### VAPOR, WATER, AND ICE

Water has sometimes been described (by scholars who don't know it very well) as the "ideal" liquid, the standard to which all other liquids are compared. This is not a description favored by water scientists. The naïve proposal that water be considered as an ideal liquid, that ice is an ideal solid, and that water vapor is an ideal gas is sufficient to give convulsive shudders to most water scientists. Water is not an ideal liquid; it is not a typical liquid; it is not a normal liquid. Water is strange. Many scholars who study it would go so far as to say that it is downright weird.

### **Enthalpic Characteristics of the Water Molecule**

As a tri-atomic molecule, water vapor has a minimum of six degrees of freedom: three of translation, three of rotation and—at temperatures normally encountered in the free atmosphere—a fractional degree of vibration (that is, some molecules in a population will be vibrating along some axes, but not all axes are involved nor all molecules).

The mean total kinetic energy ( $\overline{u}$ ) of a population of water molecules may thus be approximated by the equation:

$$\overline{u} = \overline{f}_{\circ} \frac{1}{2} \mathbf{k}_{\mathrm{B}} \overline{T}$$
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Here,  $\overline{f}_{\circ}$  is the mean number of degrees of freedom,  $\mathbf{k}_{B}$  is Boltzmann's Constant, and  $\overline{T}$  is the mean temperature of the population in kelvins. Values for the degrees of freedom and the kinetic energy content of a kilogram of water (any phase) at various temperatures are found in the Tables that follow the text in this paper.

### Vapor, Water, and Ice

It should be noted that these values are essentially independent of the phase. This independence is mandated by the convention that gases, liquids, and solids at the same temperature have the same kinetic energies normal to the sensing surface; that is:

$$\overline{T} = \frac{\overline{u}_i^{\Sigma}}{\mathbf{k}_{\mathrm{B}}} \qquad \text{NGT04}$$

Here,  $\overline{u}_i^{\Sigma}$  is the mean total kinetic energy of all kinds (translational, rotational, and vibrational) measured normal to the thermometric surface (see <u>Nature of Gas</u> <u>Temperatures</u>). In the hard sphere model of an ideal gas, this energy would apply only to the kinetic energy of translation normal to the sensing surface. However, real molecules sometimes transfer energies of rotation and energies of vibration to sensing surfaces when they "impact" on those surfaces (see <u>The Equipartition</u> <u>Conundrum</u>).

Differences in phase and temperature create different proportions of these three modes, but the total kinetic energy remains essentially the same for different phases at the same temperature.

The differences in specific heats  $(C_p)$  between the three phases at the same temperature are all accounted for by the different amounts of work being done under constant pressure and the work done in loosening and breaking the various bonding energies.

### **VAPOR**

Water vapor is the most ubiquitous of the three phases of water in the Earth's atmosphere. No part of the atmosphere is free of it. Water vapor can and does exist within the atmosphere at every combination of temperature and pressure found within the atmosphere.

**Intermolecular Bonds**: This vapor phase is generally characterized by the absence of long-term intermolecular bonds. Indeed, this has been the defining characteristic of the vapor phase in classical mechanics. However, recent studies suggest that dimers and polymers may make up as much as a tenth of a percent of vapor formations. It is not known whether these dimers and polymers persist

Vapor, Water, and Ice through intermolecular collisions, or whether they are continuously being destroyed and reformed.

The molecules (and clusters of molecules) of water vapor move about freely from place to place essentially independently of one another. The mean distances between them depend upon the number density, but are on the order of at least ten times or more of the mean molecular diameter at number densities normally encountered in the free atmosphere. Generally speaking, a vapor molecule travels some three hundred molecular diameters between collisions at normal temperatures and pressures.

**Thermal Agitation**: Virtually all vapor molecules have kinetic energies of translation and rotation. Some (but not all) possess kinetic energies of vibration, as well. These vapor molecules move through space from place to place spinning and tumbling and (on occasion) vibrating and librating.

The distribution of molecular velocities and speeds along any single axis follows the standard normal curve (see <u>Molecular Speeds and Velocities</u>) when presented in terms of their standard deviation.

$$\Phi(v_p) = \frac{1}{\sigma} \frac{1}{\sqrt{2\pi}} \exp{-\frac{v_p^2}{2\sigma^2}}$$
 MSV04

Here,  $\Phi(v_p)$  is the probability of a randomly selected molecule having a component of velocity  $v_p$  along the proximity axis.

This means that the most probable speed relative to some object of interest (another molecule or a condensation nucleus, for instance) is zero, with increasing relative speeds becoming increasingly less probable. Given the strengths of both hydrogen bonding and ionic bonding, the formation of at least some clusters is virtually certain. Add in the strong hygroscopic properties of some condensation nuclei, and virtual certainty becomes certainty.

**Phase Changes**: Thus, vapor molecules can and do form small clusters within the free atmosphere. These clusters can have the characteristics of either liquid water or ice, depending upon the temperature and other considerations.

Vapor, Water, and Ice

Both simple experience and the mathematics of probability tell us that some of these agglomerations do go on to generate larger and longer-lived forms of condensation. Everything has to start somewhere.

**Humidity**: *Humidity* is the general term for the concentration of water vapor in the atmosphere. Humidity can be measured and calculated in any of the many ways that we have developed over the years: vapor pressure, relative humidity, specific humidity, absolute humidity, mixing ratio, molecular number density, dew point, and so on.

### WATER

Liquid water is less common in the free atmosphere than is water vapor. The higher reaches of the atmosphere are virtually free of it; as are significant portions of the polar deserts. On the other hand, clouds (mostly droplets of liquid water) cover more than sixty percent of the Earth's surface at any given time. And, where clouds are absent, water haze, mist, and fog are often found. Finally, even clear skies give rise to dew.

**Intermolecular Bonds**: As a phase, liquid water is characterized by loose and ephemeral hydrogen bonding between water molecules. Individual molecules are simultaneously bonding and breaking bonds in rapid sequence with a variety of neighboring molecules whose populations change more or less constantly on the human time scale. The distance between neighboring molecules depends upon the number and nature of the hydrogen bonding at that time and place. It will vary slightly with the water temperature.

The strength of the intermolecular hydrogen bonding is such that the density of real water is some 15% greater than would be the case in a simple van der Waals ideal liquid.

Over the range of water temperatures from 0°C to 100°C, the bonding energies are approximately twice the kinetic energies. Thus, when heat is added to liquid water, about a third of it goes to increasing the temperature and about two-thirds goes toward loosening the intermolecular bonds.

Vapor, Water, and Ice

During isothermal vaporization at constant volume, all of the heat energy goes to breaking the bonding energies.

**Thermal Agitation**: Virtually all water molecules possess both kinetic energies of translation and rotation. Rotation may involve actual rotation of the molecule when the hydrogen bonds break; or it may simply involve rocking back and forth within the restrictions imposed by the very flexible hydrogen bond (libration). Again, some (but not all) water molecules will possess kinetic energies of vibration, as well. Liquid water molecules move about from place to place in the body of water, both singly and in clusters. As in the vapor phase, the populations of molecules possess a wide distribution of kinetic energies; with individual molecules changing their energies billions of times per second.

**Impulses**: These various movements coupled with the close proximity of the individual molecules generate a multitude of molecular impulses. These impulses travel with the speed of sound through the liquid. Thus, any individual molecule in liquid water is continuously subject to millions of impulses of greater or lesser vigor coming from every possible direction. Some of these impulses will amplify one another, some will diminish one another. It is no wonder that the relatively weak hydrogen bonds should break so frequently.

**Phase Changes**: Simple mathematics tells us that some portion of the molecules will have sufficient kinetic energy of translation normal to one another to break the intermolecular bonds and become vapor molecules<sup>1</sup>. In the free atmosphere, liquid droplets of water almost always contain microscopic bubbles of water vapor. They usually contain microscopic bubbles of dissolved atmospheric gases, as well—but that is another story.

In additions these same mathematics tell us that some agglomerations of water molecules will possess sufficiently low kinetic energies that the forces of attraction will cause their hydrogen atoms to start to align in proto-crystal arrangements. This is the start of the freezing process.

Finally, some of the molecules on the surface of the droplet or ice crystal will receive impulses from below that will give them sufficient kinetic energy of

<sup>&</sup>lt;sup>1</sup> A hydrogen bond is assumed to be "broken" when the bonding distance exceeds 310 pm.

Vapor, Water, and Ice

translation normal to that surface to break free and become vapor molecules. This is gross evaporation.

### **ICE**

In an ice crystal, the intermolecular distances represent equilibrium positions between attractive and repulsive forces when the molecules are strongly aligned along the projecting axes of their constituent hydrogen atoms. This alignment is what makes ice less dense than liquid water.

**Intermolecular Bonding**: This bonding of ice molecules is due to the extremely intense covalent bonding between the oxygen atom and its two hydrogen atoms. This bonding is so strong that it carries over to adjacent water molecules as well. The strength of this bond is what gives water its anomalous (very high) freezing and boiling points when compared to similar hydrogen compounds.

The role of ionization cannot be overlooked. It appears that the presence of a single hydronium cation  $(H_3O^+)$  can induce intermolecular hydrogen bonding in at least a hundred surrounding water molecules. The presence of the icing cation  $(H_{15}O_7^+)$  appears to be necessary before freezing can be initiated. In the icing process, this cation is usually structured  $H_3O^+(H_2O_6)$ . It is this structure that gives the common ice crystal and the snowflake its hexagonal shape.

In ice, a touch under two thirds of the total enthalpy is devoted to maintaining the intermolecular bonds.

**Thermal Agitation**: Most of the thermal energy will be made manifest as kinetic energy of vibration and libration. In vibration, the molecules move toward and away from one another rhythmically along the hydrogen axes, stretching and compressing the hydrogen bonds. In libration, they rock side to side, bending and stretching the hydrogen bonds. In addition, many of the ice molecules will have *intra*molecular energies of vibration and libration, with the constituent atoms altering their mutual orientations in a rhythmic fashion.

In ice, just about a third of the total enthalpy is manifest in the kinetic energies of the molecules.

**Phase Changes**: The thermal energies of the individual molecules are not uniform. Ordinarily, the mathematical distribution of these thermal energies will be such that some molecules will possess sufficient kinetic energies of rotation and translation to break these bonds and rotate, tumble, and move about from place to place within the larger crystalline structure—much as they do in liquid water. This is made manifest by the old experiment of placing a drop of water-based ink on the surface of an ice cube and watching the ink diffuse readily through the ice.

As the ice temperature increases toward the melting point, more and more groups of molecules behave essentially as liquid water. At the melting point, the process increases exponentially both in space and time and the ice turns to liquid water.

Breaking the bonds between ice molecules and converting the ice into liquid water isothermally requires some 6.01 Joules per mole.

When molecules on the surface of the ice possess sufficient kinetic energy of translation normal to that surface to completely overcome the local forces of attraction they will leave the solid phase to become gas molecules. This is gross vaporization, or—in this case—sublimation.

Breaking the bonds between water molecules and converting the water into water vapor isothermally requires some 40.7 Joules per mole at atmospheric pressure in a laboratory container. In the free atmosphere, this process only requires some 24.0 Joules per mole. The difference here is that—in the absence of a "moveable lid"—no work is done against pressure in the evaporation process, the molecules simply diffuse into the surrounding air.

### **TABLES**

The tables that follow have been compiled from a wide variety of sources. These sources are given in the references that follow the tables.

**TABLE VMI01A** 

## MACROSCOPIC PARAMETERS OF WATER VAPOR

ENTHALPY OF PHASE CHANGE VAPOR TO/FROM WATER	¢Ã	kJ kg <sup>-1</sup>	2351	2365	2379	2392	2405	2417	2430	2442	2454	2465	2477	2489	2501	
TOTAL KINETIC ENERGY	$ec{U}_i^{\Sigma}$	kJ kg <sup>-1</sup>	471	463	456	448	440	433	425	418	411	403	396	389	382	
MEAN DEGREES OF FREEDOM	ا <b>ئى</b> د	o	6.1205	6.1127	6.1058	6.0997	6.0936	6.0876	6.0815	6.0759	6.0715	6.0672	6.0629	6.0585	6.0546	
GAMMA	λ		1.32677	1.32719	1.32756	1.32789	1.32821	1.32854	1.32887	1.32917	1.32941	1.32964	1.32988	1.33011	1.33033	
SPECIFIC HEAT AT CONSTANT VOLUME	<i>Č</i>	J kg <sup>-1</sup>	1412.4	1410.6	1409.0	1407.6	1406.2	1404.8	1403.4	1402.1	1401.1	1400.1	1399.1	1398.1	1397.2	
SPECIFIC HEAT AT CONSTANT PRESSURE	${ ilde C}_p$	J kg <sup>-1</sup>	1873.9	1872.1	1870.5	1869.1	1867.7	1866.3	1864.9	1863.6	1862.6	1861.6	1860.6	1859.6	1858.7	
WATER TEMP	Ĩ	Х°	333.15	328.15	323.15	318.15	313.15	308.15	303.15	298.15	293.15	288.15	283.15	278.15	273.15	
WATER TEMP		ç	60	55	50	45	40	35	30	25	20	15	10	05	00	

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## **TABLE VMI01B**

## MACROSCOPIC PARAMETERS OF WATER VAPOR

ENTHALPY OF PHASE CHANGE VAPOR TO/FROM ICE	$\bar{M}$	kJ kg <sup>-1</sup>	2834	2836	2837	2838	2838	2838	2838	2839	2839	2839	2840	2840	2841	2841	28 42	2842	
ENTHALPY OF PHASE CHANGE VAPOR TO/FROM WATER	¢Ã	kJ kg <sup>-1</sup>	2501	2513	2525	2537	2549	2562	2575	2588	2600		Atmospheric	liquid water does	not exist at air	temperatures	below -42°C.		
TOTAL KINETIC ENERGY	$ar{U}_i^{\Sigma}$	kJ kg <sup>-l</sup>	382	374	367	360	353	346	339	332	324	317	310	303	296	289	282	275	
MEAN DEGREES OF FREEDOM	آ <b>ب</b> ر	o	6.0546	6.0512	6.0477	6.0442	6.0408	6.0376	6.0350	6.0324	6.0298	6.0286	6.0253	6.0244	6.0235	6.0227	6.0218	6.0209	
GAMMA	Ĩ		1.330326	1.330515	1.330705	1.330894	1.331084	1.331250	1.331393	1.331536	1.331684	1.331827	1.331934	1.331982	1.332030	1.332078	1.332125	1.332173	
SPECIFIC HEAT AT CONSTANT VOLUME	<sup>4</sup> آ	J kg <sup>-1</sup>	1397.177	1396.377	1395.577	1394.777	1393.977	1393.277	1392.677	1392.077	1391.457	1390.857	1390.407	1390.207	1390.007	1389.807	1389.607	1389.407	
SPECIFIC HEAT AT CONSTANT PRESSURE	${ ilde C}_p$	J kg <sup>-1</sup>	1858.7	1857.9	1857.1	1856.3	1855.5	1854.8	1854.2	1853.6	1853.0	1852.4	1851.9	1851.7	1851.5	1851.3	1851.1	1850.9	
WATER TEMP	$\tilde{L}$	$ m M_{\circ}$	273.15	268.15	263.15	258.15	253.15	248.15	243.15	238.15	233.15	228.15	223.15	218.15	213.15	208.15	203.15	198.15	
WATER TEMP		°C	00-	-05	-10	-15	-20	-25	-30	-35	-40	-45	-50	-55	-60	-65	-70	-75	

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**TABLE VMI02A** 

# MOLECULAR PARAMETERS OF WATER VAPOR OVER LIQUID WATER

VAPOR FLUX	$\tilde{J}_{i}^{t}e$	$ ext{x} 10^{24}$ impacts $ ext{m}^{-2}  ext{sec}^{-1}$	677.90	539.78	426.24	334.06	259.04	199.05	151.42	113.97	84.82	62.39	45.32	32.49	22.97	
EQUILIBRIUM VAPOR PRESSURE OVER WATER	$ ilde{m{p}}^{e}_{water}$	pascals m <sup>-2</sup>	20105	15867	12421	9640	7415	5649	4261	3180	2347	1712	1233	876	614	
MEAN IMPULSE AT IMPACT	$\overline{ ilde{0}}_i$	x 10 <sup>-23</sup> Newtons molecule <sup>-1</sup>	2.9394	2.9173	2.8950	2.8725	2.8498	2.8270	2.8040	2.7807	2.7573	2.7337	2.7099	2.6859	2.6616	
MEAN IMPULSE VELOCITY	$\overline{v_i}$	m sec <sup>-1</sup>	492	488	484	480	477	473	469	465	461	457	453	449	445	
MEAN AXIAL VELOCITY	$\frac{d\tilde{\lambda}}{d}$	m sec <sup>-1</sup>	313	311	308	306	303	301	299	296	294	291	289	286	283	
RMS AXIAL VELOCITY	ũ	m sec <sup>-1</sup>	392	389	386	383	380	377	374	371	368	365	362	358	355	
THERMAL TERM	${ m k_{B}}\overline{T}$	x 10 <sup>-21</sup> Joules molecule <sup>-1</sup>	4.5996	4.5306	4.4616	4.3925	4.3235	4.2545	4.1854	4.1164	4.0474	3.9783	3.9093	3.8403	3.7712	
WATER TEMP		°C	60	55	50	45	40	35	30	25	20	15	10	05	00	

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10

## **TABLE VMI02B**

# MOLECULAR PARAMETERS OF WATER VAPOR OVER ICE

VAPOR FLUX	$\tilde{f}_{i}^{e}$	$x 10^{21}$ impacts $m^{-2}$ sec <sup>-1</sup>	22944.74	15255.16	9979.19	6419.32	4052.97	2510.95	1523.97	905.34	525.33	297.47	164.07	87.99	45.79	23.07	11.23	5.26	11	
EQUILIBRIUM VAPOR PRESSURE OVER ICE	$ ilde{P}^{e}_{ice}$	pascals m <sup>-2</sup>	610.70	402.30	260.70	166.10	103.85	63.70	38.27	22.50	12.92	7.24	3.95	2.09	1.08	0.54	0.26	0.12		
MEAN IMPULSE AT IMPACT	<u>َطٌ</u>	x 10 <sup>-23</sup> Newtons molecule <sup>-1</sup>	2.6616	2.6371	2.6124	2.5875	2.5623	2.5369	2.5112	2.4852	2.4590	2.4325	2.4057	2.3786	2.3512	2.3234	2.2954	2.2669		
MEAN IMPULSE VELOCITY	ž.	m sec <sup>-1</sup>	445	441	437	433	428	424	420	416	114	407	402	398	293	388	384	379		
MEAN AXIAL VELOCITY	$\frac{d}{d}\tilde{\lambda}$	m sec <sup>-1</sup>	283	281	278	275	273	270	267	265	262	259	256	253	250	247	244	241	ates.com	
RMS AXIAL VELOCITY	ũ	m sec <sup>-1</sup>	355	352	348	345	342	338	335	332	328	324	321	212	314	310	90E	302	yson www.clima	
THERMAL TERM	${ m k_{B}}\overline{T}$	x 10 <sup>-20</sup> Joules molecule <sup>-1</sup>	3.7712	3.7022	3.6332	3.5641	3.4951	3.4261	3.3571	3.2880	3.2190	3.1500	3.0809	3.0119	2.9429	2.8738	2.8048	2.7358	08 by Patrick J. T.	in August of 2011
WATER TEMP		С,	-00	-05	-10	-15	-20	-25	-30	-35	-40	-45	-50	-55	-60	-65	-70	-75	Copyright 20	Last revised i

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**INTERNAL REFERENCES**: These are other papers in this collection that are either cited or linked during the course of the discussion or whose content is especially relevant to the current discussion.

[25] *The Nature of Atmospheric Temperatures* – This paper develops a universal gas temperature equation and shows how the ideal gas definition is a special case of the universal equation.

[22] <u>*The Equipartition Conundrum*</u> – This paper discusses the equipartition conundrum; that is, why molecular collisions appear to transfer only kinetic energies of translation and not kinetic energies of either rotation or vibration. Possible mechanisms for the transfer of internal energies to external energies and from external energies to internal energies are explored.

[12] <u>Molecular Speeds and Velocities</u> – This absolutely essential paper defines the various velocity terms  $(\sigma, \overline{\nu}_p, \overline{\nu}_i)$  used throughout this collection of papers and shows how they are derived and how they relate to one another mathematically.

[20] <u>Kinetic Energies of Translation</u> – This paper is a fundamental paper in this collection. It defines the various molecular kinetic energies of translation  $(\bar{u}, \bar{u}_{\sigma}, \bar{u}_{p}, \bar{u}_{i}, \bar{u}_{i'})$  and shows how each is derived. It goes on to show the mathematical relationships between the various energies and their relation to the thermal term  $(k_{\rm B}\bar{T})$ .

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### Vapor, Water, and Ice

**GENERAL REFERENCES:** These are works by other authors that contain general treatments of kinetic gas theory, statistical mechanics and thermodynamics, atmospheric physics, and other scientific fields that are used in the current paper. They primarily contribute conceptual frameworks; but offer specific scientific data on occasion.

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**Computational System**: All calculations were carried out by Microsoft's© Excel Program 2003 (SP3). The reader should be alerted to the fact that this computational system used fifteen significant figures for all calculations—whether or not such precision was warranted by the accuracy of the data. For areas under the normal curve, the NORMSDIST function was used and the ERF and ERFC functions were not used.

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