Liquids and their vapors

A Chem1 Reference Text
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Contents

substance	formula	mp	bp	ΔH_{fus}, kJ	ΔH_{vap}, kJ
neon	Ne	24.5 K	27.1 K	0.41	1.7
mercury	Hg	357	396	2.3	59.1
sodium	Na	98	889	2.63	59.1
iron	Fe	1530	3000	13.8	340
tungsten	W	3380	5900		
chlorine	CL_2	239 K	271 K	6.41	10.4
water	H_2O	0	100	6.0	44.0
methane	CH_4	89 K	112 K	0.94	8.2
benzene	C_6H_6	5.5	80	10.6	30.8
sodium chloride	NaCl	801	1410	3.55	

Melting and boiling points are in °C except as indicated; ΔH_{fusion} values are at 20 °C or at the boiling point, whichever is smaller.

Table 1: Liquid ranges and heats of fusion and vaporization of several substances.

1   Special physical properties of liquids

Liquids occupy a rather peculiar place in the trinity of solid, liquid and gas; like solids, their molecules are in direct contact, and so their densities are similar, but the abilitiy of their components to slip and slide around each other gives liquids something of the mobility of a gas. From the standpoint of chemistry, this represents the best of two worlds; rapid chemical change requires intimate contact between the agents undergoing reaction, but these agents, along with the reaction products, must be free to move away to allow new contacts and further reaction to take place.

We also recognize the liquid as being the preferred state of a substance at temperatures intermediate between the realms of the solid and the gas. But if you look at the melting and boiling points of a variety of substances (Table 1), you will notice that the temperature range within which many liquids can exist tends to be rather small. In this, and in a number of other ways, the liquid state appears to be somewhat tenuous and insecure, as if it had no clear right to exist at all. Certainly the liquid state is the most complicated of the three states of matter to analyze and to understand. But just as people whose personalities are more complicated and enigmatic are often the most interesting ones to kknow, it is these same features that make the liquid state of matter the most fascinating to study.

How do we know it's a liquid?   Anyone can usually tell if a substance is a liquid simply by looking at it. What special physical properties do liquids possess that make them so easy to recognize? One obvious property is their *mobility*, which refers to their ability to move around, to change their shape to conform to that of a container, to flow in response to a pressure gradient, and to be displaced by other objects. But these properties are shared by gases, the other member of the two *fluid* states of matter. The real giveaway is that a liquid occupies a *fixed volume*, with the consequence that a liquid possesses a definite *surface*. Gases, of course, do not; the volume and shape of a gas are simply those of the container in which it is confined. Of course, the higher density of a liquid also plays a role here; it is only because of the large density difference between a liquid and the space above it that we can see the surface at all. (What we are really seeing, of course, is the reflection and refraction that occurs when light passes across the boundary between two phases differing in density, or more precisely, in *refractive index*.)

1.1   Flow properties of liquids: the viscosity

The term *viscosity* is a measure of resistance to flow. You have undoubtedly observed the relative ease at which water, pancake syrup, liquid detergent and molasses are able to pour out of a container. The

substance	formula	viscosity, cp	surface tension, dynes/cm
benzene	C_6H_6	.652	28.9
bromine	Br_2	1.0	.995
carbon tetrachloride	CCl_4	.87	.97
ethanol	C_2H_5OH	1.20	22.8
ether	$(C_2H_5)_2O$	.23	17.0
glycerol	$C_3H_5(OH)_3$	1.49	40.4
water	H_2O	1.00	73
helium	He		0.18
neon	Ne		5.5
argon	Ar		13.2

Temperatures are 20 °C except for noble gas elements that are at their boiling points.

Table 2: Viscosity and surface tension of several liquids

viscosity of a substance is related to the strength of the forces acting between its molecular units. The two edible substances mentioned above are concentrated solutions of sugar molecules. Sugars are studded with hydroxyl groups (–OH) which can form multiple hydrogen bonds with water and with each other, producing a sticky disordered network. To pour these liquid easily, it helps to warm them; hydrogen bonds are easily disrupted by thermal agitation. Lubricating oils (whose action we will discuss later) are mostly long hydrocarbon molecules which interact through dispersion forces, and to some extent simply by becoming entangled.

The temperature dependence of the viscosity of liquids is well known to anyone who has tried to pour cold syrup on a pancake. Automotive lubricating oils can similarly be too viscous at low temperatures (making it harder for your car to operate on a cold day), while losing so much viscosity at engine operating temperatures that their lubricating properties become impaired. These engine oils are sold in a wide range of viscosities; the higher-viscosity oils are used in warmer weather and the lower-viscosity oils in colder weather. The idea is to achieve a fairly constant viscosity that is ideal for the particular application. By blending in certain ingredients, lubricant manufacturers are able to formulate "multigrade" oils whose viscosities are less sensitive to temperatures, thus making a single product useful over a much wider temperature range.

How viscosity impedes flow. *The next time you pour a viscous liquid such as syrup out of a container, notice how different parts of the liquid move at different rates and sometimes in different directions. In order to flow freely, the particles making up a fluid must be able to move independently. Intermolecular attractive forces work against this, making it difficult for one molecule to pull away from its neighbors and force its way in between new neighbors.*

The pressure drop that is observed when a liquid flows through a pipe is a direct consequence of viscosity. Those molecules that happen to be near the inner walls of a tube tend to spend much of their time attached to the walls by intermolecular forces, and thus move very slowly. Movement of the next layer of molecules is impeded as they slip and slide over the non-movers; this process continues across successive layers of molecules as we move toward the center of the tube, where the velocity is greatest. This effect is called viscous drag, and is directly responsible for the pressure drop that can be quite noticeable when you are taking a shower bath and someone else in the house suddenly turns on the water in the kitchen.

Viscosity of gases *One might suppose that gases, in which the molecules are too far apart to exert attractive forces on each other, would possess zero viscosity, but this is not the case: the long*
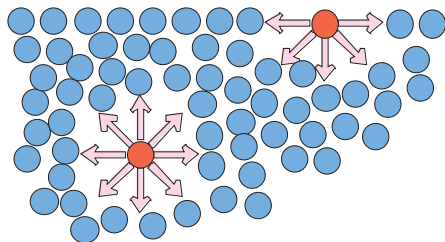
A molecule located at the surface has fewer neighbors than one in the bulk liquid. The resulting unbalance of attractive forces draws the surface molecules together, creating what is in effect an elastic surface film that tries to minimize its area. If the amount of water is small enough to allow surface tension to overcome gravitational forces (which work to flatten the surface), the water will form a spherical drop.

Figure 1: Origin of surface tension.

pipelines that carry natural gas across the continent require pumping stations to compensate for pressure drop just as do the oil pipelines. It is interesting, however, that the origin and behavior of viscosity in gases is completely different than for liquids.

When a gas flows through a tube, the molecules in contact with the walls tend to have their forward velocities reduced just as happens in liquids. Unlike the molecules in a liquid, however, the gas molecules can also move freely in a direction normal to the direction of flow. As the slowed-down molecules are released from the walls of the container, they tend to move toward the center of the tube and in doing so they collide with other, faster-moving molecules and slow them down. Thus the cause of viscosity in gases is intermolecular collisions rather than attractive forces between the molecules of the fluid. One important consequence of this is that the viscosity of gases always]it increases with the temperature. This happens because the higher the temperature, the more rapidly will be the migration toward the center of the tube of those molecules whose direction-of-flow velocities have been reduced, thus increasing the collision rate.

1.2 Surface tension

A molecule within the bulk of a liquid experiences attractions to neighboring molecules in all directions, but since these average out to zero, there is no net force on the molecule it is, on the average, as energetically comfortable in one location within the liquid as in another.

Liquids have surfaces, however, and a molecule that finds itself in such a location is attracted to its neighbors below and to either side, but there is no attraction operating in the 180° solid angle above the surface. As a consequence, a molecule at the surface will tend to be drawn into the bulk of the liquid. Clearly there must always be *some* molecules at the surface, but the smaller the surface area, the lower the potential energy. Thus intermolecular attractive forces act to minimize the surface area of a liquid. The geometric shape that has the smallest ratio of surface area to volume is the *sphere*, so very small quantities of liquids tend to form spherical *drops*. As the drops get bigger, their weight deforms them into the typical tear shape.

If a molecule within the bulk of the liquid is moved to the surface, work must be done to break some of the intermolecular attractions. This is the same as saying that creation of additional surface requires an input of energy. The *surface tension* is defined as the amount of work that must be done in order to increase the surface by unit area:

$$\gamma = -\frac{dw}{dA}$$

The SI units of surface tension are $\mathrm{J\,m^{-2}}$ or $\mathrm{N\,m^{-1}}$. Surface tension, like the viscosity, decreases with temperature, and for the same reasons.

1.3 Interactions between liquid and solid surfaces

The effects related to the surface tension occur at the liquid-air interface; these are only a special case of *interfacial tensions* that are present at any phase boundary: liquid-liquid, solid-solid, solid-gas, and
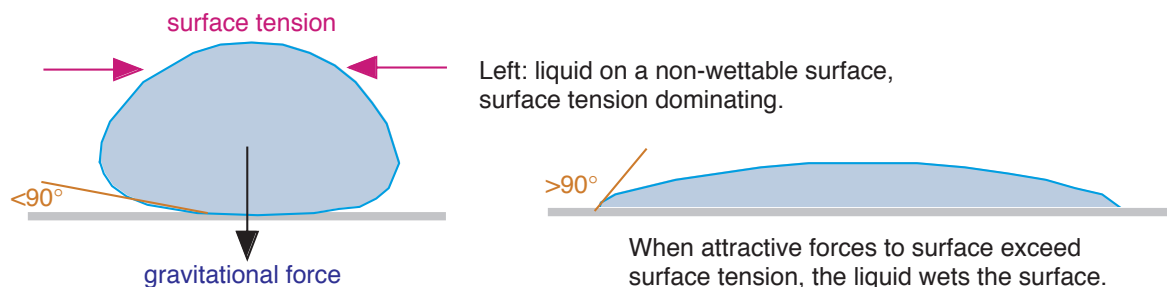
Figure 2: Liquids on wettable and non-wettable surfaces.

liquid-solid.

Wetting   Take a plastic mixing bowl from your kitchen, and splash some water around in it. You will probably observe that the water does not cover the inside surface uniformly, but remains dispersed into drops. The same effect is seen on a dirty windshield; running the wipers simply breaks hundreds of drops into thousands. By contrast, water poured over a clean glass surface will *wet* it, leaving a uniform film.

When a molecule of a liquid is in contact with another phase, its behavior depends on the relative attractive strengths of its neighbors on the two sides of the phase boundary. If the molecule is more strongly attracted to its own kind, then interfacial tension will act to minimize the area of contact by increasing the curvature of the surface. This is what happens at the interface between water and a hydrophobic surface such as a plastic mixing bowl or a windshield coated with oily material. A clean glass surface, by contrast, has -OH groups sticking out of it which readily attach to water molecules through hydrogen bonding; the lowest potential energy now occurs when the contact area between the glass and water is maximized. This causes the water to spread out evenly over the surface, or to *wet* it.

A liquid will wet a surface if the angle at which it makes contact with the surface is less than 90°. The value of this *contact angle* can be predicted from the properties of the liquid and solid separately.

Water repellency   Water is quite strongly attracted to many natural fibers such as cotton and linen; a droplet that falls on such a material will flatten out and be drawn through the fabric (Fig. **??**.) One way to prevent this is to coat the fibers with a polymeric material that is not readily wetted. The water tends to curve away from the fibers so as to minimize the area of contact, so the droplets are supported on the gridwork of the fabric but tend not to fall through.
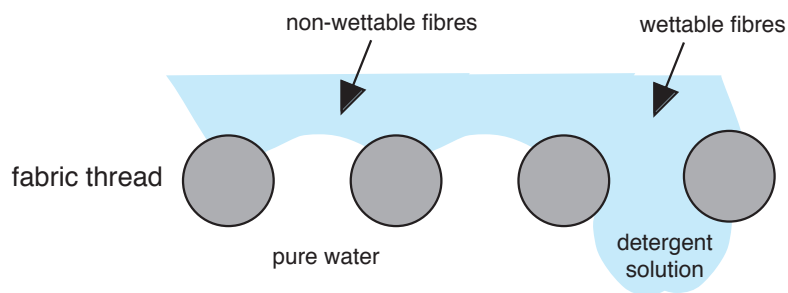

Figure 3: Water repellency and penetration of fabrics.

Capillary rise If the walls of a container can be efficiently wetted by a liquid, then the liquid tends to creep up the sides of the container above the surface; this effect is responsible for the curved *meniscus* that is seen in a narrow container such as a burette.

1. Liquid wets walls of tube, increasing surface area.

2. Surface tension acts to decrease, surface area, pulling liquid up.

3. Wetting continues from higher level, causing liquid

4. Eventually the liquid reaches a height at which its its weight is exactly balanced by surface tension, resulting in a constant height.
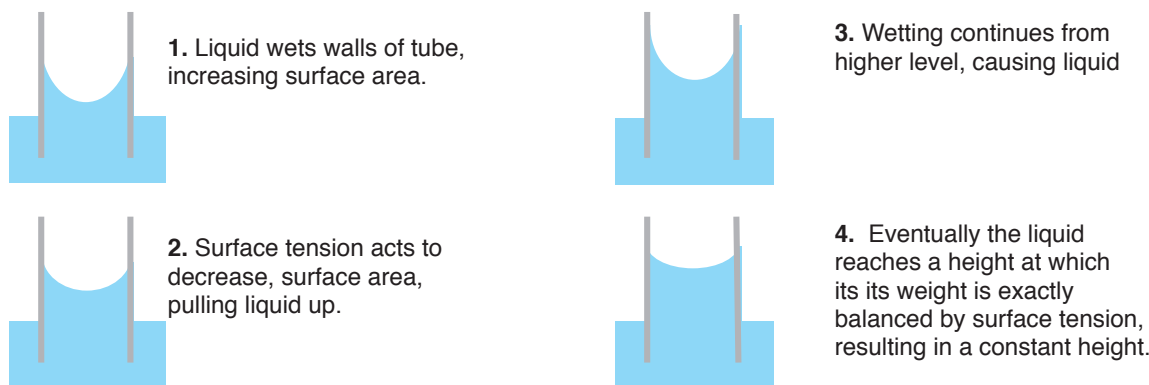
Figure 4: Capillary rise.

Suppose that a glass tube of small cross-section is inserted into an open container of water (Fig. 4.) The attraction of the water to the inner wall of the tube pulls the edges of the water up, creating a meniscus whose cross-section area is greater than that of the tube. The surface tension of the water acts against this by attempting to reduce the curvature, stretching the meniscus into a flatter shape by pulling the liquid farther up into the tube. This process continues until the weight of the liquid column becomes equal to the surface tension force, and the system reaches mechanical equilibrium. This effect is only significant when the diameter of the container is very small, as in a small-bore glass *capillary* tube, or in the interstices of porous or fibrous materials. If the diameter is large, the weight of the liquid prevents any noticeable capillary rise.

The meniscus. If you look closely at the upper surface of a liquid in a graduated cylinder or other fairly narrow glass tube, you will noticed that it is curved; this upper surface is known as the *meniscus*. This is just another manifestation of tendency of a liquid to minimize its surface area; that is, of surface tension. A clean glass surface is highly attractive to most molecules, so most liquids display a concave meniscus in a glass tube (Fig. 5).

The only commonly seen exception to this is metallic mercury, in which the atoms are more strongly attracted to each other than to the glass. The meniscus at the top of a mercury column in a glass tube has a negative curvature; the high part is at the center, rather than at the edges. The capillary rise of

water (and most liquids) in glass

Surface tension causes the surface of a liquid in a narrow tube to assume a spherical shape. The sign of the curvature depends on the relative attractions of the liquid molecules to each other and to the walls of the tube.
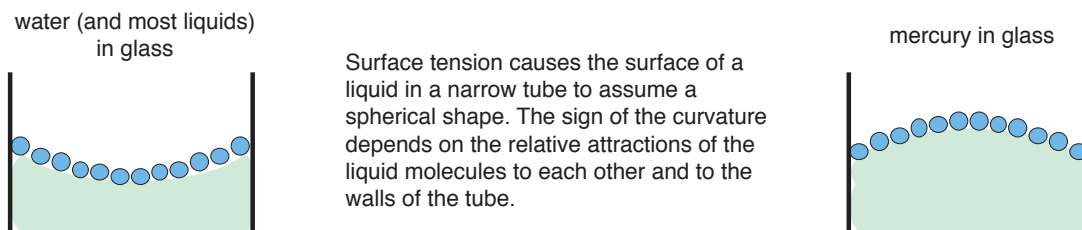
mercury in glass

Figure 5: Formation of a meniscus in a glass tube.

mercury in a very narrow tube is also negative; the height of the column will be less than that in a larger container in which the narrow tube is immersed.

2 Surface properties of solids

When we think of solids we usually think of the bulk material. The *surfaces* of solids have unique structures, properties, and chemical behaviors of their own, which become especially evident when the solids are finely divided, so that the ratio of surface to volume is larger.

Sintering The surfaces of solids are not nearly as uniform as those of liquids. The regularity and uniformity that characterizes crystals is interrupted at the surface; there will always be corners, edges, steps, pits, and other irregularities. At the molecular level, a surface is more like a mountain range. Atoms or molecules located at corners, edges, or near the tops of the "hills" have fewer neighbors, and there thus less tightly bound than others, and will therefore have slightly lower melting points.

If finely-powdered crystals are packed tightly together and heated to a temperature that is somewhat less than the melting point, the molecules in these more exposed locations will undergo a kind of localized melting that acts to weld the particles together at these points of contact. This process is known as *sintering*. The resulting materials possesses a rigid but open sponge-like structure that can have useful properties, such as ability to absorb and retain lubricating oils.

Adsorption The molecules at the surface of a solid can attract foreign molecules in an adjoining gaseous or liquid phase; the foreign molecules are said to be *adsorbed* to the surface. The average residence time of an adsorbed molecule depends on the temperature and on the energy released when adsorption occurs; the latter quantity (the *heat of adsorption*) can be determined experimentally by measuring the rise in temperature of a thin film of the solid when a suitable gas is introduced.

If the adsorbed molecules are bound by weak van der Waals forces, the process is called *physical adsorption*. Physical adsorption of air molecules onto the inner walls of containers poses a real problem where high vacuums are required; as the molecules slowly desorb, the vacuum is reduced. One solution is to *degas* the apparatus by heating it while it is being pumped; another is to place within it a highly reactive metal (known as a "getter") that will react with the gas molecules as they are released.

> *If you are a non-smoker, you have probably noticed the unpleasant odor that remains for some time on your hair and clothing after you have left a room in which people have been smoking. This is a common example of adsorption followed by desorption.*

Chemisorption Many solids attract other molecules so strongly to their surfaces that chemical bonds are formed. *Chemisorption* is a very widespread and important phenomenon; it is the basis of much of catalysis and electrochemistry.

All metals except gold quickly become acquire a chemisorbed layer oxygen when exposed to the air. Metal oxides, clays, and ordinary glass have –OH groups projecting from their surfaces. These tend to be highly active chemically, acting as acids or bases depending on the conditions.

Catalysts The transition metals and their oxides tend to chemisorb a wide variety of substances. One reason for their high surface activity is the presence of a number of partially occupied d-orbitals that extend above the surface, making it possible for substances in an adjacent phase to form covalent chemical bonds with the surface. Ni, V, and especially Pd and Pt are particularly active in this respect. These metals chemisorb hydrogen atoms so strongly that these atoms are removed from gases such as H_2 and hydrocarbon fuels that come into contact with these metals. The resulting fragments tend to

be highly reactive, so that when other components are introduced, a reaction can take place that would otherwise be impossible. The solid that mediates this sequence of chemisorption followed by a reaction is a *heterogeneous catalyst*.

Catalysts of this type are widely employed in petroleum refining, in which long-chain hydrocarbon molecules CH_3-$(CH_2)_n$-CH_3 are broken down ("cracked") into smaller fragments. The same principle used in the platinum-based catalytic converters of automobiles to remove uncombusted hydrocarbons from the exhaust. When a fuel gas is brought into contact with platinum in the presence of oxygen, the highly exothermic oxidation of the hydrogen atoms and fuel gas fragments produces enough heat to sustain flameless combustion.

Adhesion If the molecules at all solid surfaces can attract and hold foreign molecules, why do the solids themselves not tend to stick together? The answer is that they do, as long as their surfaces are extremely smooth. You may have noticed how microscope slides tend to stick together, and if you have taken a machine shop course, you may be familiar with the way that two smooth steel gauge blocks can be stuck together by sliding one over the other in a circular motion which machinists call "wringing". Ordinary surfaces are too uneven to allow two bodies to be in contact over more than a small fraction of the total surface, so the molecule-to-molecule van der Waals forces are not strong enough to have any noticeable effect.

If you want to join two solid objects together, you use a glue or adhesive. A *glue* is a substance that flows onto a surface and evens out the hills and valleys, and then hardens into a high-strength solid. An *adhesive* works in much the same way; most adhesives are highly viscous polymeric materials that are sufficiently flexible to conform to the solid surface. Metals are often joined by means of a *solder*, which is usually a low-melting alloy of tin and lead. Before soldering, the two metals are usually coated with a *flux*. This is usually a weak acid (such as the abietic acid, $C_{19}H_{29}COOH$, found in rosin) that reacts with and removes the surface oxide coating.

2.1   Friction and lubrication

Although the surfaces of ordinary solids are too unclean and uneven to allow them to adhere to each other, their high points and protuberances can come into contact, forming temporary, localized "bonds" that give rise to the familiar phenomenon of *friction*. When one solid slides over another, the potential energy that is released as the surface attractions are broken is liberated in the form of heat; this is the familiar frictional heating. This heating can lead to localized sintering, as described above. This in turn causes the surfaces to temporarily weld together; breaking and remaking of the welds often occurs at a frequency high enough to produce an intermittent motion that results in squeaking. It sometimes happens that the surfaces of a metal shaft and its bearing will sinter together so strongly that the bearing seizes. This is less likely to occur when the two surfaces are of different materials, so that one is softer than the other. When a new engine or machine is "broken in" under a light load, the softer material is worn down to a more even surface which presents fewer points at which sintering and subsequent welding can occur.

In order to reduce friction, we use a *lubricant*. A good lubricant must keep the two bearing surfaces apart, while at the same time offering a minimum of resistance to the shearing motion between them. There is a certain amount of conflict between these two criteria; the second is favored by low-viscosity liquids made of small molecules which do not tend to entangle and which have low intermolecular forces, while the first criterion is often best met by larger molecules whose intermolecular forces promote adsorption onto the surface; without this adhesion, the liquid simply gets squeezed out.

Lubricants are designed for specific applications by balancing molecular size and reactivity with surfaces. The latter is often increased by adding a heavy-metal soap, such as calcium stearate. (A mixture of a lubricating oil and a soap is called a lubricating grease). The calcium ions will be strongly attracted to the oxide surface of the metal, and will at the same time hold onto the long-chain stearate

ions, $CH_3(CH_2)_{16}COO^-$, that have the desired flow properties. Any exposed metal atoms, which tend to have positive charges, will bind to the negatively-charged ends of the stearate ions. For very heavy loads where ordinary lubricants would get squeezed out of the bearings, layered-type "slippery" solid lubricants such as graphite and MoS_2 are used.

The proper lubrication of aluminum has always been a problem because the oxide coating does not adhere very well to the metal and the negative ions of the lubricant are not strongly attracted to the bare aluminum. Special lubricants have been developed that employ different means of bonding to the aluminum atoms.

3   Changes of state

A given substance responds to changes in temperature and pressure by moving between these states, occupying whichever one best fits the conditions. In this unit, we will learn what common factors govern the preferred state of matter under a particular set of conditions, and we will examine the way in which one phase gives way to another when these conditions change We will also look at some of the interesting effects that occur at the surfaces where two phases meet.

3.1   Stability of a phase

The molecular units in a solid are arranged more compactly and closely than are those in a liquid, and are therefore at the lowest possible potential energy. Thermal energy, always present at temperaturs above absolute zero, is generally insufficient to knock the molecules out of their energetically favorable locations, so its only effect is to cause the molecules to twist and vibrate around their equilibrium positions. Thus in solids, both the potential and the kinetic energy are low, compared to liquids and especially gases.

If solids are the lowest-energy states of matter, why can substances exist as liquids or gases at all? The obvious answer is that although low energy is always favored, energy alone is not the determining factor; if it were, all matter would be permanently frozen. The other factor that wins out is the amount of *disorder*. A crystalline solid phase contains very little disorder, whereas the molecules of a gas are in almost total disorder.

Just as low-energy configurations of matter are more probable, or likely, than high-energy configurations, so are high-disorder arrangements more probable than low-disorder ones; the latter principle is just a matter of simple statistics, well known to any card player. Although disordered states of molecules are always favored statistically, they cannot be realized unless there is sufficient thermal energy available to overcome the attractive forces that otherwise lock them into more ordered configurations. Thus the "energy" and "disorder" factors act in opposition; the outcome is determined by the temperature in relation to the strength of the intermolecular attractive forces.

This helps us understand why substances exist as solids at low temperatures, as gases at high temperatures, and as liquids in between. At most temperatures, one phase will be more stable than the others and this will be the only phase that exists. At the melting point, the solid and liquid phases are equally stable, and can coexist. The same applies to the liquid and gas phases at a higher temperature, the boiling point.

3.2   The escaping tendency

The extent to which the effects of disorder prevail in a given solid, liquid, or gas can be expressed in terms of the tendency of molecules to leave that phase; we will call this the *escaping tendency* of the molecules from the phase. The escaping tendency is a quantity of fundamental importance in understanding all chemical equilibria and transformations. We have not defined the term in a formal way, and in fact
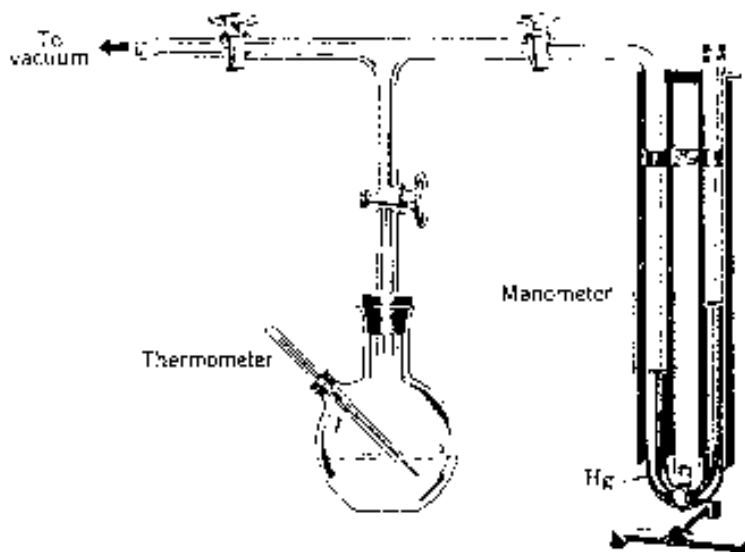
The most straightforward way of measuring the vapor pressure of the liquid in the flask is to begin with both limbs of the manometer at atmospheric pressure, with the two stopcocks on the right side open and the leftmost one closed. (The right limb of the manometer is permanently open to the atmosphere. The vapor pressure of the liquid is then just the difference in height of the two mercury columns

Figure 6: Apparatus for measuring the vapor pressure of a liquid.

will not do so in this course. What is important for now is how we can observe and compare escaping tendencies.

Think first of a gas: what property of the gas constitutes the best measure of its tendency to escape from a container? It does not require much reflection to conclude that the greater the *pressure* of the gas, the more frequently will they collide with the walls of the container and possibly find their way through an opening to the outside. Thus the *pressure* confining a gas is a direct measure of the tendency of molecules to *escape* from a gaseous phase.

What about liquids and solids? Although we think of the molecules of condensed phases as permanently confined within them, these molecules still possess some thermal energy, and there is always a chance that one that is near the surface will occasionally fly loose and escape into the space outside the solid or liquid. We can observe the tendency for this to happen by placing the substance in a closed, evacuated container connected to a manometer for measuring gas pressure. Gradually, a pressure will build up as molecules escape from the substance and enter the vapor phase. This pressure will eventually stabilize at a fixed value that depends on the substance and on the temperature; this fixed value is known as the *equilibrium vapor pressure*, or simply as the "vapor pressure" of the liquid or solid. The vapor pressure is a direct measure of the escaping tendency of molecules from a condensed state of matter.

Vapor pressure and temperature   The escaping tendency of molecules from a phase always increases with the temperature; therefore the vapor pressure of a liquid or solid will be greater at higher temperatures. As Fig. 8 shows, the variation of the vapor pressure on the temperature is not linear. However, a plot of the logarithm of the vapor pressure as a function of the reciprocal temperature is linear.

3.3   Vapor pressure of water: relative humidity

The vapor pressure of water at 24 °C is about 24 torr, or around .03 atm. This is the partial pressure of H_2O that will be found in the vapor space within a closed container of water at this temperature; the air in this space is said to be *saturated* with water vapor.

Using a monometer to measure the vapor pressure of water. The water vapor in the closed limb exerts a force in opposition to the atmospheric pressure; the difference in the height

When the container has just been closed, the vapor pressure rises as molecules move from the liquid into the vapor. As more molecules appear in the vapor, some of them will return to the liquid. Eventually the rates at which molcules move in the two directions are identical; at this point, no further change in the number of molecules in the vapor space occurs, and the vapor pressure remains at its equilibrium value indefinitely.
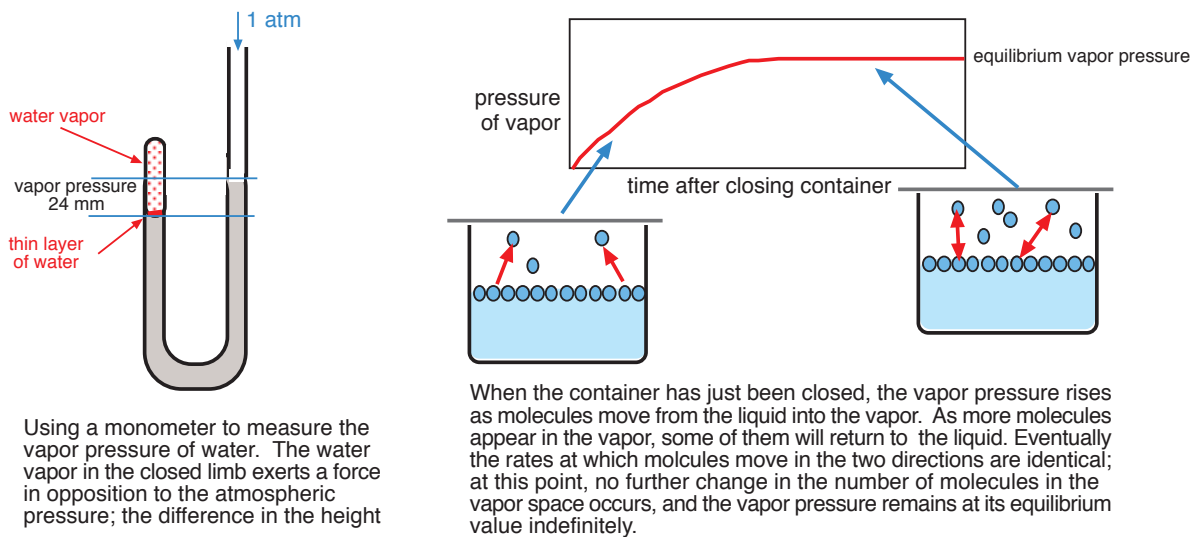
Figure 7: Partial pressure of vapor and the equilibrium vapor pressure.
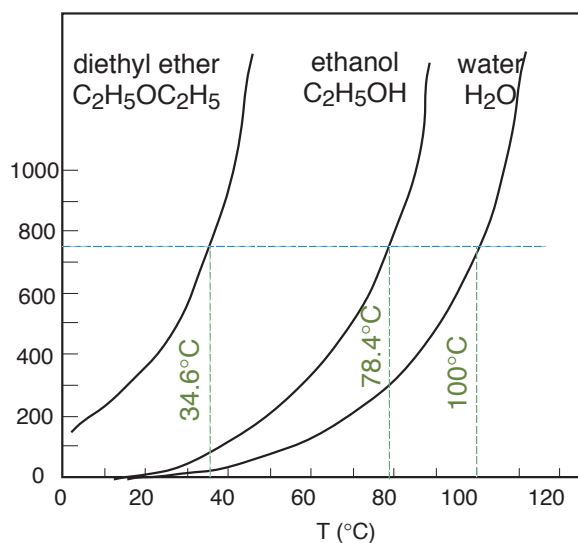

Figure 8: Vapor pressure as a function of temperature.

In ordinary air, the partial pressure of water vapor is normally less than its saturation or equilibrium value. The ratio of the partial pressure of H_2O in the air to its (equilibrium) vapor pressure at any given temperature is known as the *relative humidity*. Water enters the atmosphere through evaporation from the ocean and other bodies of water, and from water-saturated soils. The resulting vapor tends to get dissipated and diluted by atmospheric circulation, so the relative humidity rarely reaches 100 percent. When it does, especially in warm weather, we are very uncomfortable because vaporization of water from the skin is inhibited; if the air is already saturated with water, then there is no place for our perspiration to go, other than to drip down our face.

Because the vapor pressure increases with temperature, a parcel of air containing a fixed partial pressure of water vapor will have a larger relative humidity at low temperatures than at high temperatures. Thus when cold air enters a heated house, its water content remains unchanged but the relative humidity drops. In climates with cold winters, this promotes increased moisture loss from house plants and from mucous membranes, leading to wilting of the former and irritation of the latter.

The *dew point* is the temperature at which the relative humidity is 100 percent. In the evening, especially on clear nights, solid objects lose heat to the sky more rapidly than does the air. When their temperature falls below the dew point, some of the water vapor will condense out on their surfaces. For water to condense directly out of the atmosphere as rain, the air must be at or below the dew point, but this is not of itself the only requirement for the formation of rain, as we will see shortly.

3.4   Vapor pressures of solid hydrates

Many solid salts incorporate water molecules into their crystal lattices; the resulting compounds are known as *hydrates*. These solid hydrates possess definite vapor pressures which correspond to equilibrium between the hydrated and anhydrous compounds and water vapor. For example:

$$SrCl_2 \cdot 6\,H_2O \;\longrightarrow\; SrCl_2 \;+\; 6\,H_2O$$
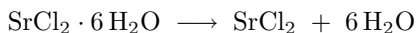
The vapor pressure of this hydrate is 8.4 torr at $25\,°C$. Only at this unique partial pressure of water vapor can the two solids coexist at $25\,°C$. If the partial pressure of water in the air is greater than 8.4 torr, a sample of anhydrous $SrCl_2$ will absorb moisture from the air and change into the hydrate.

> **Problem Example 1** ———————————————————————
>
> What will be the relative humidity of air in an enclosed vessel containing solid $SrCl_2 \cdot 6\,H_2O$ at $25\,°C$?
>
> *Solution: What fraction of the vapor pressure of water at this temperature (23.8 torr) is the vapor pressure of the hydrate (8.4 torr)? Expressed in percent, this is the relative humidity.*

If the partial pressure of H_2O in the air is less than the vapor pressure of the hydrate, the latter will tend to lose moisture and revert back to its anhydrous form. This process is sometimes accompanied by a breakup of the crystal into a powdery form, and effect known as *efflorescence.*

3.5   Boiling point and melting point

When the vapor pressure of a liquid becomes equal to the total pressure in the vapor space above the liquid, the liquid will boil. The *normal boiling point* is the temperature at which a liquid will boil under a total pressure of 1 atm; that is, it is the temperature at which the vapor pressure of the liquid is 1 atm. At the boiling point, the tendency of molecules to escape from the liquid phase and from the vapor phase is the same; the two phases are in equilibrium and can coexist indefinitely.

> *This explains why you cannot raise the temperature of a pot of boiling water above $100°C$. Supplying more heat will make it boil faster, but as long as the two phases (liquid and vapor) are present, the temperature will not rise above the boiling point as long as the total pressure remains at 1 atm.*
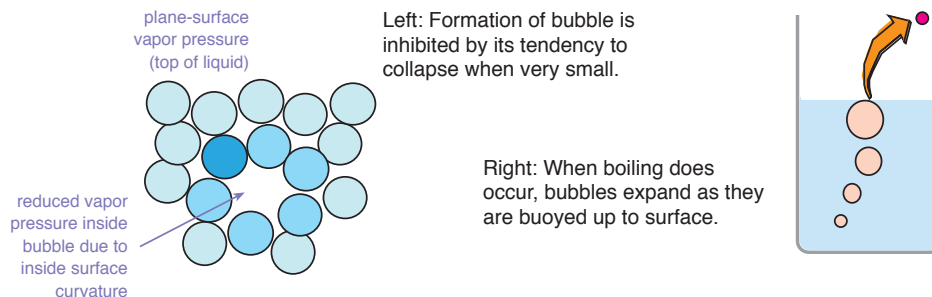
plane-surface
vapor pressure
(top of liquid)

Left: Formation of bubble is
inhibited by its tendency to
collapse when very small.

reduced vapor
pressure inside
bubble due to
inside surface
curvature

Right: When boiling does
occur, bubbles expand as they
are buoyed up to surface.

Figure 9: Bubble formation and boiling.

3.6 Condensation and boiling: nucleation

Suppose that a substance is at a temperature and pressure that falls within the vapor region of the phase diagram for that substance. We then decrease the temperature so as to move the state point toward the liquid region. When the state point falls on the vapor pressure line, the two phases can coexist and we would expect some liquid to condense. Once the state point moves to the left of the vapor pressure line, the substance will be entirely in the liquid phase. This is supposedly what happens when rain forms from atmospheric water vapor that has been cooled to its dew point.

The reverse process should work the same way: starting with a temperature in the liquid region, nothing happens until we reach the vapor pressure line, at which point the liquid begins to change into vapor. At higher temperatures, only the vapor remains.

This is the theory. The fact is that a vapor will generally *not* condense to a liquid at the boiling point (also called the condensation point or dew point), and a liquid will generally not boil at its boiling point.

The reason for the discrepancy is that the vapor pressure, as we normally use the term and as it is depicted by the liquid-vapor line on the phase diagram, refers to the partial pressure of vapor in equilibrium with a liquid whose surface is reasonably flat, as it would be in a partially filled container. In a drop of liquid or in a bubble of vapor within a liquid, the surface of the liquid is not flat, but curved. For drops or bubbles that are of reasonable size, this does not make much difference, but these drops and bubbles must grow from smaller ones, and these from tinier ones still. Eventually, one gets down to the primordial drops and bubbles having only a few molecular dimensions, and it is here that we run into a problem: this is the problem of *nucleation.*

Vapor pressure of drops   The vapor pressure of a liquid is determined by the attractive forces that act over a 180° solid angle at the surface of a liquid. In a very small drop, the liquid surface is curved in such a way that each molecule experiences fewer nearest-neighbor attractions than is the case for the bulk liquid. The outermost molecules of the liquid are bound to the droplet less tightly, and the drop has a larger vapor pressure than does the bulk liquid. If the vapor pressure of the drop is greater than the partial pressure of vapor in the gas phase, the drop will evaporate. Thus it is highly unlikely that a droplet will ever form within a vapor as it is cooled.

If this is so, then why do vapors ever condense, and why does it rain? If you cool a vapor in a container, condensation takes place not within the vapor itself, but on the inner surface of the container. What happens here is that intermolecular attractions between the solid surface will cause vapor molecules to *adsorb* to the surface and stabilize the incipient drop until it grows to a size at which it can be self-sustaining. This is the origin of the condensation on the outside of a cool drink, or of the dew that appears on the grass.

In the region of the atmosphere where rain forms there are large numbers of solid particles, mostly of microscopic size. Some of these are particles of salt produced by evaporation of spray from the ocean

surface. There are particles of ammonium sulfate that are believed to be of biological origin, there is volcanic dust, and of course there is dust and smoke due to the activities of humans. These particles tend to adsorb water vapor, and some may even dissolve to form a droplet of concentrated solution. In either case, the vapor pressure of the water is reduced below its equilibrium value, thus stabilizing the aggregate until it can grow to self-sustaining size and become fog, rain, or snow.

This, by the way, is why fog is an irritant to the nose and throat; each fog droplet carries within it a particle of dust or (in air polluted by the burning of sulfur-containing fossil fuels) a droplet of sulfuric acid, which it efficiently deposits on your sensitive mucous membranes. If you own a car which is left outside on a foggy night, you may have noticed how dirty the windshield is in the morning.

Superheating and boiling of liquids   What is the difference between the evaporation and boiling of a liquid? When a liquid evaporates at a temperature below its boiling point, the molecules that enter the vapor phase do so directly from the surface. When a liquid boils, bubbles of vapor form in the interior of the liquid, and are propelled to the surface by their lower density (buoyancy). As they rise, the diminishing hydrostatic pressure causes the bubbles to expand, reducing their density (and increasing their buoyancy) even more.

A bubble, like a drop, must start small and grow larger, but there is a difficulty here that is similar to the one with bubbles. A bubble is a hole in a liquid; molecules at the liquid boundary are curved inward, so that they experience nearest-neighbor attractions over a solid angle *greater* than 180°. As a consequence, the vapor pressure of the liquid facing into a bubble is always *less* than that of the bulk liquid at the same temperature. When the bulk liquid is at its boiling point (that is, when its vapor pressure is 1 atm), the pressure of the vapor within the bubble will be less than 1 atm, so the bubble will tend to collapse. Also, since the bubble is formed within the liquid, the hydrostatic pressure of the overlaying liquid will add to this effect. For both of these reasons, a liquid will not boil until the temperature is raised *above* the boiling point, a phenomenon known as *superheating*.

In large quantities, superheated liquids can be very dangerous, because the introduction of an impurity (such as release of an air bubble from the container surface) or even a mechanical disturbance can trigger nucleation and cause boiling to occur suddenly and almost explosively. If you have had experience in an organic chemistry laboratory, you probably know this as *"bumping"*, and have been taught to take precautions against it.

The *melting point* of a solid is the temperature at which the escaping tendencies of molecules from the solid and from the liquid phases are the same. Since the vapor pressure is a measure of escaping tendency, it follows that the vapor pressures of the solid and liquid phases will be identical at the melting point.

Sublimation   Some solid have such high vapor pressures that heating leads to a substantial amount of direct vaporization even before the melting point is reached. This is the case for solid iodine, for example. I_2 melts at 115 °C and boils at 183 °C, is easily *sublimed* at temperatures around 100 °C. Even *ice* has a measurable vapor pressure near its freezing point, as evidenced by the tendency of snow to evaporate in cold dry weather.

There are other solids whose vapor pressure overtakes that of the liquid before melting can occur. Such substances sublime without melting; a common example is solid carbon dioxide ("Dry Ice") at 1 atm.

4   Phase maps

The temperatures and pressures at which a given phase of a substance is stable (that is, from which the molecules have the lowest escaping tendency) is an important property of any substance. Because both
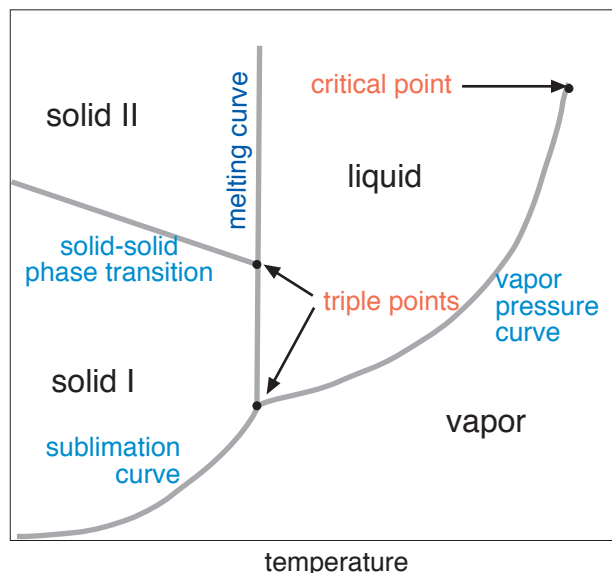
Figure 10: Schematic phase diagram for a one-component system

You can think of this phase diagram (for a hypothetical substance) as a "map" on which every point corresponds to some combination of (P, T). Reading a phase diagram becomes quite easy if you understand these rules:

1. The regions bounded by lines on the diagram are the values of pressure and temperature at which the corresponding phase is the only stable one.

2. The *lines* define all values of (P, T) at which *two phases* can coexist (i.e., be in equilibrium). The slope of the line depends on the difference in density of the two phases. This is why the lines bounding the vapor region are curved; the density of the gas is itself a sensitive function of the temperature, whereas the density of a condensed phase remains relatively constant. As a result the density difference, and hence the slope of the curve bounding the gaseous region, increases with temperature.

3. Where two lines *intersect*, *three* phases can coexist. This condition can only occur at a unique value of (P, T) known as the *triple point*. Since all three phases are in equilibrium at the triple point, their vapor pressures will be identical at this temperature.

4. The line that separates the liquid and vapor regions ends at the *critical point*. At temperatures and pressures greater than the critical temperature and pressure, no separate liquid phase exists.

the temperature and pressure are factors, it is customary to plot the regions of stability of the three phases in P-T coordinates.

The best way of making sure you understand a phase diagram is to imagine that you are starting at a certain temperature and pressure, and then change just one of these parameters, keeping the other constant. You will be traversing a horizontal or vertical path on the phase map, and there will be a change in state every time your path crosses a line. Of special importance is the horizontal path corresponding to a pressure of 1 atmosphere; this line defines the normal melting and boiling temperatures of a substance.

Because pressures can vary over an extremely wide range, it is common practice to draw phase diagrams with non-linear pressure coordinates. This enables us to visualize the phase behavior of a substance at both very low and very high pressures.
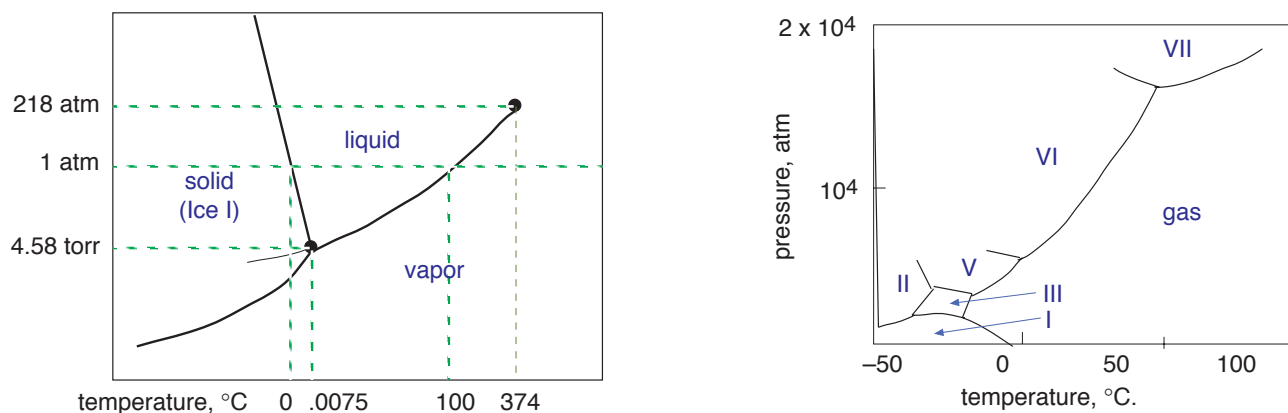
Phase diagram of water. Notice the following features of this very important phase diagram:

1. The slope of the line separating the solid and liquid regions is *positive;* this reflects the unusual property that the density of the liquid is greater than that of the solid, and it means that the melting point of ice decreases as the pressure increases. Thus if ice at $0\,°C$ is subjected to a high pressure, it will find itself above its melting point and it will melt. (Contrary to what is sometimes taught, however, this is not the reason that ice melts under the pressure of ice skates or skis, providing a lubricating film which makes these modes of transportation so enjoyable. The melting in these cases arises from frictional heating.)

2. The *triple point* of water is just $0.0075°$ above the freezing point; only at this temperature and pressure can all three phases of water coexist indefinitely.

3. Above the critical temperature of $374\,°C$, no separate liquid phase of water exists.

Figure 11: Phase diagrams for water at low and high pressures.
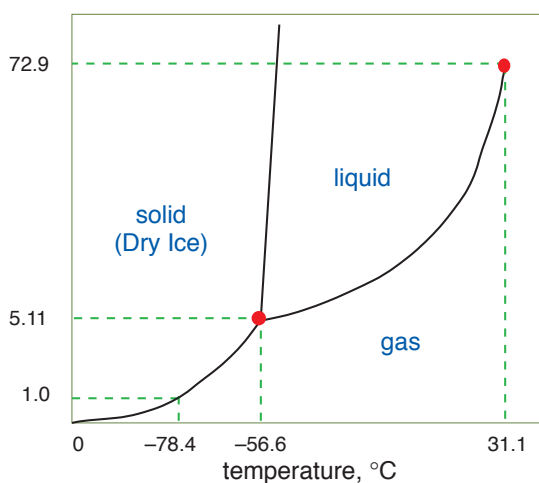

Dry Ice, solid **carbon dioxide**, is widely used as a refrigerant. The phase diagram shows why it is "dry". The triple point pressure is at 5.11 atm, so below this pressure, liquid CO_2 cannot exist; the solid can only sublime directly to vapor. CO_2 vapor at a partial pressure of 1 atm is in equilibrium with the solid at $195\,°K(-79\,°C)$; this is the *normal sublimation temperature* of carbon dioxide.

The surface temperature of Dry Ice will be slightly less than this, since the partial pressure of CO_2 in contact with the solid will usually be less than 1 atm. Notice also that the critical temperature of CO_2 is only $31\,°C$. This means that on a very warm day, the CO_2 in a fire extinguisher will be entirely vaporized; the vessel must therefore be strong enough to withstand a pressure of 73 atm.

Supercritical carbon dioxide (CO_2 at pressures above 73.9 atm) possesses the solvent properties of a liquid and the penetrating properties of a gas; one major use is to remove caffiene from coffee beans.

Figure 12: Phase diagram of carbon dioxide.
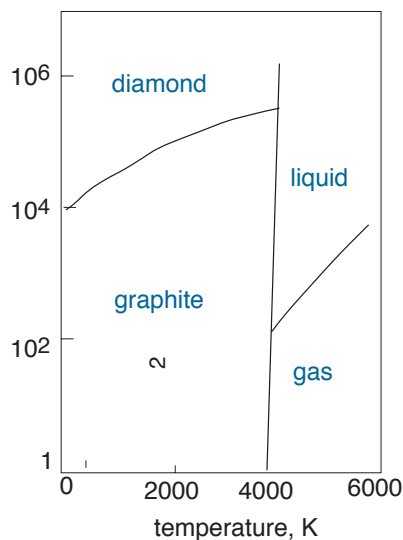
The phase diagram of **carbon** contains a new feature: there are *two* solid phases, diamond and graphite. Graphite is the stable solid at low pressures, but the rate at which diamond converts to carbon is immeasurably slow under ordinary environmental conditions; the diamond phase is said to be *metastable*. Diamond can only be formed at pressures above 10^4 atm, but to manufacture synthetic diamonds at a reasonable rate, a pressure of 200,000 atm and a temperature of about $4000\,°$K would be required. Since no apparatus can survive these conditions, the process is carried out commercially at 70,000 atm and $2300\,°$K in a solution of molten nickel, which also acts as a catalyst. Traces of Ni in the finished product serve to distinguish synthetic diamonds from natural ones.

Figure 13: Phase diagram of carbon

4.1 Phase studies at high pressures

We tend to think of the properties of substances as they exist at the low to moderate pressures encountered in everyday life, forgetting that most of the matter that makes up our world is situated inside the Earth, where pressures are orders of magnitude higher. Geochemists and planetary scientists need to know about the phase behavior of substances in order to develop useful models to test their theories about the structure and evolution of the Earth and of the solar system.

The study of matter at high pressures is not an easy task; the general techniques were pioneered by P.W. Bridgeman of Harvard University between 1901-1960. The more recent development of the diamond anvil cell has greatly extended the range of pressures attainable and the kinds of observations that can be made.

These studies have revealed that many molecular substances such as hydrogen and water change to solid phases having melting points well above room temperature at very high pressures; there is a solid form of ice that remains frozen even at $100\,°$C. At still higher pressures, many of these substances become metals. It is believed that much of the inner portion of the largest planets consists of hydrogen, possibly in a metallic state.

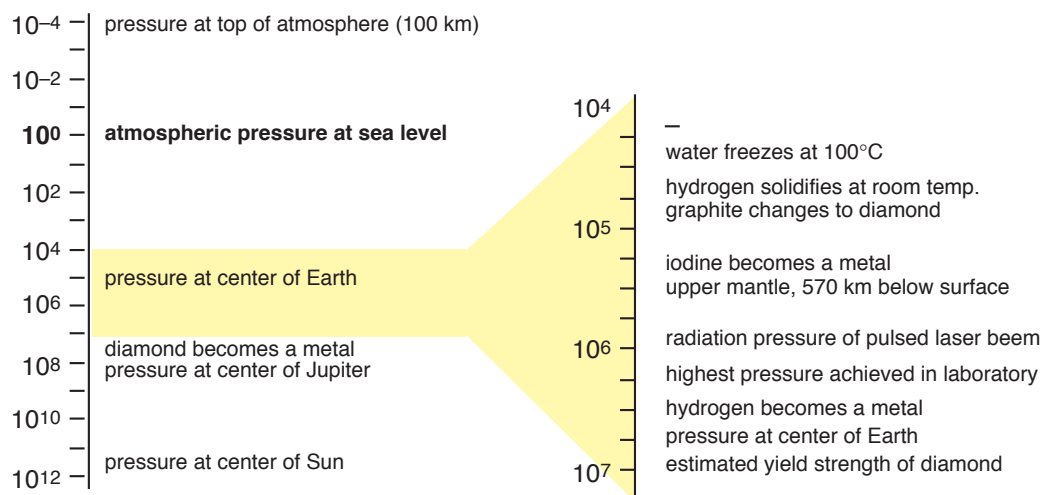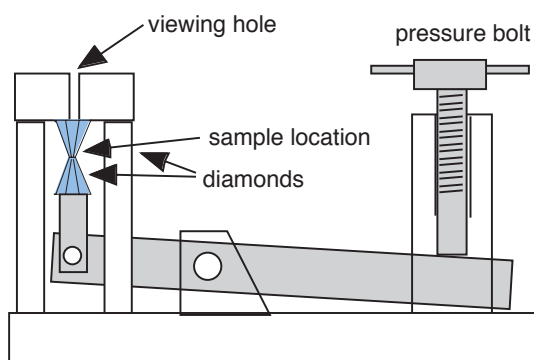|	
10^{-4} — pressure at top of atmosphere (100 km)	
10^{-2} —	
	10^4 —
10^0 — **atmospheric pressure at sea level**	— water freezes at 100°C
10^2 —	hydrogen solidifies at room temp. graphite changes to diamond
	10^5 —
10^4 —	iodine becomes a metal upper mantle, 570 km below surface
pressure at center of Earth	
10^6 —	
diamond becomes a metal	radiation pressure of pulsed laser beem
10^8 — pressure at center of Jupiter	10^6 — highest pressure achieved in laboratory
10^{10} —	hydrogen becomes a metal pressure at center of Earth
pressure at center of Sun	estimated yield strength of diamond
10^{12} —	10^7 —

Figure 14: Range of pressures encountered in nature.

The diamond anvil cell, developed in 1959, produces the highest static pressures available in the laboratory. Diamond is used because of its extreme hardness and its transparency, which allows the sample to be viewed through a microscope. Thrust generated by the pressure bolt is transmitted to the diamonds through a lever arm, piston, and rocker mounts. The cell itself is a hole in a thin sheet of metal placed between the diamond surfaces; the metal serves as a gasket to prevent the contents of the cell from being squeezed out. (See Scientific American, April 1984, pp 54-62.)

Figure 15: The diamond anvil cell.