 'triple point', when three phases stably coexist (having identical Gibbs free energies),^d but may abruptly and totally change

into each other given a slight change in temperature or pressure. Under the singular conditions of temperature and pressure where liquid water, gaseous water and hexagonal ice stably coexist, there is a 'triple point' where both the boiling point of water and melting point of ice are equal. Four phase lines cannot meet at a single point. A 'critical point' occurs at the end of a phase line where the properties of the two phases become indistinguishable from each other, for example when, under singular conditions of temperature and pressure, liquid water is hot enough and gaseous water is under sufficient pressure that their densities are identical (0.322 g cm^{-3}). At temperatures above the critical temperature a gas cannot be liquefied. Critical points are usually found at the high temperature end of the liquid-gas phase line.

The phase diagram of water

The phase diagram of water is complex, ^{a, b, c, e, f} having a number of triple points and one, or possibly two, critical points. Many of the crystalline forms may remain metastable in much of the low-temperature phase space at lower pressures. A thermodynamic model of water and ices Ih, III, V and VI [1320] and thermodynamic functions of the phase transitions [1658] have been described. The known ices can be divided, by cluster analysis of their structures [1717], into the low-pressure ices (hexagonal ice, cubic ice and ice-eleven), the high-pressure ices (ice-seven, ice-eight and ice-ten) and the others (found in the relatively narrow range of moderate pressures between about 200-2000 MPa). It is noticeable that most phase boundaries between the ices that share phase boundaries, particularly with the liquid, are parallel to the temperature axis, implying density-driven phase transformations [2465]; entropy-driven phase transformations showing phase boundaries parallel to the pressure axis. All phases that share phase boundaries with liquid water (ices Ih, III, V and VI and VII) have disordered hydrogen bonding. The phases with ordered hydrogen bonding are found at lower temperatures and are indicated in light blue below. The structural transformation conditions of some of these ices during compression have been described [1795]. As pressure increases, the ice phases become denser. They achieve this by initially bending bonds, forming tighter ring or helical networks, and finally including greater amounts of network inter-penetration. This is particularly evident when comparing ice-five with the metastable ices (ice-four and ice-twelve) that may exist in its phase space. Note that, in the phase diagram below, only the stable phases are shown and that the vertical axis has a logarithmic scale for pressure, as the required pressures vary over more than ten orders of magnitude.

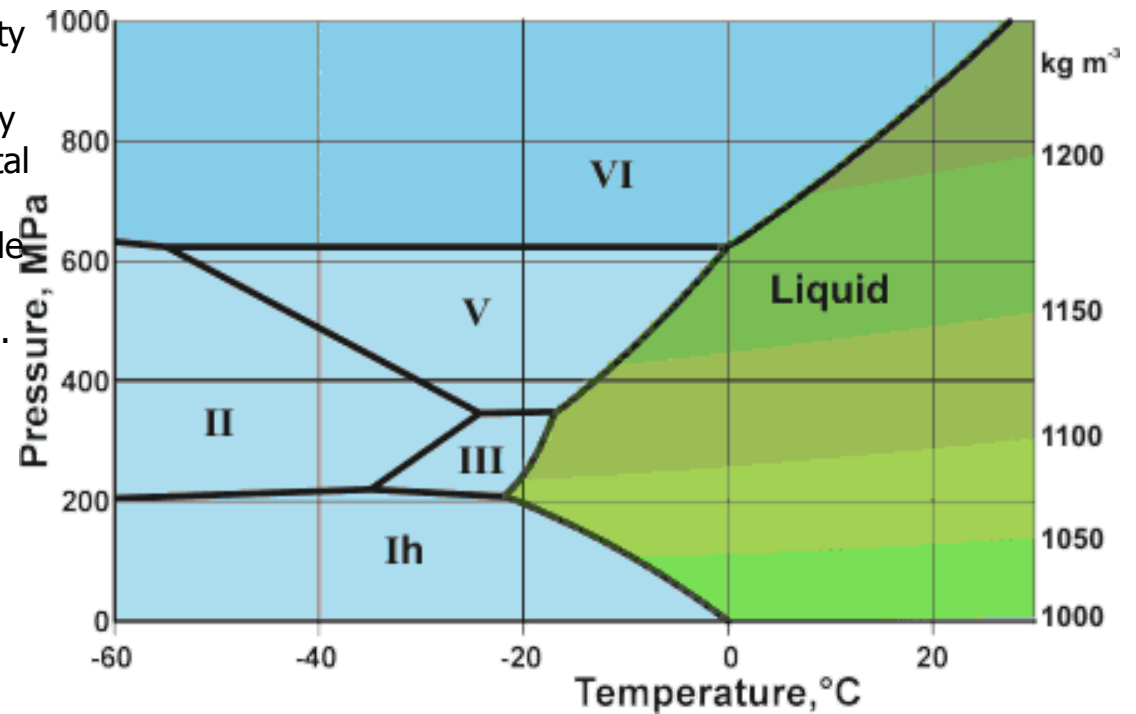
The phase diagram of water



Detail of the water phase diagram

The mean surface conditions on **E**arth, (also atmospheric conditions, **M**ars and **V**enus on mousing over Earth) are indicated. The complex central part of the phase diagram is expanded opposite. The critical point and the orange line in

the ice-one phase space refer to the low-density (LDA) and high-density (HDA) forms of amorphous water (ice) [16]. Although generally accepted and supported by diverse experimental evidence [754a, 861], the existence of this second, if metastable, critical point is impossible to prove absolutely at the present time and is **disputed by some** [200, 618, 628, 754b, 1115]. The transition between LDA and HDA is due to the increased entropy and attractive van der Waals contacts in HDA compensating for the reduced strength of its hydrogen bonding.



Mouse over border for D₂O phase lines

The high-pressure phase line between **ice-ten** (X) and **ice-eleven** (XI) [81] is still subject to experimental verification. The melting point line between **supercritical water** and **high-pressure ice** has been established [691, 2096]. Ice VII possesses **higher and lower pressure forms** [1428]. A phase diagram of water at higher temperatures, up to 9000 K, has been proposed [1671].

Both the critical points are shown as red circles in the phase diagram, above.

Many properties of cold liquid water change above about 200 MPa (for example, **viscosity**, **self-diffusion**, **compressibility**, **Raman spectra** and **molecular separation**), which may be explained by the presence of a high-density liquid phase containing interpenetrating hydrogen bonds. The chemical properties of water are also greatly changed at high temperatures and pressures due to the changes in **dissociation**, **solubility**, **diffusivity** and reactivity due to decreasing **hydrogen-bonding** [1116].]

Triple points

Triple points occur where three phase lines join and the three (stable) phases may coexist at equilibrium. As the triple point (gas:liquid:ice Ih) can be precisely reproduced in the laboratory, its temperature (defined to be exactly 273.16 K), together with the absolute zero of temperature (0 K) determine the thermodynamic temperature scale and the size of the kelvin.

Thermodynamic data for the triple points of water

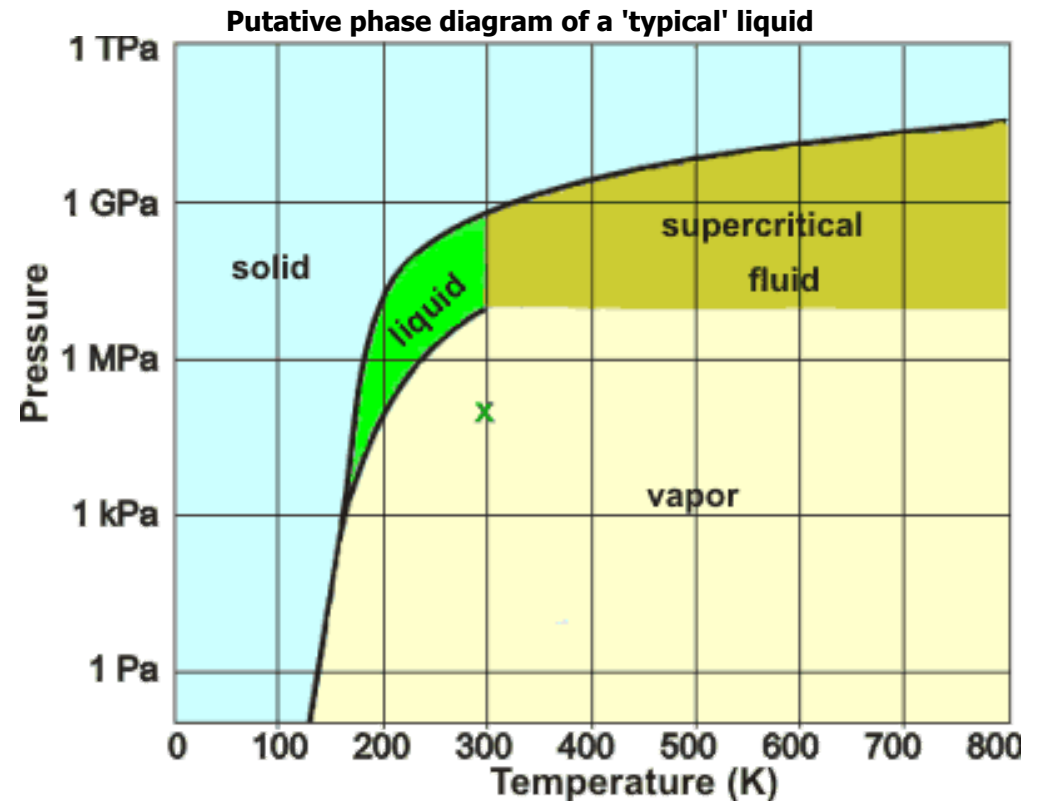
Triple points			MPa	°C	$\Delta H,$ kJ \times mol ⁻¹	$\Delta S,$ J mol ⁻¹ K ⁻¹	ΔV cm ³ mol ⁻¹	Ref.	D ₂ O [717]
gas	liquid	Ih	0.000611657	0.010				536	661 Pa, 3.82 °C [70]
			gas → liquid		-44.9	-165	-22050	1833	
			gas → Ih		-50.9	-186	-22048		
			liquid → Ih		-5.98	-22	1.634		
gas	Ih	XI	0	-201.0				717	0 MPa, -197 °C
			Ih → XI				0		
liquid	Ih	III	209.9	-21.985				537	220 MPa, -18.8 °C
			liquid → Ih		-4.23	-16.9	2.434	1833	
			liquid → III		-3.83	-15.3	-0.839		
			Ih → III		0.39	1.6	-3.273		
Ih	II	XI	70	-199.8				2300	80 MPa, -195 °C [2300]
Ih	II	III	212.9	-34.7				537	225 MPa, -31.0 °C
			Ih → II		-0.75	-3.2	-3.919	1833	
			Ih → III		0.17	0.7	-3.532		
			II → III		0.92	3.8	0.387		
II	III	V	344.3	-24.3				537	347 MPa, -21.5 °C
			II → III		1.27	5.1	0.261	1833	
			II → V		1.20	4.8	-0.721		

			III→V		-0.07	-0.2	-0.982		
II	VI	XV						1582	~0.8 GPa, -143 °C
liquid	III	V	350.1	-16.986				537	348 MPa, -14.5 °C
			liquid→III		-4.61	-18.0	-0.434	1833	
			liquid→V		-4.69	-18.3	-1.419		
			III→V		-0.07	-0.2	-0.985		
II	V	VI	~620	~-55				539	
liquid	V	VI	632.4	0.16				537	629 MPa, 2.4 °C
			liquid→V		-5.27	-19.3	-0.949	1833	
			liquid→VI		-5.29	-19.4	-1.649		
			V→VI		-0.02	-0.5	-0.700		
VI	VIII	XV						1582	~1.5 GPa, -143 °C
VI	VII	VIII	2,100	~5				8	1950 MPa, ~0 °C
			VI→VII		-0.09	-0.3	-1.0	1833	
			VI→VIII		-1.20	-4.2	-1.0		
			VII→VIII		-1.10	-3.9	0.0		
liquid	VI	VII	2,216	81.85				537	2060 MPa, 78 °C
			liquid→VI		-6.36	-18.0	-0.59	1833	
			liquid→VII		-6.36	-18.0	-1.64		
			VI→VII		0.0	0.0	-1.05		
VII	VIII	X	62,000	-173				538	
super-critical fluid	VII	X	43,000	>700				612a	
			47,000	~727				612b	
super-critical fluid	VII	Superionic	~40,000	~1000				1572	

Footnotes

^a If water behaved more typically as a low relative molecular mass (molecular weight) material, its phase diagram may have looked rather like this (where 'x' marks ambient conditions on earth).

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^b The metastable phases ([Ice Ic](#), [ice IV](#), [Ice IX](#) and [Ice XIII](#)) do not belong in a phase diagram. However, [Ice Ic](#) (cubic ice) has been found in the [hexagonal ice](#) phase space below -80 °C, [ice IV](#) has been found within the [ice-three](#), [ice-five](#) and [ice-six](#) phase spaces and [Ice IX](#) and [Ice XIII](#) have been found within the [ice-two](#) phase space. As with the stable ice phases, at low enough temperatures these phases may be stable for extensive periods as there is insufficient energy available to overcome the necessary activation barriers. [[Back](#)]

^c Note that phase diagrams originating from this site have been copied by various sources including to and then from Wikipedia without proper citation (or inherent permissions) of their source. Such poor scientific etiquette is easy for me to detect and reflects badly on these authors. [[Back](#)]

^d On a phase line the Gibbs free energies of the two phases (G_1 , G_2) must be equal and remain equal if conditions change causing movement along the phase line. Thus

$$\left(\frac{\partial G_1}{\partial T}\right)_P dT + \left(\frac{\partial G_1}{\partial P}\right)_T dP = \left(\frac{\partial G_2}{\partial T}\right)_P dT + \left(\frac{\partial G_2}{\partial P}\right)_T dP$$

But, $\left(\frac{\partial G}{\partial T}\right)_P = S$ where S is the entropy, and $\left(\frac{\partial G}{\partial P}\right)_T = V$ where V is the volume

Therefore $\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{L}{T\Delta V}$ where L is the latent heat (enthalpy change) for the phase change. This is the **Clausius-**

Clapeyron equation. At a triple point, the Gibbs free energies of the three phases (G_1, G_2, G_3) must be equal and the entropy and enthalpy (latent heat) changes for all three phase changes ($1 \longrightarrow 2, 2 \longrightarrow 3, 1 \longrightarrow 3$) at that point may be calculated, given the pressure, temperature $\left(\frac{dP}{dT}\right)$ and volume changes. [[Back](#)]

^e The phase diagram for heavy water (D_2O) differs little from the [diagram for \$H_2O\$](#) given the scales used in the diagram. A more accurate representation would be by shifting the temperature scale by about 3.6 K as most of the **triple points** for D_2O are 3 - 4 K warmer than those for H_2O (see [above](#)). The pressure differences are positive or negative but not significant given the logarithmic scale used. [[Back](#)]

^f The phase diagram of water for **negative pressure** has been described [[2666](#)]. [[Back](#)]

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