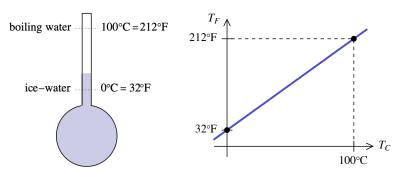
Chapter M

Temperature, Heat and Phase

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M.1 - Temperature Scales

Fahrenheit and Celsius Scales



Two commonly used temperature scales are Fahrenheit and Celsius. In the Fahrenheit scale the temperature of the freezing point of water (at one atmosphere) is 32 °F and the boiling point is 212 °F. For Celsius these two temperatures are 0 °C and 100 °C. It is straightforward to convert between the two. Consider a graph of T_F vs. T_C . We insist that these two scales are linearly related; this implies that the graph is a line. The slope of the line is

slope =
$$\frac{\Delta T_F}{\Delta T_C} = \frac{212 - 32}{100 - 0} = \frac{9}{5}$$
.

The intercept is 32. It follows that the conversion is

$$T_F = \frac{9}{5} T_C + 32.$$

Note that for temperature difference we get

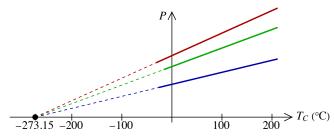
$$\Delta T_F = \frac{9}{5} \Delta T_C.$$

Constant Volume Gas Thermometers

A thermometer based on the expansion of a gas at constant volume was introduced. It was seen that a plot of pressure vs. temperature for different gases gave lines that had a common T-intercept, the temperature at zero pressure, at a very cold negative temperature.

Pressure vs. Temperature

for Different Gases at Constant Volume



This was the first hint of a coldest temperature that we now call absolute zero. It should be mentioned that absolute zero is much more fundamental than just a property of cold gases. It is a very fundamental value and the coldest temperature in *all* thermal experiments. In the

Celsius scale the value of absolute zero is now defined exactly as

$$T_{\text{absolute zero}} = -273.15 \,^{\circ}\text{C}.$$

Absolute Temperature and Kelvin

An absolute temperature scale is one that is shifted to make absolute zero, zero in that scale. The absolute scale associated with Celsius is called the Kelvin scale. The conversion between Celsius and Kelvin is

$$T_K = T_C + 273.15$$
.

Temperatures in Kelvin are given as K and not °K. We usually will take the above number to be just 273. Note that temperature differences in Kelvin are the same as in Celsius. We will give these Celsius temperature differences in K.

Example M.1 - Simple Conversions

(a) The temperature of liquid nitrogen at one atmosphere of pressure is 77 K. What is this in Celsius and in Fahrenheit?

Solution

$$T_C = T_K - 273 \text{ K} = 77 \text{ K} - 273 \text{ K} = -196 \text{ °C}$$

$$T_F = \frac{9}{5} T_C + 32 = -321 \text{ °F}$$

(b) The nominal value for healthy human body temperature is 98.6 °F. What is this in Celsius and in Kelvin?

Solution

$$T_F = 98.6 \,^{\circ}\text{F} \text{ and } T_F = \frac{9}{5} T_C + 32 \implies T_C = \frac{5}{9} (T_F - 32) = 37 \,^{\circ}\text{C}$$

 $T_K = T_C + 273 \,\text{K} = 37 \,^{\circ}\text{C} + 273 \,\text{K} = 310 \,\text{K}$

M.2 - Heat

Heat is thermal energy that flows from hot to cold, or more precisely, from higher temperature to lower temperature. It is an essential point that heat is thermal energy that moves. The static notion of thermal energy is a quite different thing which we will define later as *internal energy*. We will use Q to denote heat. We will choose the convention that Q is the heat *added* to a thermodynamic system. When heat is removed from something we take Q to be negative.

What is the effect of heat on a system? Suppose you add heat to a pot of water. The heat will increase the temperature of the water, usually. But if the water is at the boiling point the heat doesn't change the temperature; it changes the phase. Thus, when heat is added to a system it can either change the temperature of the system or change it's phase.

Temperature Change - Specific Heat

To raise the temperature of a fixed quantity (mass) of a material by some amount ΔT requires heat that is roughly proportional to the temperature change $Q \propto \Delta T$. This is precise as the ΔT becomes small. Moreover, to raise a substance by a fixed temperature requires an amount of heat proportional to m, the mass of the substance, $Q \propto m$. We can combine these proportionalities and get

$$Q = m c \Delta T$$
.

c, the constant of proportionality is called the specific heat; it is a property of a material. Generally, it varies somewhat with the temperature and pressure of the substance, but we will typically neglect this change as small.

The specific heat c is a property of a material. The heat capacity C is a property of an object.

$$Q = C \Delta T$$

For example, a thermos has a heat capacity; the glass in a thermos has a specific heat. If an object is made of one material then C = mc. If it is made of several then $C = m_1 c_1 + m_2 c_2 + ...$.

Units: The SI unit for heat is: J = joule

Alternative units for heat are cal (calories), kcal or BTU.

- 1 cal raises 1 g of water by 1 K.
- 1 kcal raises 1 kg of water by 1 K.
- 1 BTU raises 1 lb_m (pound mass) by 1 F° (Fahrenheit degree).

(BTU is awkwardly also used as a unit of power for stoves and air conditioners; in that context a BTU is implied to be BTU/h and should be written as such.)

Water has a high specific heat. Its value is:

$$c_{\text{water}} = 4186 \frac{J}{\text{kg} \cdot \text{K}} = 1 \frac{\text{kcal}}{\text{kg} \cdot \text{K}} = 1 \frac{\text{cal}}{\text{g} \cdot \text{K}} = 1 \frac{\text{BTU}}{\text{lb}_{\text{m}} \text{ F}^{\circ}}$$

Note that the specific heat of ice is different than liquid water $c_{ice} = 2100 \frac{J}{ko \cdot K}$

Substance	Specific Heat $\left(\frac{J}{\ker K}\right)$
Water	4186
Ice (≤ 0 °C)	2100
Lead	130
Copper	390
Silver	234
Aluminum	910
Ethanol	2428
Iron	470

Specific Heats at 20 °C and 1 atm

Example M.2 - Hot Coffee, Cold Mug

0.25-kg of coffee at 82 °C, the official Starbucks temperature, is added to a 0.15-kg glass coffee mug at 20 °C. Assuming no heat exchange with the environment, what is the equilibrium temperature of the coffee/mug system? Take the specific heat of coffee to be that of water. For glass: $c_G = 0.20 \text{ kcal/(kg} \cdot \text{K)}$.

Solution

$$c_W = 1 \frac{\text{kcal}}{\text{kg} \cdot \text{K}}$$
, $c_G = 0.20 \frac{\text{kcal}}{\text{kg} \cdot \text{K}}$, $m_W = 0.25 \text{ kg}$, $m_G = 0.15 \text{ kg}$, $T_W = 82 \text{ °C}$ and $T_G = 20 \text{ °C}$

The total heat exchange between the coffee and mug is zero. Since Q is the heat added, it will be negative for the coffee.

$$0 = Q_{\text{tot}} = m_W c_W (T - T_W) + m_G c_G (T - T_G)$$

We can solve for the final temperature T.

$$T = \frac{m_W c_W T_W + m_G c_G T_G}{m_W c_W + m_G c_G} = 75.4 \,^{\circ}\text{C}$$

Note that since the specific formulas involve temperature differences we can do the calculations without converting to Kelvins.

Example M.3 - Time to Boil Water

(a) How long does it take to boil a pot of water? To make this a good question we must know more information. Take there to be 2 kg of water (2 liters) initially at room temperature, 20 °C. We also need to know the rate at which heat is delivered; take the burner to be 2000 W, meaning that it delivers 2000 J of heat each second. Furthermore, we will neglect the heat capacity of the pot and ignore heat exchange with the environment.

Solution

$$c = 4186 \frac{J}{\text{kg} \cdot \text{K}}$$
, $m = 2 \text{ kg}$, $\Delta T = T_f - T_i = 100 \text{ °C} - 20 \text{ °C} = 80 \text{ K}$ and $\mathcal{P} = 2000 \text{ W}$

The heat is the power times the time: $Q = \mathcal{P} t$.

$$\mathcal{P} t = m c \Delta T \implies t = m c \Delta T / \mathcal{P} = 335 \text{ s} = 5.58 \text{ min}$$

Phase Change - Latent Heat

The phase change between solids and liquids is called fusion. The liquid-gas transition is called vaporization. At the temperature of a phase transition the latent heat is the amount of heat per mass needed to change the phase.

$$O = \pm m L$$

The sign must be added by hand. When going from solid to liquid heat is added, so Q is positive and from liquid to solid it is negative. Similarly, from liquid to gas Q > 0 and from gas to liquid Q < 0.

		L_f – Latent Heat	Boiling Point	L_v – Latent Heat
Substance	(Fusion)	of Fusion	(Vaporization)	of Vaporization
	Temperature	(J/kg)	Temperature	(J/kg)
Helium	-	-	$-269 ^{\circ}\text{C} = 4.2 \text{K}$	20.7×10^3
Hydrogen	$-259 ^{\circ}\text{C} = 14 \text{K}$	59.5×10^3	-252.9 °C = 20.3 K	445×10^3
Nitrogen	-210.0 °C = 63.2 K	25.3×10^3	-195.8 °C = 77.3 K	201×10^{3}
Oxygen	-219 °C = 54 K	13.7×10^3	$-183 ^{\circ}\text{C} = 90 \text{K}$	213×10^{3}
Methane	$-182 ^{\circ}\text{C} = 91 \text{K}$	58.4×10^3	-164 °C = 109 K	112×10^3
Ethanol	-114 °C = 159 K	104×10^3	78 °C = 351 K	854×10^{3}
Water	$0 ^{\circ}\text{C} = 273 \text{K}$	334×10^{3}	100 °C = 373 K	2260×10^{3}
Lead	327 °C = 600 K	24.5×10^3	1750 °C = 2023 K	179.5×10^3
Silver	962 °C = 1235 K	105×10^3	2163 °C = 2436 K	2390×10^{3}
Copper	1084 °C = 1357 K	209×10^{3}	2562 °C = 2835 K	4730×10^{3}
Gold	1064 °C = 1337 K	63.7×10^3	2856 °C = 3229 K	1645×10^3
Iron	1538 °C = 1811 K	247×10^{3}	2861 °C = 3134 K	6090×10^3
Silicon	1414 °C = 1687 K	1790×10^3	3265 °C = 3538 K	12800×10^3

Latent heats and phase transition temperatures for different substances at 1 atm. (Reference)

Latent heats and phase transition temperatures for different substances at 1 atm. (Reference)

From the table above, we can see the following.

■ For water: fusion at $0 \,^{\circ}$ C $L_f = 334 \times 10^3 \, \text{J/kg}$

vaporization at 100 °C $L_v = 2260 \times 10^3 \text{ J/kg}$

■ For lead: fusion at 327 °C $L_f = 24.5 \times 10^3 \text{ J/kg}$

vaporization at 1750 °C $L_v = 179.5 \times 10^3 \text{ J/kg}$

Note that L_f for lead is much less than for that for water. One could easily conclude, absurdly, that it is easier to melt lead than water, however it takes considerable heat to raise its temperature to 327 °C.

Not all materials have all three phases at one atmosphere. At that pressure, helium does not have a solid phase. Also at one atmosphere, carbon dioxide lacks a liquid phase; the direct transition from solid to gas is known as sublimation and there is a latent heat of sublimation.

■ For CO₂: sublimation at -78.5 °C $L_s = 571 \times 10^3$ J/kg

Example M.4 - Time to Boil Water (Continued)

(b) To continue the previous example: How much longer does it take to boil away all the water?

Solution

$$L_v = 2260 \times 10^3 \frac{J}{\text{kg}}$$
, $m = 2 \text{ kg}$ and $\mathcal{P} = 2000 \text{ W}$

The heat is the power times the time: $Q = \mathcal{P} t$.

$$\mathcal{P} t = m L_v \implies t = m L_v / \mathcal{P} = 2260 \text{ s} = 37.7 \text{ min}$$

(c) What is the ratio of the time it takes to boil away water to the time it takes to bring it from 20 °C to a boil? This is the ratio of the time for part (b) to the time for part (a). This will be independent of both the mass of water and the power of the burner.

Solution

$$c = 4186 \frac{J}{\text{kg} \cdot \text{K}}$$
, $\Delta T = 80 \text{ K}$ and $L_v = 2.26 \times 10^6 \frac{J}{\text{kg}}$

The heat is the power times the time: $Q = \mathcal{P} t$.

$$t_b/t_a = \frac{m L_v/\mathcal{P}}{m c \Delta T/\mathcal{P}} = \frac{L_v}{c \Delta T} = 6.75$$

Example M.5 - Add Ice to Water

A quantity of mass m of ice at -25 °C is added to 5-kg of water at 20 °C. There are three possible final states, depending on the value of m. For small m all the ice will melt and you will end up with water at some temperature less than 20°C. If there is a lot of ice then all the water will freeze and this results in ice at a temperature higher than -25 °C. Between the two cases you end up with ice-water, meaning ice and water in equilibrium at 0 °C. Which ranges of values of m will give each of the three outcomes.

Solution

The relevant constants and given information is

$$m_W = 5 \text{ kg}$$
, $c_I = 2100 \frac{J}{\text{kg} \cdot \text{K}}$, $c_W = 4186 \frac{J}{\text{kg} \cdot \text{K}}$ and $L_f = 334 \times 10^3 \frac{J}{\text{kg}}$

It suffices to find m_1 , the critical initial amount of ice to melt all the ice and end up with all water at 0 °C and m_2 , the critical amount to end up with all ice at 0 °C.

The three ranges of m-values are

$$m < m_1 \Longrightarrow$$
 all water, $m_1 \le m \le m_2 \Longrightarrow$ ice – water and $m > m_2 \Longrightarrow$ all ice

To find m_1 we have three steps to consider

 m_1 of ice at -25° C $\stackrel{1}{\Longrightarrow} m_1$ of ice at 0° C $\stackrel{2}{\Longrightarrow} m_1$ of water at 0° C and m_W of water at 20° C $\stackrel{3}{\Longrightarrow} m_W$ of water at 0° C

The total heat exchange is zero. Summing over the heats added in each of the three steps above gives.

$$0 = Q_{\text{tot}} = Q_1 + Q_2 + Q_3 = m_1 c_I \Delta T_I + m_1 L_f + m_W c_W \Delta T_W$$

Solve for m_1 using $\Delta T_I = +25$ K and $\Delta T_W = -20$ K.

$$m_1 = -\frac{m_W c_W \Delta T_W}{c_I \Delta T_I + L_f} = 1.08 \text{ kg}$$

We can find m_2 similarly but the three steps are now

 m_2 of ice at -25° C $\stackrel{1}{\Longrightarrow} m_2$ of ice at 0° C and m_W of water at 20° C $\stackrel{2}{\Longrightarrow} m_W$ of water at 0° C $\stackrel{3}{\Longrightarrow} m_W$ of ice at 0° C

The total heat exchange is zero. Summing over the heats added in each of the three steps above gives,

$$0 = Q_{\text{tot}} = Q_1 + Q_2 + Q_3 = m_2 c_I \Delta T_I + m_W c_W \Delta T_W - m_W L_f$$

Solve for m_2 using the same ΔT values $\Delta T_I = +25$ K and $\Delta T_W = -20$ K.

$$m_2 = \frac{-m_W c_W \Delta T_W + m_W L_f}{c_I \Delta T_I} = 39.8 \text{ kg}$$

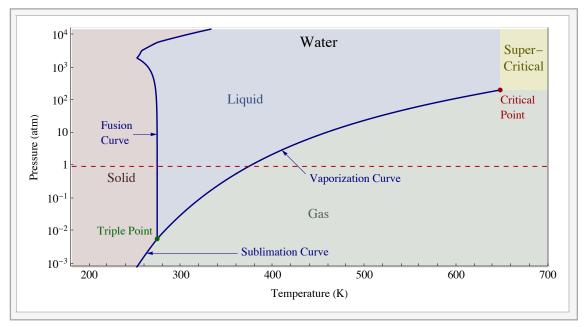
We define two systems to be in *thermal equilibrium* when no heat will flow between them when they are brought into thermal contact. Thermal contact means that the systems are linked in such a way where heat (and only heat) can flow from one to another. This linking could be some wall that conducts heat or it could be a conducting rod. Two systems are in thermal equilibrium if and only if they are at the same temperature.

After the three laws of thermodynamics were well established, it was realized that there was an additional assumption implicit in the notion of temperature; this became the "zeroth law." If system A is in thermal equilibrium with system B and system B is in thermal equilibrium with system C, then A is in thermal equilibrium with C. Physically, this allows us to make a thermometer. Think of system B as a thermometer. If systems A and C read the same value on B then they must be at the same temperature.

When two systems are brought into thermal contact, heat will flow from one system to the other until they reach thermal equilibrium. The time it takes to reach thermal equilibrium depends on the nature of the thermal contact. Regardless of the details of the thermal contact, the systems will eventually reach thermal equilibrium but the time required will depend on the quality of the thermal contact.

M.3 - Phase Diagrams

Phase Diagram for Water and Other Substances



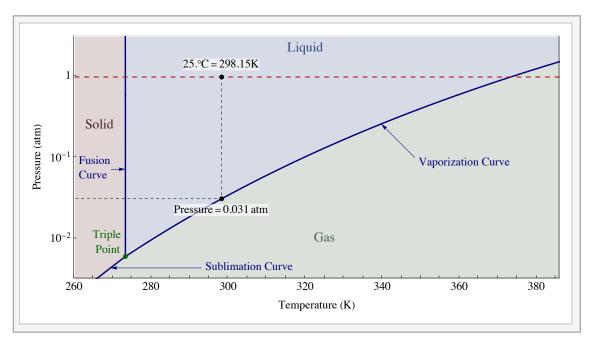
Interactive Figure - The Phase Diagram for Water and Other Substances

A phase diagram is a plot of pressure versus temperature showing how the phase of a substance varies with its temperature and pressure. The phase diagram above is for water and, when used interactively, shows other substances. We have discussed phases and phase transitions at 1 atm; in the diagram, the red dashed line is 1 atm. As the temperature at 1 atm increases, water changes phase from solid to liquid at 0 °C and from liquid to vapor at 100 °C. The phase diagram illustrates these phase transitions at all pressures.

At a low pressure, there is a point called the *triple point*, where all three phases of water, or any substance, can coexist; this is at 273.16 K and 0.0060 atm for water. Below that pressure there is no liquid phase and there is a direct sublimation phase transition from solid to gas. It should be clear from the phase diagram that the temperatures of the phase transitions vary with pressure. The phase diagram shows why water boils at a lower temperature at higher altitudes, since the pressure is lower. A pressure cooker exploits the fact that at higher pressure water boils at a higher temperature and food cooks more rapidly.

Latent heat is the energy needed to cross a phase transition curve at some pressure. Latent heats vary with pressure. The latent heat of vaporization gets smaller with increasing pressure. Surprisingly, the latent heat of vaporization goes to zero at a point known as the *critical point*. For water this is at 217.8 atm and 647.1 K. At temperatures and pressures higher than at the critical point there is no distinction between the liquid and gas phases; this is the *super-critical* region of a phase diagram.

Partial Pressure of Water and Humidity



Suppose you had a closed container with water and air and pulled all the air out to make a vacuum above the water level. Some of the water will evaporate and the region above the water would not be a perfect vacuum after the system reaches equilibrium. With the phase diagram we can see that at some temperature there is a low pressure where vapor and liquid water would be at equilibrium. This is the pressure of the vaporization curve at that temperature and it would be the small pressure above the water in the closed container.

In air at 1 atm, this becomes the vapor pressure, or partial pressure of water, when the air and water are at equilibrium. A relative humidity of 100% corresponds to this equilibrium state. Normally the air and water are not at equilibrium and the partial pressure of water vapor is less than its equilibrium value. The relative humidity is the fraction of the partial pressure of water to its equilibrium partial pressure.

Relative Humidity =
$$\frac{\text{partial pressure of water in air}}{\text{equilibrium partial pressure of water in air}} \times 100\%$$