

2 Temperature and thermal equilibrium

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Heat and temperature

Sensations of warmth and coldness are familiar and needed for survival. We learn very early their significance and what to do about them. They are not very reproducible; if you have one hot hand and one cold hand, lukewarm water feels hot to the cold hand and cool to the hot hand. If you have a fever and the environment is at a temperature you would normally regard as comfortable, you may feel much too hot or much too cold.

Thermometers allow comparisons of temperature to be made, and we can unambiguously say which of two bodies has the higher temperature, regardless of what kind of thermometer we use, provided the thermometer can come into thermal equilibrium with the body.

Some simple and familiar thermometers rely on thermal expansion, usually magnified in some way, since thermal expansion coefficients of solids and liquids are quite small. Liquid (ethanol or mercury) in glass thermometers have a wide bulb, and the liquid expands into a narrow uniform tube; the small change in volume of liquid is converted into a large change of length of the liquid in the narrow tube. Two strips of different metals welded together convert a small differential expansion into a larger deflection of a pointer.

Thermometers of this sort depend on an *equation of state* of a material; the percentage expansion of a solid or fluid is a characteristic of the material which may vary with temperature and pressure, but does not depend on the shape or size of the body.

2.1 Zeroth law

Bodies in thermal contact tend to a common temperature, so thermometers generally take up the temperature of their surroundings, preferably without causing much disturbance.

Things in thermal equilibrium with the same thing are in thermal equilibrium with each other.

Heat flows from higher temperature to lower temperature.

How fast thermal equilibrium is established between two bodies depends on how they are separated. Metals are good conductors of heat, so a piece of metal connecting them will make them equilibrate faster. Materials that trap air are poor conductors, and such materials can be used to insulate

two bodies from one another. A vacuum is not a good transmitter of heat, particularly over short distances.

2.2 Thermometers and thermometry

Some examples of thermometers are:

- Ethanol in glass (below 78 C) or mercury in glass (above -39 C);
- Air or other gases (constant pressure or constant volume);
- Bimetallic strip (two different sorts of metal welded together) bends as the temperature is changed because of differential expansion;
- Electrical resistance of platinum or carbon;
- Radiation measurement;
- Thermocouple: generates voltage proportional to temperature difference between two junctions in a circuit made up of two different metals;
- Nuclear resonance absorption (particularly useful at very low temperatures);
- Color of cholesteric liquid crystal;
- Color of hot iron bar;

Water in glass would not make a good thermometer, since the coefficient of expansion changes sign at 4 C, so that it expands as it cools from 4 C to 0 C.

For calibration of thermometers it is useful to have clearly defined fixed points for temperature. Some examples of fixed points are:

- Freezing point of gold, 1063 C;
- Melting point of NaCl, 801 C;
- Boiling point of water, 100 C;
- Triple point of water (where solid, liquid and vapor are in equilibrium), 0.01 C;
- Superfluid transition in liquid helium, -270.98 C.

A temperature scale can be defined in terms of two fixed points, such as the freezing point of water (zero in the Celsius scale) and the boiling point of water (100 in the Celsius scale), both at 760 torr pressure. Intermediate temperatures can then be defined by a linear interpolation, and temperatures outside the range can be defined by extrapolation. There is, however, no guarantee that different types of thermometers will give the same extrapolations or interpolations.

Most thermometric techniques have a limited range of applicability, and if different thermometers disagree with one another we have so far given no criterion for preferring one thermometer to another. Later we will show that thermodynamics and statistical mechanics constrain our choice of temperature scales. The gas thermometer, radiation measurements, and nuclear resonance measurements can all be related to the preferred scale, whereas the other methods I have listed are all dependent on specific materials properties. The carbon resistor actually does very well in approximating the ideal temperature scale over a wide range.

If there is no thermal equilibrium, different thermometers will not correspond to one another. For example, mercury and alcohol thermometers placed in sunlight will give different readings, neither of which corresponds to air or ground temperature. Different components of the solar corona or of the earth's upper atmosphere are at quite different temperatures, in a sense we will define in terms of the kinetic theory of gases. In some electronic devices electrons can have much higher temperatures than the rest of the solid.

2.3 Thermal expansion

Thermal expansion is used as the basis for several sorts of thermometers. For liquids and gases we generally quote the volume coefficient of expansion β , which is the rate of change in volume (at constant pressure) with temperature, divided by the volume;

$$\beta = \frac{1}{V} \frac{\partial V}{\partial T} = \frac{\partial \ln V}{\partial T} = -\frac{\partial \ln \rho}{\partial T}. \quad (1)$$

If the temperature is measured in either the Kelvin scale or the Celsius scale the units are $1/C^\circ$, since temperature intervals are the same in both. For gases at room temperature the volume coefficient of expansion is about $3.3 \times 10^{-3}/C^\circ$, according to the ideal gas laws discussed in the next two sections. For ethanol it is $1.1 \times 10^{-3}/C^\circ$, and for mercury it is $.18 \times 10^{-3}/C^\circ$. Water is special, since it contracts a little just above the freezing point, reaches a

maximum density at 4 C, and then begins expanding, with a coefficient of expansion that is strongly temperature-dependent. This maximum density, combined with the fact that ice is less dense than water, helps to ensure that deep water in lakes rarely goes below 4 C.

For solids it is usually the linear coefficient of expansion α that is quoted. This is defined as

$$\alpha = \frac{1}{L} \frac{\partial L}{\partial T} = \frac{\partial \ln L}{\partial T}, \quad (2)$$

where L is one of the linear dimensions. For an isotropic material $\beta = 3\alpha$, since $\ln V = 3 \ln L$ for a cube. For both iron and concrete the linear expansion coefficient is $18 \times 10^{-6}/\text{C}^\circ$, which is why iron rods can be used to reinforce concrete — if the expansion coefficients were different changes in temperature would lead to internal stresses in these structures, and the bonding between the different materials could be lost. The alloy invar has an expansion coefficient of $1 \times 10^{-6}/\text{C}^\circ$, ordinary glass has $8.5 \times 10^{-6}/\text{C}^\circ$.

Thermal expansion in solids seems small, and it has to be magnified somehow or other for use in a thermometer, but it is a major problem in construction. Railroads used to be laid with a gap between rails to allow for this, and the noise of wheels passing over this gap made one of the characteristic sounds of a train. In modern track the rails are welded together, so that the rails are held under compression at high temperatures, where there is danger of buckling, and they are under tension at low temperatures. Buildings and bridges have expansion joints to allow for this movement — you can see such joints on the passages joining the Physics–Astronomy Tower to the B building.

Typical problem. *A rail has length L , cross-sectional area A , at temperature T when it is not under stress. The temperature then goes up to $T + \delta T$ while it is held in place by the neighboring rails, so its length does not change. What force must each of its neighbors exert on it?*

You can do this by asking how much the length would change if it were free to change. This can be found from the linear coefficient of expansion α to be $\delta L = \alpha \delta T L$. Then you can use the Young's modulus Y to calculate the compressive stress which would be needed to compress the rail to its original length, and this is $Y \delta L / L = Y \alpha \delta T$. This stress is a force per unit area, so we have to multiply the stress by the area A to get the force at each end of the rail as $Y A \alpha \delta T$.

2.4 Ideal gas thermometry

Two hundred years ago studies by Gay-Lussac, Charles and Avogadro showed that “good” gases at low pressures all behave similarly, and they can be used to define a common temperature scale by the relation

$$pV = nR(T + T_0) . \quad (3)$$

where n is the number of moles (number of molecules divided by Avogadro’s number $N_0 = 6.02 \times 10^{23}$, or mass in grams divided by the molecular weight of a molecule), and R is the gas constant, which is 8.315 J/mole C°. The constant T_0 is 273.15 C°, and this suggests that the minimum possible temperature, *absolute zero*, is -273.15 C.

The constant on the right side of Eq. (3) can also be written as $nR = Nk_B$, where N is the number of molecules in the volume V , and $k_B = R/N_0$ is Boltzmann’s constant, N_0 is the Avogadro number, the number of molecules per mole. The Boltzmann constant has the value 1.38×10^{-23} J/C°.

Equation (3) is an idealization which is true at low enough pressures. We need a procedure for recognizing when the pressure is low enough, or, rather, for extrapolating to the zero pressure limit. If we write the volume per mole as $v = V/n$ we can in general write an expansion of pv in powers of p ,

$$pv = R(T + T_0) + B(T)p + C(T)p^2 + \dots , \quad (4)$$

and this is one form of what is known as the *virial expansion*. The leading coefficients in this expansion can be determined either from experimental measurements, or by calculation from intermolecular potentials. If measurements of the volume V as a function of pressure are made at a fixed temperature, and the results plotted for pV as a function of p , as shown in fig. 1, a straight line should give a good fit at low pressures. The slope of this line should give n times the coefficient $B(T)$, and the intercept for $p = 0$ should give the ideal gas limit $nR(T + T_0)$.

From such measurements taken at different temperatures an ideal gas temperature scale can be deduced. Real experiments have to take careful account of corrections due to the thermal expansion of the solid container of the gas. A gas thermometer of this sort is awkward to use, but it has the great advantage that it does not depend on the particular gas which is used. This gas thermometer can be used to calibrate more practical thermometers, so that a temperature scale independent of the particular material can be constructed. This scale is called the *ideal gas scale*.

The measured value of T_0 was approximately 273.15 C°. Nowadays, it has this value by the definition of the Celsius scale. For many purposes we use

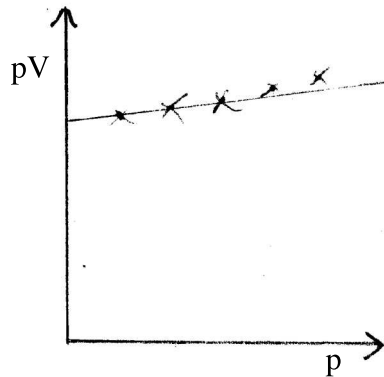


Figure 1: A plot of pressure times volume as a function of pressure at fixed temperature for a gas. The slope gives the first virial coefficient, while the intercept gives $nR(T + T_0)$.

the Kelvin scale, in which the temperature is measured by the amount it is above the absolute zero, $-T_0$. In this scale only one fixed point is needed, not the two which were used to define the Celsius scale, and the fixed point is the *triple point* of water, the temperature and pressure at which a mixture of ice, liquid water, and water vapor, with no air present, are all in equilibrium; this is, by definition, a temperature of 273.16 K, just above the zero of the Celsius scale.

Later we shall see that the Kelvin scale, based on the properties of the ideal gas, is a very natural one to use both for thermodynamics and for the kinetic theory of gases.

2.5 Equations of state for gases

The ideal gas law (3) says $pV = nRT$, where T is the temperature on the ideal gas (Kelvin) scale, and R is the gas constant. For a gas with just one species of molecules of molecular weight M this can be changed into the form

$$\rho(p, T) = 10^{-3}Mp/RT, \quad (5)$$

which is an equation for the density ρ as a function of pressure and temperature. This is a simple example of an *equation of state*. The factor 10^{-3} here, and the factor of 10^3 in Eq. (6) come from the fact that the mole is

defined in terms of grams of material, not kilograms.

For a gas with several components, such as air, the ideal gas equation of state can be written as

$$p = 10^3 \sum_j RT \frac{\rho_j}{M_j}, \quad (6)$$

where the pressure is a sum of contributions from a concentration ρ_j of the molecule of type j with molecular weight M_j . Each separate contribution to this sum is known as the *partial pressure* of the particular component. In dry air at atmospheric pressure the partial pressure of nitrogen is 78×10^3 Pa, the partial pressure of oxygen is 21×10^3 Pa, and the partial pressure of argon is $.93 \times 10^3$ Pa.

Various people have produced more accurate equations of state for gases which reduce to Eq. (3) in the low pressure limit, and you can find some of these in any physical chemistry text-book. One example is given by the virial equation (4), but the equation most physicists like best, because we think we can explain how it comes about, is the van der Waals equation

$$(p + a/v^2)(v - b) = RT, \quad (7)$$

where v is the volume per mole and a, b are constants. Figure 18–11 in Giancoli shows, in a p – V diagram, the curves of constant temperature given by this equation, with the liquid and vapor phases separated by a line of constant pressure at the lower temperatures.

The van der Waals equation can also be used to get a correction to the gas law in the low pressure limit, which gives a virial expansion in the form

$$pv = RT + bp - a/v + ab/v^2 \approx RT + \left(b - \frac{a}{RT}\right)p + \text{terms in } p^2.$$

Comparison of the with Eq. (4) shows that $B(T) = b - a/RT$.

2.6 Solids and liquids

We know that solids and liquids also change their densities, although much less than gases do, when either the pressure or the temperature is changed. We can make a two-variable Taylor series expansion of the density, ρ , in powers of the pressure p , and the deviation δT of the temperature from some standard value T . This has the form

$$\rho(p, T + \delta T) = \rho(0, T) + \frac{\partial \rho}{\partial p} p + \frac{\partial \rho}{\partial T} \delta T + \dots$$

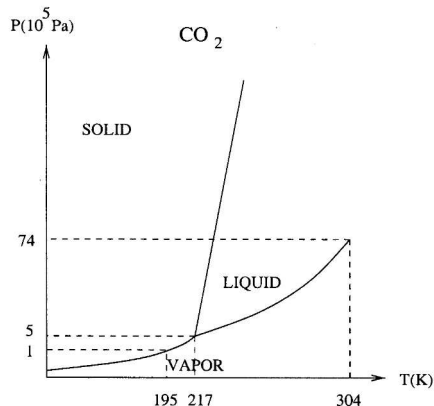


Figure 2: Phase diagram for CO₂

Since the bulk modulus is defined as $K = \rho \partial p / \partial \rho$, and the volume coefficient of thermal expansion is defined as $\beta = -(1/\rho) \partial \rho / \partial T$, this equation can be rewritten as

$$\rho(p, T + \delta T) \approx \rho(0, T) + \frac{\rho}{K} p - \beta \rho \delta T + \dots \quad (8)$$

This is only approximate, as large changes in pressure or temperature will produce corrections of higher order in $p, \delta T$. Yes, at fixed temperature it is all right to write $\partial \rho / \partial p = 1 / (\partial p / \partial \rho)$.

2.7 Phase diagrams for simple substances.

Almost any simple substance, like water, CO₂, or nitrogen, can exist as a solid, a liquid, or a gas. Which of these three it is depends on the pressure and temperature. Everything except helium becomes a solid at sufficiently low temperature, and everything, including helium, solidifies if the pressure is high enough. Everything is a gas at sufficiently low pressure. Figure 2 shows a schematic representation of the boundaries in the pressure-temperature plane between these three phases of matter for CO₂, which is a typical example. Figure 3 shows water, which is anomalous but very important, and fig. 4 shows helium, which is very unusual. The plot is schematic because a plot drawn properly on a linear scale would be very hard to see. Look at the phase diagram for CO₂, which is the typical case. There is a line separating the solid phase from the liquid phase, which shows

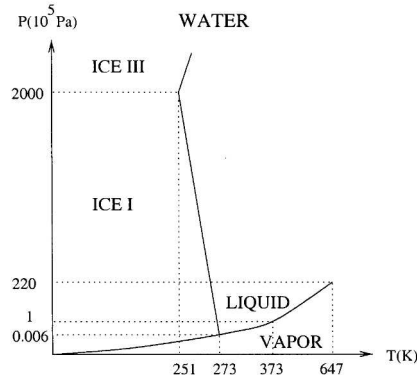


Figure 3: Phase diagram for H_2O

that the melting point of the solid, the temperature at which liquid and solid coexist, increases a little as the pressure is increased. There is a curve separating the solid from the gas which gives the pressure and temperature at which solid and gas can coexist, and this gives the *saturated vapor pressure* of the solid. This generally drops exponentially as the temperature drops. Thirdly there is a curve separating the gas from the liquid, and this gives the saturated vapor pressure of the liquid, which again increases exponentially with temperature, but comes to a stop at a point known as the *critical point*, where the distinction between gas and liquid disappears. In the case of CO_2 the critical point comes at the critical pressure $p_c = 74$ bar and critical temperature $T_c = 31$ C. The point at the other end of this line is where solid, liquid and gas can all coexist, and this is known as the *triple point*. The triple point for CO_2 is at $p_t = 5.1$ bar and $T_t = -57$ C. Because the pressure of the triple point is higher than atmospheric pressure, liquid CO_2 can only be stored under pressure, and when it is released from this pressure it evaporates rapidly, cooling the remaining liquid until it forms *dry ice*, which is the solid phase. It is dry because instead of warming up and melting it only warms up to the temperature at which it is in equilibrium with its own vapor at atmospheric pressure, a temperature of about -78 C, and then evaporates. On these three coexistence curves between two phases the density is not a unique function of pressure and temperature, because on the vapor–liquid coexistence curve, for example, the composition can be anywhere between pure vapor and pure liquid.

If you look at fig. 3 for water you can see some similar features, and some differences. The critical point is at $p_c = 221$ bar, $T_c = 374$ C, and the triple point at $p_t = 611$ Pa and $T_t = 0.01$ C (the triple point temperature is exact, since the Kelvin scale is defined by the triple point, and Celsius is defined in terms of the Kelvin scale). The boiling point of water, at 100 C, is where the vapor pressure reaches atmospheric pressure. The melting curve, where liquid water and ice are in equilibrium, slopes the other way, so that ice melts under pressure instead of solidifying, as most substances do. The liquid–vapor coexistence curve is needed to understand a lot of important things. The relative humidity is the amount of water vapor in the air relative to the saturated vapor pressure – if the relative vapor pressure is too high you cannot keep cool by sweating, and if it is too low you may get uncomfortably dry. The dew point is the temperature at which the actual pressure of water vapor in the air becomes equal to the saturated vapor pressure; dew or frost form because the ground is colder than the dew point of the surrounding air.

I have shown another phase boundary, where ordinary ice (ice I) turns into a more dense solid phase known as ice III above a pressure of about 2000 bar. There is another triple point where the liquid, ice I and ice III coexist at this pressure and -22 C temperature. This is the lowest temperature, as far as I know, at which pure liquid water can exist in equilibrium. Ice III changes to ice II when it is cooled below about -35 C, and there are many other forms of ice at even higher pressures. There is a complicated figure showing these on page 33 of Zemansky and Dittman, *Heat and thermodynamics : an intermediate textbook*.

Figure 4 for helium shows no triple point, because helium is only solidified under a pressure of about 25 bar, which is far higher than its vapor pressure. The critical pressure is 2.3 bar, and the critical temperature 5.2 K. This diagram has another unusual feature, which is two different liquid phases coexisting on the *lambda line*, which cuts the vapor pressure line at 2.177 K. The high temperature phase is a normal liquid, but the low temperature phase has many strange properties and is known as a *superfluid*.

2.8 Representations of the equation of state.

Since we need to represent density or volume as a function of both pressure and temperature, we need either to have three-dimensional diagrams, which can be found in more detailed books, or to represent one of the variables in the same way that heights are represented on a map, by drawing contours to represent curves of constant height. The contours of constant temperature

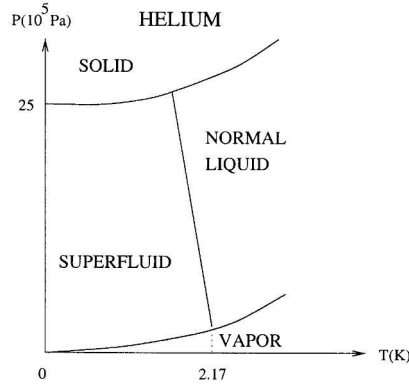


Figure 4: Phase diagram for helium

in a p - V diagram are known as *isotherms*, and we shall need them again when we discuss work and energy.

The plots of p against V are particularly useful, because the work done on a substance is $W = -\int p dV$, so, when a substance is moved along a curve in the p - V plane, the work done on the substance is given by minus the area under the curve.

For an ideal gas the isotherms are just given by the hyperbolas $pV = nRT$. Figure 5 shows the isotherms for a gas-liquid system near its critical point. At lower temperatures the isotherms have flat portions where liquid and vapor coexist at the same pressure, and the effect of an increase in volume at constant temperature is simply to evaporate more liquid without changing the pressure. At the critical point this flat portion disappears, but the slope is zero. Above the critical temperature the curves have negative slope everywhere.

Figure 6 shows isotherms for a solid which expands on melting. These again have a flat portion where the liquid and solid can coexist at the same pressure – melting of part of the solid increases the volume without changing temperature or pressure. If the isotherms were plotted on the same scale as the isotherms for a gas they would look very steep, because the bulk modulus of the solid or of the liquid near its melting point is so large.

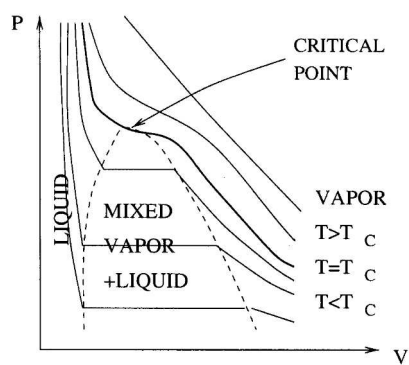


Figure 5: Isotherms near a gas-liquid critical point

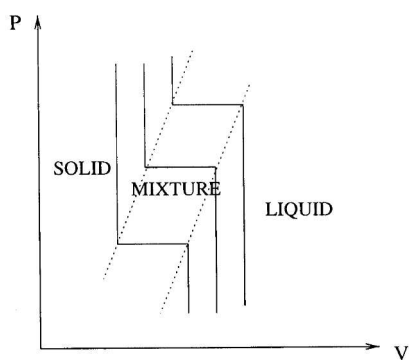


Figure 6: Isotherms near the melting point of a solid