THE LATENT HEAT FALLACY

Introduction

Latent heat is one of the many forms of potential energy required by the principle of the conservation of energy. This principle states that although the energy in a system and its environment may be converted from one form to another, the total energy in the system and its environment remains the same.

In many physical and chemical processes, that part of the energy that can be measured does change, and the measurable total changes as well. The problem is that the two don't jibe. The principle of conservation of energy is maintained by assigning the missing energy or the extra energy to the category of potential energy. Potential energy thus can be calculated, but it cannot be measured.

Heat energy is that energy that is involved in a net transfer of energy from a hotter body to a cooler one solely because of the difference in temperature. In a process that involves either a loss or a gain of measurable heat energy, the missing or extra heat energy is commonly termed "latent" heat.

It should be noted that current thermodynamic practice has abandoned the term "latent heat". What used to be called the latent heat of a process is now termed the "enthalpy" of that process. We will use both terms—sometimes together, and sometimes separately.

When vaporization occurs, the total kinetic energy of the resulting water vapor is less than the total kinetic energy of the water or ice vaporized plus the total heat required to vaporize the water or ice. This missing energy is termed the latent heat of vaporization (enthalpy of vaporization). When condensation occurs, the total kinetic energy plus the total bonding energy of the condensed water or ice is greater than the kinetic energy of the vapor that gave rise to it. This added energy is termed the latent heat of condensation (enthalpy of condensation).

Similarly, when ice melts, the total kinetic energy plus the bonding energy of the resulting water is less than the total kinetic energy plus the bonding energy of the ice that preceded it. This missing energy is termed the latent heat of fusion (enthalpy of fusion). When freezing occurs, the total kinetic energy plus the bonding energy of the ice is greater than the total kinetic energy plus the bonding energy of the water that produced it. This added energy is termed the enthalpy of freezing.

The total energy content of the system and its environment before vaporization is equal to the total energy content of the system and its environment after condensation. Similarly, the total energy content of the system and its environment before melting is equal to the total energy content of the system and its environment after freezing. The principle of conservation of energy is thus maintained.

Phenomena to be Explained

01. When ice is heated, the increase in kinetic energy of the ice molecules (as measured by the increase in temperature) is less than the energy absorbed by the system.

02. When ice is allowed to vaporize (sublimate) naturally, the kinetic energy of the vapor molecules is less than the loss of thermal energy in the ice substrate.

03. When ice is melted isothermally, energy is absorbed by the process that is not manifest in the kinetic energy of the liquid water produced by the melting.

04. When water is heated, the increase in kinetic energy of the water molecules (as measured by the increase in temperature) is less than the energy absorbed by the system.

05. When water is allowed to vaporize naturally, the kinetic energy of the vapor molecules is less than the loss of thermal energy in the water substrate.

06. When water is vaporized isothermally, energy is absorbed by the process that is not manifest in the kinetic energy of the water vapor produced by the vaporization.

07. When condensation occurs, the temperature of the air surrounding the condensate either increases or decreases at lesser rate. This is manifest in the observation that the wet adiabatic lapse rate is less than the dry adiabatic lapse rate.

08. When freezing occurs, the temperature of the water surrounding the ice either increases or decreases at a lesser rate.

The Conventional Hypothesis

The conventional hypothesis is that when water is changed from a more organized phase to a less organized phase, the energy necessary to effect that change (to melt ice or vaporize water) is stored somehow in the newly liberated molecules. This energy cannot be observed or measured. Hence, the Scottish physicist Joseph Black called it “latent” heat. The term “latent” is derived from the Latin ***latere***, “to lie hidden”.

The molecules retain this latent energy in some unknown fashion throughout their billions of collisions and possible chemical and physical reactions. At some later time, when they again reunite with other water molecules, this energy is released to the substrate or to the surrounding medium, or to both.

Problems with the Conventional Hypothesis

There are two major problems with the conventional hypothesis. They concern the manner in which molecules “carry” the latent heat that they are supposed to have gained in the heating process, and how that heat is released at condensation or fusion.

The “Carrying” Problem – We know a great deal more about the inner workings of molecules and atoms than was known at the time Black first proposed his hypothesis in the 1850's. Quantum physics has given us a pretty good insight into both the internal and external mechanisms by which energy is stored and expressed by molecules. There has been no convincing evidence of any latent heat or enthalpy of transformation stored in liquid or gas molecules.

A vapor molecule of total kinetic energy ***U*** that came from the sublimation of an icicle hanging on Uncle Ivan's *dacha* in Verkhoyansk when the temperature was 233°K has exactly the same energy content (as far as we can tell) as a vapor molecule of the identical total kinetic energy ***U*** that came from Aunt Tillie's teakettle at 373° K in Tunbridge Wells.

The conventional theory says that the former molecule must bear a greater "latent" energy than the former, since it takes more energy to vaporize an ice molecule from 233°K than it does to vaporize a water molecule at 373°K. Nevertheless, we have been unable to find any trace of that energy in the molecules themselves. Nor has any convincing mechanism of internal storage been proposed.

The "Release" Problem – To the best of my knowledge (admittedly, quite limited) there are only three methods by which energy can be transmitted from place A to place B in the atmosphere. These are net radiation, net conduction, and the net movement of mass and its attendant energies from A to B.

If heat is "released" during condensation or freezing, what exactly is the manner of its release? And where is the hotter object that is transferring heat to the surrounding air or water?

Radiative heat transfer involves the emission of photons at place A and their absorption at place B. When cloud droplets condense from water vapor, there is no unusual increase in the radiative emissions of either the condensate or the surrounding air. Each continues to radiate in keeping with the Stefan-Boltzmann equation.

Both condensation and freezing often occur isothermally. Under isothermal conditions, there is no hotter object to lose heat and no cooler object to gain it. This situation eliminates any possibility of net heat transfer by any known method. Even when the processes of condensation and freezing are not isothermal, it is the less organized phase that is the cooler of the two. How then, can cooler cloud droplets warm the air or cooler ice warm the water?

Finally, when vapor condenses or water freezes, there is a net transfer of mass (and all of that mass's energies) from the less organized phase to the more highly organized phase. Consequently, mass transfer cannot account for the warming or either the residual air or the residual water during condensation and freezing. The transfer of enthalpy is in exactly the wrong direction.

This point is worth elaboration. When water freezes, enthalpy is transferred from the liquid phase to the solid phase. When vapor condenses in cloud droplets, enthalpy is transferred from the gaseous phase to the liquid phase. And yet, it is the residual phase—the phase that is losing energy—that is either actually warmed or caused to cool at a lesser rate. What is happening?

An Alternative Hypothesis

Those of you who have read my previous essays in this series already know my explanation for these phenomena. I maintain that the processes of phase transformation are both symmetrical and selective. This involves only a slight adjustment in what physicists already accept. Let's take a look at our "phenomena to be explained" through the lens of this alternative hypothesis.

01. *When ice is heated, the increase in kinetic energy of the ice molecules (as measured by the increase in temperature) is less than the energy absorbed by the system.* Some of the heat energy ($\Delta \boldsymbol{Q}$) goes to increasing the kinetic energy of the ice molecules ($\Delta \boldsymbol{U}$). Under constant pressure conditions, some of the energy may go to doing work by expansion against that constant pressure ($\boldsymbol{W_p}$). The remaining energy goes to doing work by stretching, bending, and or breaking the intermolecular bonds ($\boldsymbol{W_a}$). These allocations are described by the expression:

$$\boldsymbol{\Delta Q = \Delta U + W_p + W_a} \qquad \text{LHF01}$$

02. *When ice is allowed to vaporize (sublimate) naturally, the kinetic energy of the vapor molecules is less than the loss of thermal energy in the ice substrate*. Vaporization is selective. The intermolecular bonds of attraction in ice are quite strong. It takes a considerable amount of energy to break them and to escape from them. Only the more energetic molecules have this necessary energy—but they don't have it for long. As these vapor molecules leave the surface of the ice, their velocity normal to the surface is diminished by these same attractive forces. This results in a vapor molecule whose kinetic energy is less than that of the ice molecule that produced it. This process is given by the expression:

$$\underset{\sim}{\boldsymbol{u}}_{-i}^{\boldsymbol{vapor}} = \underset{\sim}{\boldsymbol{u}}_{-i}^{\boldsymbol{substrate}} - \underset{\sim}{\boldsymbol{u}}_{-i}^{\boldsymbol{escape}} \qquad \text{VAP06}$$

The escape energy per molecule may be readily obtained by dividing the heat of vaporization per unit mass by the number of molecules per unit mass:

$$\underset{\sim}{\boldsymbol{u}}_{-i}^{\boldsymbol{escape}} = \frac{\underset{\sim}{\boldsymbol{Q}}^{\boldsymbol{vaporization}}}{\underset{\sim}{\boldsymbol{N}}} \qquad \text{VAP07}$$

This escape energy, of course, must be carried on the books as the enthalpy (latent heat) of vaporization.

03. *When ice is melted isothermally, energy is absorbed by the process that is not manifest in the kinetic energy of the liquid water produced by the melting.* In this case, all of the energy added to the system is used to loosen and break the bonds that hold the molecules in their ice configuration.

$$\Delta \boldsymbol{Q} = \underset{\sim}{\boldsymbol{Q}}^{\boldsymbol{fusion}} \ (\bar{\boldsymbol{T}} \ \text{constant}) \qquad \text{LHF02}$$

This energy is carried on the books as the enthalpy (latent heat) of fusion.

04. *When water is heated, the increase in kinetic energy of the water molecules (as measured by the increase in temperature) is less than the energy absorbed by*

the system. . Some of the heat energy ($\Delta \boldsymbol{Q}$) goes to increasing the kinetic energy of the water molecules ($\Delta \boldsymbol{U}$). Under constant pressure conditions, some of the energy may go to doing work by expansion against that constant pressure ($\boldsymbol{W_p}$). The remaining energy goes to doing work by stretching, bending, and or breaking the intermolecular bonds ($\boldsymbol{W_a}$). These allocations are described by the expression:

$$\Delta Q = \Delta U + W_p + W_a \qquad \text{LHF01}$$

05. *When water is allowed to vaporize naturally, the kinetic energy of the vapor molecules is less than the loss of thermal energy in the water substrate.* Vaporization is selective. The intermolecular bonds of attraction in water are quite strong. It takes a considerable amount of energy to break them and to escape from them. Only the more energetic molecules have this necessary energy—but they don't have it for long. As these vapor molecules leave the surface of the water, their velocity normal to the surface is diminished by these same attractive forces. This results in a vapor molecule whose kinetic energy is less than that of the water molecule that produced it. This process is given by the expression:

$$\underset{\sim}{u}_{-i}^{vapor} = \underset{\sim}{u}_{-i}^{substrate} - \underset{\sim}{u}_{-i}^{escape} \qquad \text{VAP06}$$

The escape energy per molecule may be readily obtained by dividing the heat of vaporization per unit mass by the number of molecules per unit mass:

$$\underset{\sim}{u}_{-i}^{escape} = \frac{\underset{\sim}{Q}^{vaporization}}{\underset{\sim}{N}} \qquad \text{VAP07}$$

This escape energy, of course, must be carried on the books as the enthalpy (latent heat) of vaporization.

06. *When water is vaporized isothermally, energy is absorbed by the process that is not manifest in the kinetic energy of the water vapor produced by the vaporization.* In this case, all of the energy added to the system is used to

loosen and break the bonds that hold the molecules in their liquid configurations.

$$\Delta \boldsymbol{Q} = \underset{\sim}{\boldsymbol{Q}}^{vaporization} \ (\bar{\boldsymbol{T}} \ \text{constant}) \qquad \text{LHF03}$$

This energy is carried on the books as the enthalpy (latent heat) of vaporization. Under laboratory conditions of constant pressure, a term for the work done in expanding under constant pressure must be added to the right-hand side of the equation. In the free atmosphere, this term is unnecessary, since no such work is being done.

07. When condensation occurs, the temperature of the air surrounding the condensate either increases or decreases at lesser rate. This is manifest in the observation that the wet adiabatic lapse rate is less than the dry adiabatic lapse rate. Condensation, like vaporization, is a selective process. The less energetic molecules are the ones most likely to condense out. They are the most common molecules in the zone of attraction surrounding the substrate, and they are the least likely to have velocities away from the substrate that are greater than the attractive forces. Since temperature is an average, the removal of the "cooler" molecules increases the mean temperature of the residual vapor molecules. No other transfer of heat is necessary.

08. When freezing occurs, the temperature of the water surrounding the ice either increases or decreases at a lesser rate. Freezing, like condensation, is a selective process. The less energetic molecules are the ones most likely to start to form proto-crystal structures. They are far more numerous than the more energetic ones, and they are the least likely to have kinetic energies away from the icing nuclei and embryo crystals that are greater than the attractive forces of these nuclei. Since temperature is an average, the removal of the "cooler" molecules increases the mean temperature of the residual water molecules. No other transfer of heat is necessary.

Summary

Vaporization, condensation, melting, and freezing are all selective processes. In vaporization and melting, the most energetic molecules and the most loosely bonded molecules are the first to make the phase change. Since temperature is a measure of average kinetic energy of translation, the removal of the "hotter" molecules reduces the temperature of those remaining.

In condensation and freezing, the least energetic molecules are the first to make the phase change. The removal of the "cooler" molecules either raises the temperature of those remaining or reduces the rate of cooling.

Molecules do not carry latent heat as they change from a more organized phase to a less organized one; i. e., from ice to water or from water to vapor or from ice to vapor. Molecules do not release heat as they change from a less organized phase to a more organized one; i. e., from vapor to water or ice and from water to ice.

Let me offer an analogy. Imagine a large room containing a considerable number of people. Each individual has a certain amount of money on their person. The **total** amount of money in the room is analogous to the enthalpy content of a mass of humid air. The **average** amount per person is analogous to the temperature of our mass of humid air. We request that every individual with less than a certain amount of money step into the lobby for a moment. After they leave, the total amount of money in the room is diminished, but the average has gone up.

So it is with both condensation and freezing. You remove heat (enthalpy) and the temperature goes up. A rather nice paradox.

A Note of Caution: When we take the free atmosphere as our system, we must also take in the entire physical universe as our environment. The atmosphere is continuously gaining both radiant and kinetic energy from extraterrestrial sources and losing it to extraterrestrial sinks. We have no evidence that supports a long-term equality; and it is obvious that no short-term equilibrium exists.

TABLES

The two tables that follow are borrowed from essays on ***Gross Vaporization*** and ***Gross Sublimation***. Table LHF01 is an exact copy of Table VAO09 and Table LHF02 is an exact copy of Table SUB09. The derivations of the values in these two tables are given very briefly following each table in this paper.

However, this derivation is brief. Readers wishing a more thorough examination of how the values were obtained are referred to the above two papers from which the data were obtained.

TABLE LHF01

SPECIFIC ENTHALPIES OF WATER VAPORIZATION

SYSTEM TEMP	SYSTEM TEMP	ENTHALPY OF PHASE CHANGE	ENTHALPY GAIN BY VAPOR PHASE	ENTHALPY LOSS BY LIQUID PHASE
°C	$\bar{T}$	$\dot{\underset{\sim}{W}}_{kg}^{\leftrightarrow}$	$\Delta \underset{\sim}{U}$	$\Delta \underset{\sim}{Q}$
	K	**kJ kg^{-1}**	**kJ kg^{-1}**	**kJ kg^{-1}**
40	**313.15**	**2405**	**440**	**2845**
35	**308.15**	**2417**	**433**	**2850**
30	**303.15**	**2430**	**425**	**2855**
25	**298.15**	**2442**	**418**	**2860**
20	**293.15**	**2454**	**411**	**2864**
15	**288.15**	**2465**	**403**	**2869**
10	**283.15**	**2477**	**396**	**2873**
05	**278.15**	**2489**	**389**	**2878**
00	**273.15**	**2501**	**382**	**2882**
-05	**268.15**	**2513**	**374**	**2887**
-10	**263.15**	**2525**	**367**	**2892**
-15	**258.15**	**2537**	**360**	**2897**
-20	**253.15**	**2549**	**353**	**2902**
-25	**248.15**	**2562**	**346**	**2908**
-30	**243.15**	**2575**	**339**	**2913**
-35	**238.15**	**2588**	**332**	**2920**

All table values are for a system consisting of clean humid air at a pressure of 10^5 Pascals in contact with a pure natural water surface. Note that these values are dependent only on the mass vaporized and not upon the rate of vaporization.

SPECIFIC ENTHALPIES OF WATER VAPORIZATION

$$\dot{\underset{\sim}{\boldsymbol{W}}}_{kg}^{\leftrightarrow} = -6.14342 \text{ x } 10^{-5}\boldsymbol{C}^{3} + 1.58927 \text{ x } 10^{-3}\boldsymbol{C}^{2} - 2.36418\boldsymbol{C} + 2500.79$$

This is the enthalpy of phase change in kilojoules per kilogram. **C** is in degrees Celsius. This is the enthalpy that is converted into latent heat by the vaporization of one kilogram of water at the specified water temperature. The formula is a cubic fit to the data in Table 2.1 of R. R. Rogers and M. K. Yau, *A Short Course in Cloud Physics*, Butterworth & Heinemann, 1988, page 16.

$$\Delta\underset{\sim}{\boldsymbol{U}} = \underset{\sim}{\overline{\boldsymbol{N}}}_{kg}\,\underset{\sim}{\overline{\boldsymbol{u}}}_{-i}^{\Sigma}$$

This is the total vapor kinetic energy in Joules per kilogram, although the table shows it in kilojoules. This is the enthalpy gained by the humid air consequent to the vaporization of one kilogram of water at the specified system temperature.

$$\Delta\underset{\sim}{\boldsymbol{Q}} = \Delta\underset{\sim}{\boldsymbol{U}} + \dot{\underset{\sim}{\boldsymbol{W}}}_{kg}^{\leftrightarrow}$$

This is the total enthalpic (heat) loss by the liquid water surface consequent to the vaporization of one kilogram of water at the specified system temperature.

TABLE LHF02

SPECIFIC ENTHALPIES OF ICE SUBLIMATION

SYSTEM TEMP	SYSTEM TEMP	ENTHALPY OF PHASE CHANGE	ENTHALPY GAIN BY VAPOR PHASE	ENTHALPY LOSS BY ICE PHASE
°C	$\bar{T}$	$\underset{\sim}{\dot{W}}{}_{kg}^{\leftrightarrow}$	$\Delta \underset{\sim}{U}$	$\Delta \underset{\sim}{Q}$
	K	**kJ kg^{-1}**	**kJ kg^{-1}**	**kJ kg^{-1}**
00	273.15	2834	382	3216
-05	268.15	2836	374	3210
-10	263.15	2837	367	3204
-15	258.15	2838	360	3198
-20	253.15	2838	353	3191
-25	248.15	2838	346	3184
-30	243.15	2838	339	3177
-35	238.15	2839	332	3170
-40	233.15	2839	324	3163
-45	228.15	2839	317	3157
-50	223.15	2840	310	3150
-55	218.15	2840	303	3144
-60	213.15	2841	296	3137
-65	208.15	2841	289	3130
-70	203.15	2842	282	3124
-75	198.15	2842	275	3117

All table values are for a system consisting of clean humid air at a pressure of 10^5 Pascals in contact with a pure natural ice surface. Note that these values are dependent only on the mass sublimated and not upon the rate of sublimation.

SPECIFIC ENTHALPIES OF ICE SUBLIMATION

$$\underset{\sim}{\dot{W}}{}_{kg}^{\leftrightarrow} = 0.0009059\left(\frac{\underset{\sim}{\bar{\rho}}_{ice}}{\underset{\sim}{\bar{m}}}\right)^{\frac{1}{3}}$$

This is the enthalpy of phase change in kilojoules per kilogram. It is a function of the mean intermolecular distance between the ice molecules.

$$\Delta \underset{\sim}{U} = \underset{\sim}{\bar{N}}_{kg}\,\underset{\sim}{\bar{u}}{}_{-i}^{\Sigma}$$

This is the total vapor kinetic energy in Joules per kilogram, although the table shows it in kilojoules. This is the enthalpy gained by the humid air consequent to the sublimation of one kilogram of ice at the specified system temperature.

$$\Delta \underset{\sim}{Q} = \Delta \underset{\sim}{U} + \underset{\sim}{\dot{W}}{}_{kg}^{\leftrightarrow}$$

This is the total enthalpic (heat) loss by the ice surface consequent to the sublimation of one kilogram of ice at the specified system temperature.

REFERENCES

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.

Gross Vaporization – This paper explains why selected liquid water molecules leave the surface of the water and become water vapor molecules using the concepts of kinetic gas theory and statistical mechanics. The rate of gross vaporization is seen as a dynamic balance between thermal forces (especially intermolecular impulses) that tend to drive molecules apart and binding forces that tend to draw them together. The rate of gross vaporization is then based on a statistical distribution of impulses normal to the surface and the number of those impulses that are greater than the sum of the binding forces.

Gross Sublimation – This paper explains why selected ice molecules leave the surface of the ice and become water vapor molecules using the concepts of kinetic gas theory and statistical mechanics. The rate of gross vaporization is seen as a dynamic balance between thermal forces (especially intermolecular impulses) that tend to drive molecules apart and binding forces that tend to draw them together. The rate of gross sublimation is then based on a statistical distribution of impulses normal to the surface and the number of those impulses that are greater than the sum of the binding forces.

Molecular Speeds and Velocities – This absolutely essential paper defines the various velocity terms ($\boldsymbol{\sigma}, \bar{\boldsymbol{v}}_p, \bar{\boldsymbol{v}}_i$) used throughout this collection of papers and shows how they are derived and how they relate to one another mathematically.

Kinetic Energies of Translation – This paper is a fundamental paper in this collection. It defines the various molecular kinetic energies of translation ($\bar{\boldsymbol{u}}, \bar{\boldsymbol{u}}_\sigma, \bar{\boldsymbol{u}}_p, \bar{\boldsymbol{u}}_i, \bar{\boldsymbol{u}}_{i'}$) 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 ($k_B\bar{T}$).

The Probability Density Curve – This paper discusses the significance and history of the probability density curve. It goes on to show how in its normalized form it is also the distribution function for axial velocities.

EXTERNAL REFERENCES:

These are papers by other authors that contain statements or data that are specifically incorporated into the current discussion.

Fundamental Physical Constants: 2006 CODATA – Peter J. Mohr, Barry N. Taylor, and David B. Newell; National Institute of Science and Technology (NIST), ***CODATA Recommended Values of the Fundamental Physical Constants: 2006;*** Gaithersburg, 2007. http://physics.nist.gov/cuu/Constants/codata.pdf

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 uses fifteen significant figures for all calculations—whether or not such precision is 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.

LIQUID WATER DENSITY: This is the density of one cubic meter of pure natural water in kilograms. Values of 0°C and above were taken from Table 21-2, *American Institute of Physics Handbook*, Third Edition, McGraw Hill, 1972. Below zero values were taken from htpp://en.wikipedia.org/wiki/Density on 15 May 2010.

EQUILIBRIUM VAPOR PRESSURE: Taken from Table 2.1 on page 16 of R. R. Rogers and M. K. Yau, *A Short Course in Cloud Physics*, Butterworth & Heinemann, 1988.

SURFACE ENERGY: Liquid water/humid air surface tension in millinewtons per meter. Values from 0°C to 60°C were taken from Properties of Water: Surface Tension, Wikipedia on 16/05/2010. Values from -5°C to -20°C were taken from *Experimental Values of the Surface Tension of Supercooled Water*, Paul T. Hacker, National Advisory Committee for Aeronautics, Technical Paper 2510, 1951. Values below -20°C were extrapolated from Hacker's data.

ENTHALPY OF VAPORIZATION: Enthalpy of phase change between liquid and vapor phases in kilojoules per kilogram. The formula is a cubic fit to the data in Table 2.1 of R. R. Rogers and M. K. Yau, *A Short Course in Cloud Physics*, Butterworth & Heinemann, 1988, page 16.

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 discussion.

Walter Benenson, John W. Harris, Horst Stocker, Holger Lutz, editors; **Handbook of Physics**; Springer, New York, 2006.

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