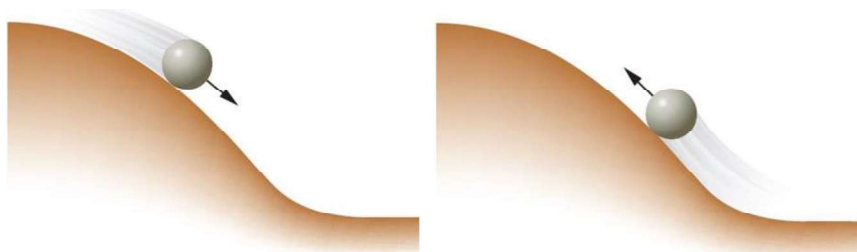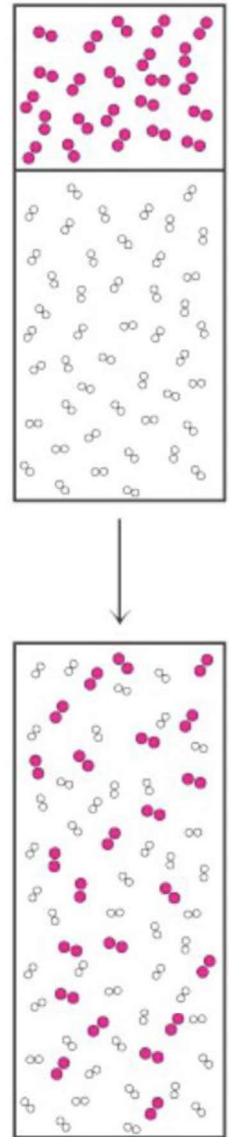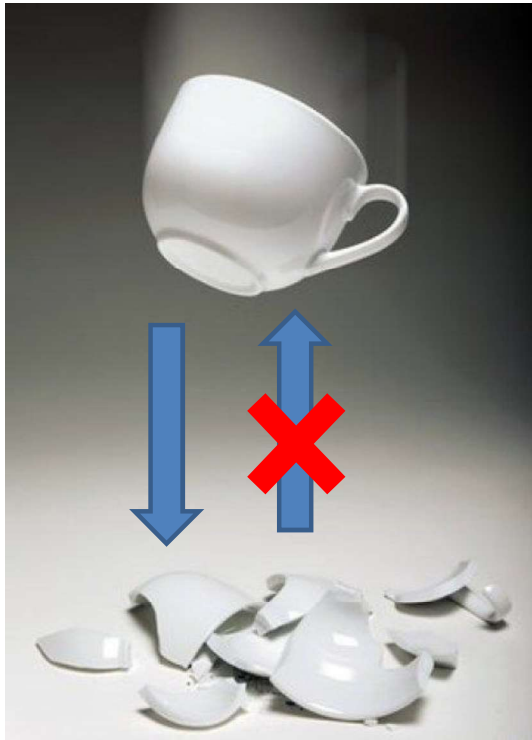# Irreversibility of Natural Processes

- A hot cup of coffee cools by virtue of heat transfer to the surroundings, but heat will not flow from the cooler surroundings to the hotter cup of coffee.

- Gasoline is used as a car drives up a hill, but the fuel level in the gasoline tank cannot be restored to its original level when the car coasts down the hill.

- Natural processes are irreversible, they have a certain direction.

Directionality of Natural Processes

- First law of thermodynamics states that the energy cannot be destroyed nor created, it can only be transferred or converted.

- It says nothing about the direction of energy transfer.

- The second law defines the direction which the process can take place.

- It also asserts that energy has quality as well as quantity.

Spontaneity

- A **spontaneous change** is a change that has a tendency to occur without work having to be done to bring it about. A spontaneous change has a natural tendency to occur.
  - Gas expands, the temperature of a hot object cools down in a cold environment, formation of water molecules from hydrogen and oxygen.
- A **non-spontaneous change** is a change that can be brought about only by doing work. A non-spontaneous change has no natural tendency to occur.
  - A gas can be compressed into a smaller volume by pushing in a piston, the temperature of a cool object can be raised by forcing an electric current through a heater attached to it, and water can be decomposed by the passage of an electric current.
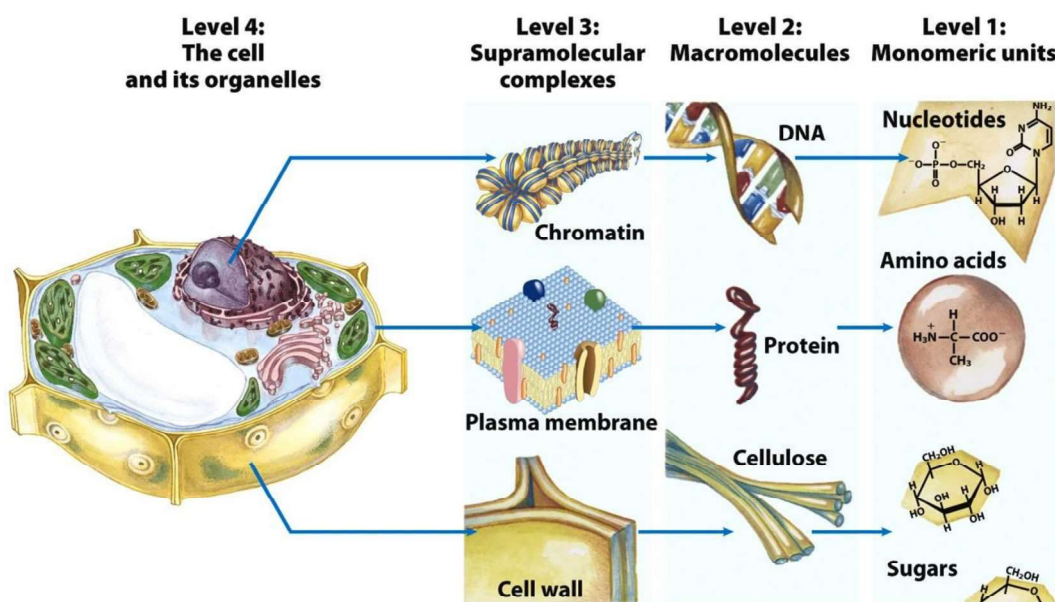
"SPONTANEOUS" REACTION
as time elapses
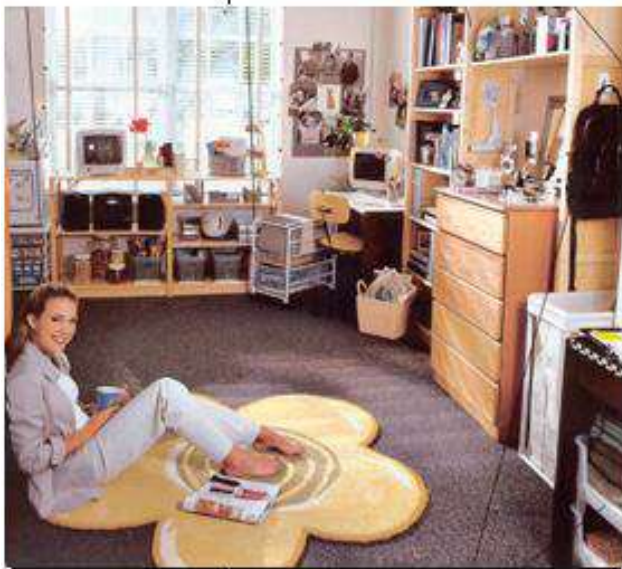
ORGANIZED EFFORT REQUIRING ENERGY INPUT

Is Life against the Second Law?

- Living organisms consist of collections of molecules much more highly organized than the surrounding materials from which they are constructed, and organisms maintain and produce order, seemingly contradictory to the second law of thermodynamics.

- In thermodynamics the term spontaneous has nothing to do with speed.
- Some spontaneous changes are very fast, such as the precipitation reaction that occurs when solutions of sodium chloride and silver nitrate are mixed.
- However, some spontaneous changes are so slow that there may be no observable change even after millions of years. For example, the decomposition of benzene into carbon and hydrogen is spontaneous although it takes millions of years.

$$W_{net} = Q_H - Q_L$$

$$Q_L = 0?$$
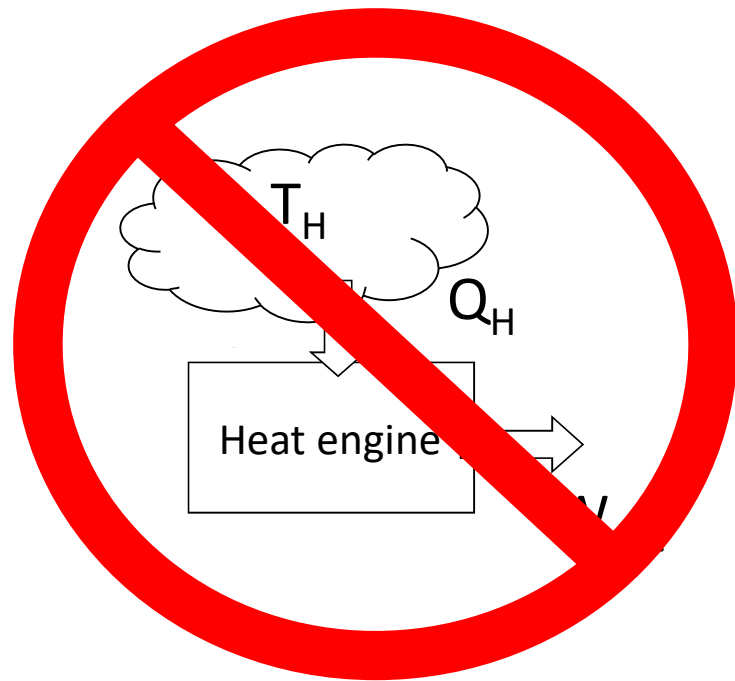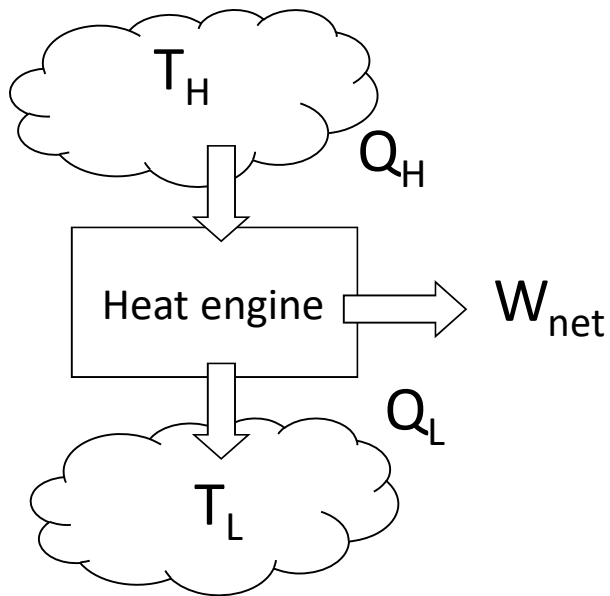
The Second Law of Thermodynamics: The Law of Entropy

- The second law of thermodynamics states that **the entropy of an isolated system tends to increase.**

Entropy

- *The apparent driving force of spontaneous change is the tendency of energy and matter to disperse*.

    1. Matter tends to become dispersed.

    2. Energy tends to become dispersed.

- The measure of the dispersal of energy or matter used in thermodynamics is called the **entropy**, *S*.

Low Disorder
Less Dispersed State
Low Entropy

Spontaneous
Favorable

High Disorder
More Dispersed State
High Entropy

Gas spreads to fill
space over time

Pile of bricks dropped from a lorry
Which arrangement is the more probable?

Disorder is
more probable
than order
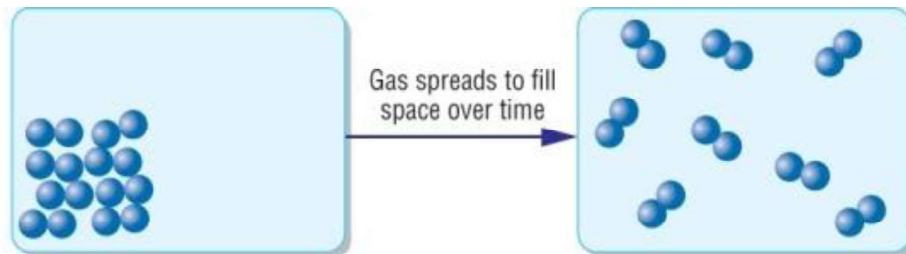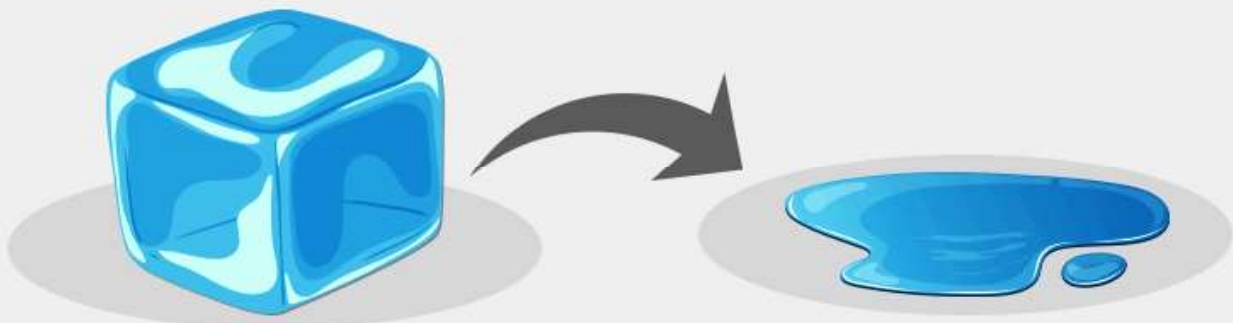
ENTHALPY

ENTHALPY IS DONATED BY 'H' REFERS TO THE MEASURE OF TOTAL HEAT CONTENT IN A THERMODYNAMIC SYSTEM UNDER CONSTANT PRESSURE.

ENTROPY

ENTROPY IS DENOTED BY 'S' REFERS TO THE MEASURE OF THE LEVEL OF DISORDER IN A THERMODYNAMIC SYSTEM.

- The entropy of an isolated system tends to increase.
- The "isolated system" may consist of a system in which we have a special interest (a beaker containing reagents) and that system's surroundings: the two components jointly form a little "universe" in the thermodynamic sense.

- The change in entropy of a system is equal to the energy transferred as heat to it *reversibly* divided by the temperature at which the transfer takes place.

$$\Delta S = \frac{q_{rev}}{T}$$

- There are three points we need to understand about the definition in entropy equation:

  1. the significance of the term "reversible,"
  2. why heat (not work) appears in the numerator,
  3. why temperature appears in the denominator.

$$\Delta S = \frac{q_{rev}}{T}$$

1

Reversible transfer of heat is smooth, careful, restrained transfer between two bodies at the same temperature. By making the transfer reversible, we ensure that there are no hot spots generated in the object that later disperse spontaneously and hence add to the entropy.

2

We make use of the random motion of molecules, whereas to transfer energy as work, we make use of orderly motion.
It should be plausible that the change in entropy—the change in the degree of dispersal of energy and matter—is proportional to the energy transfer that takes place by making use of random motion rather than orderly motion.

3

Finally, the presence of the temperature in the denominator in takes into account the randomness of motion that is already present.
If a given quantity of energy is transferred as heat to a hot object (one in which the atoms already undergo a significant amount of thermal motion), then the additional randomness of motion generated is less significant than if the same quantity of energy is transferred as heat to a cold object in which the atoms have less thermal motion.

- Calculate the change in entropy of a large mass of water upon the transfer of 100 kJ of heat reversibly at 0°C and 100°C.

At 0°C

$$\Delta S = \frac{q_{rev}}{T} = \frac{100 \times 10^3 \text{ J}}{273 \text{ K}} = +366 \text{ J K}^{-1}$$

At 100°C

$$\Delta S = \frac{100 \times 10^3 \text{ J}}{373 \text{ K}} = +268 \text{ J K}^{-1}$$

> ➤ We used a large mass of water to ensure that the temperature of the sample does not change as heat is transferred.
> ➤ The increase in entropy is greater at the lower temperature.
> ➤ Entropy is an extensive property. When we deal with molar entropy, an intensive property, the units will be joules per kelvin per mole (J / K mol).

Entropy as a state function

- The entropy is a state function, a property with a value that depends only on the present state of the system.

- The entropy is a measure of the current state of dispersal of energy and matter in the system, and how that change was achieved is not relevant to its current value.

- The implication of entropy being a state function is that a change in its value when a system undergoes a change of state is independent of how the change of state is brought about.

The temperature variation of Entropy

- The entropy of a sample is expected to increase as the temperature is raised from T_i to T_f, because the thermal motion is greater at the higher temperature.

- Provided the heat capacity is constant over the range of temperatures of interest:

$$\Delta S = C \ln \frac{T_f}{T_i}$$

  - where C is the heat capacity of the system; if the pressure is held constant during the heating, we use the constant-pressure heat capacity, C_p, and if the volume is held constant, we use the constant-volume heat capacity, C_v.

The temperature variation of Entropy

$$\Delta S = \frac{q_{rev}}{T}$$

- refers to the transfer of heat to a system at a temperature T. However, in general, the temperature changes as we heat a system.
- Suppose that we transfer only an infinitesimal energy, dq, to the system; then there is only an infinitesimal change in temperature and we introduce negligible error if we keep the temperature in the denominator of the eqn equal to T during that transfer.
- As a result, the entropy increases by an infinitesimal amount dS given by

- the heat capacity C is

$$dS = \frac{dq_{rev}}{T}$$

$$C = \frac{q}{\Delta T}$$

- where ΔT is macroscopic change in temperature. For the case of an infinitesimal change dT, we write

$$C = \frac{dq}{dT}$$

$$dq_{rev} = CdT$$

- Therefore,

$$dS = \frac{CdT}{T}$$

- The total change in entropy, S, when the temperature changes from T_i to T_f is the sum (integral) of all such infinitesimal terms:

$$\Delta S = \int_{T_i}^{T_f} \frac{CdT}{T}$$

- may be taken outside the integral and the latter evaluated as follows:

$$\Delta S = \int_{T_i}^{T_f} \frac{CdT}{T} \overset{\boxed{\text{Constant heat capacity}}}{=} C \int_{T_i}^{T_f} \frac{dT}{T} = C \ln \frac{T_f}{T_i}$$

When $T_f > T_i$, $T_f/T_i > 1$, which implies that the logarithm is positive, that $\Delta S > 0$, and therefore that the entropy increases. Note that the relation also shows a less obvious point, that the higher the heat capacity of the substance, the greater the change in entropy for a given rise in temperature.

- **Self-exercise:** Calculate the change in molar entropy when water vapor is heated from 160°C to 170°C at constant volume ($C_{V,m}$ 26.92 J / K mol).

The entropy change accompanying a phase transition

- The entropy of a substance is expected to increase when it melts and when it vaporizes because its molecules become more dispersed as it changes from solid to liquid and from liquid to vapor.

- Likewise, we expect the unfolding of a protein from a compact, active three-dimensional conformation to a more flexible conformation, to be accompanied by an increase of entropy because the polypeptide chain becomes less organized. **?**

The entropy of fusion

- The **entropy of fusion**, $\Delta_{fus}S$, the change of entropy per mole of substance, at the melting temperature, T_{fus}, is:

All enthalpies of fusion are positive (melting is endothermic: it requires heat), so all entropies of fusion are positive too: disorder increases on melting.

- The protein lysozyme, an enzyme that breaks down bacterial cell walls, unfolds at a transition temperature of 75.5°C, and the standard enthalpy of transition is 509 kJ/mol. Calculate the change in entropy accompanying denaturation of lyzozyme.

$$\Delta_{trs}S^{\ominus} = \frac{\Delta_{trs}H^{\ominus}(T_{trs})}{T_{trs}} = \frac{+509 \text{ kJ mol}^{-1}}{(273.15 + 75.5) \text{ K}} = +1.46 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

The entropy of vaporization

- The entropy of vaporization, $\Delta_{vap}S$, at the boiling temperature, T_b, of a liquid is related to its enthalpy of vaporization at that temperature by

$$\Delta_{vap}S = \frac{\Delta_{vap}H(T_b)}{T_b}$$

Because vaporization is endothermic for all substances, all entropies of vaporization are positive. The increase in entropy accompanying vaporization is in line with what we should expect when a compact liquid turns into a gas.

- Calculate the entropy of vaporization of water at 25°C.
  - First, we calculate the entropy change for heating liquid water from 25°C to 100°C:

    $$\Delta S_1 = C_{p,m}(H_2O, \text{liquid})\ln\frac{T_f}{T_i} = (75.29 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\frac{373 \text{ K}}{298 \text{ K}}$$
    $$= +16.9 \text{ J K}^{-1}\text{mol}^{-1}$$

  - Then, we calculate the entropy of transition at 100°C:

    $$\Delta S_2 = \frac{\Delta_{vap}H(T_b)}{T_b} = \frac{4.07 \times 10^4 \text{ J mol}^{-1}}{373 \text{ K}} = +1.09 \times 10^2 \text{ J K}^{-1} \text{ mol}^{-1}$$

  - Finally, we calculate the change in entropy for cooling the vapor from 100°C to 25°C:

    $$\Delta S_3 = C_{p,m}(H_2O, \text{vapor})\ln\frac{T_f}{T_i} = (33.58 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln\frac{298 \text{ K}}{373 \text{ K}}$$
    $$= -7.54 \text{ J K}^{-1} \text{ mol}^{-1}$$

  - The sum of the three entropy changes is the entropy of transition at 25°C:

    $$\Delta_{vap}S\ (298 \text{ K}) = \Delta S_1 + \Delta S_2 + \Delta S_3 = +118 \text{ J K}^{-1} \text{ mol}^{-1}$$

Entropy changes in the surroundings

- The entropy change of the surroundings in contact with the system at the temperature *T*:

$$\Delta S_{sur} = \frac{q_{sur}}{T}$$

  - The pressure of the surroundings is constant since it is very large.

- The metabolic rate is the rate at which an organism expends energy from the oxidation of food. At rest, organisms still consume energy at the so-called *basal metabolic rate*. Even a resting human being heats the surroundings, typically at a rate of 100 J/s. Estimate the entropy a resting person generates in the surroundings in the course of a day at 20°C.

  – The energy transferred by heating the surroundings in the course of a day is:

  $$q_{sur} = (86\ 400\ \text{s}) \times (100\ \text{J s}^{-1}) = 86\ 400 \times 100\ \text{J}$$

  – The increase in entropy of the surroundings is therefore

  $$\Delta S_{sur} = \frac{q_{sur}}{T} = \frac{86\ 400 \times 100\ \text{J}}{293\ \text{K}} = +2.95 \times 10^4\ \text{J K}^{-1}$$

  Just to stay alive, each person on the planet contributes about 30 kJ/K each day to the entropy of their surroundings. The use of transport, machinery, and communications generates far more in addition.

- **Self-exercise:** Suppose a small reptile operates at 0.50 J s1. What entropy does it generate in the course of a day in the water in the lake that it inhabits, where the temperature is 15°C?

- The equation is expressed in terms of the energy supplied to the *surroundings* as heat, q_{sur}.
- Normally, we have information about the heat supplied to or escaping from the system, q. The two quantities are related by $q_{sur} = -q$.
- For instance, if $q = 100$ J, an influx of 100 J, then $q_{sur} = -100$ J, indicating that the surroundings have lost that 100 J.
- Therefore, at this stage we can replace q_{sur} in eqn by $-q$ and write:

$$\Delta S_{sur} = -\frac{q}{T}$$

- If the chemical reaction or a phase transition takes place at constant pressure, we can replace q with the change in enthalpy of the system:

$$\text{For a process at constant pressure: } \Delta S_{sur} = -\frac{\Delta H}{T}$$

The Third Law of Thermodynamics

- The entropies of all perfectly crystalline substances are zero at $T = 0$.

- $S(0) = 0$ *for all perfectly ordered crystalline materials.*

- The entropy of a substance under a standard pressure (1 bar) in its standard state at the temperature of interest is called the **standard molar entropy**, $S_m^{\ominus}$.

Third-Law Entropy

- The **Third-Law entropy** at any temperature, S(T), is equal to the area under the graph of C/T between T = 0 and the temperature T.
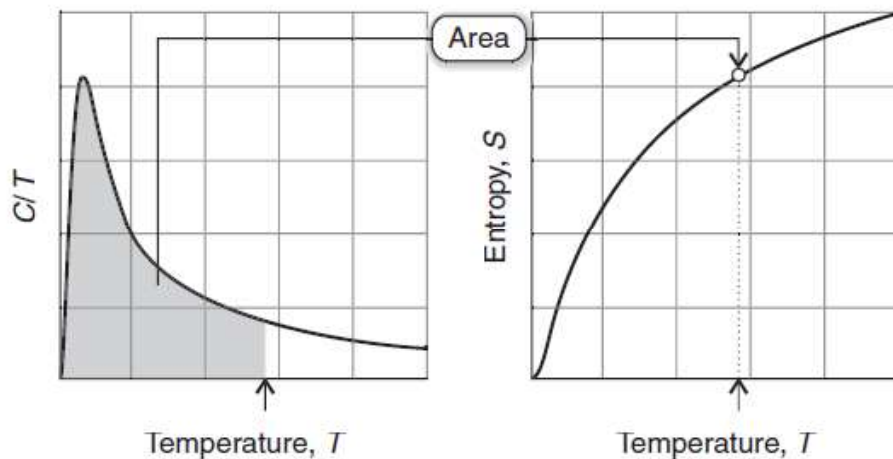
- If there are any phase transitions (for example, melting) in the temperature range of interest, then the entropy of each transition at the transition temperature is calculated like that in:

$$\text{At the melting temperature: } \Delta_{fus}S = \frac{\Delta_{fus}H(T_{fus})}{T_{fus}}$$

- and its contribution added to the contributions from each of the phases, as shown in figure:
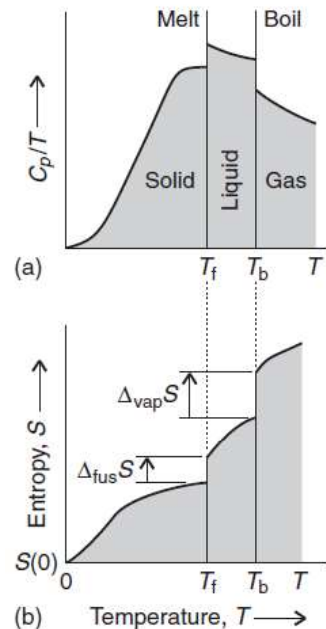
Table 2.2 Standard molar entropies of some substances at 298.15 K*

Substance	$S_m^{\ominus}/(J\ K^{-1}\ mol^{-1})$
Gases	
Ammonia, NH_3	192.5
Carbon dioxide, CO_2	213.7
Hydrogen, H_2	130.7
Nitrogen, N_2	191.6
Oxygen, O_2	205.1
Water vapor, H_2O	188.8
Liquids	
Acetic acid, CH_3COOH	159.8
Ethanol, CH_3CH_2OH	160.7
Water, H_2O	69.9
Solids	
Calcium carbonate, $CaCO_3$	92.9
Diamond, C	2.4
Glycine, $CH_2(NH_2)COOH$	103.5
Graphite, C	5.7
Sodium chloride, NaCl	72.1
Sucrose, $C_{12}H_{22}O_{11}$	360.2
Urea, $CO(NH_2)_2$	104.60

➤ All standard molar entropies are positive, because raising the temperature of a sample above T 0 invariably increases its entropy above the value $S(0) = 0$.

➤ Another feature is that the standard molar entropy of diamond (2.4 J / K mol) is lower than that of graphite (5.7 J / K mol).

➤ This difference is consistent with the atoms being linked less rigidly in graphite than in diamond and their thermal motion being correspondingly greater.

➤ The standard molar entropies of ice, water, and water vapor at 25°C are, respectively, 45, 70, and 189 J / K mol, and the increase in values corresponds to the increasing dispersal of matter and energy on going from a solid to a liquid and then to a gas.

The standard reaction entropy

- When there is a net formation of a gas in a reaction, as in a combustion, we can usually anticipate that the entropy increases.
- When there is a net consumption of gas, as in the fixation of N2 by certain microorganisms, it is usually safe to predict that the entropy decreases.
- However, for a quantitative value of the change in entropy and to predict the sign of the change when no gases are involved we need to calculate the standard reaction entropy using the standard molar enthalpies of reactants and products.
- The difference in molar entropy between the products and the reactants in their standard states is called the **standard reaction entropy**, $\Delta_r S^{\ominus}$ and expressed as:

$$\Delta_r S^{\ominus} = \sum \nu S_m{}^{\ominus}(\text{products}) - \sum \nu S_m{}^{\ominus}(\text{reactants})$$

- The enzyme carbonic anhydrase catalyzes the hydration of CO_2 gas in red blood cells. Calculate the standard reaction entropy.

Since the gas is consumed in the reaction we predict the sign of the entropy as negative.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$
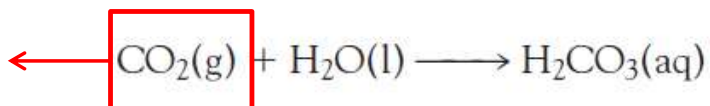
$$\Delta_r S^\ominus = S_m^\ominus(H_2CO_3, aq) - \{S_m^\ominus(CO_2, g) + S_m^\ominus(H_2O, l)\}$$
$$= (187.4 \text{ J K}^{-1} \text{ mol}^{-1})$$
$$- \{(213.74 \text{ J K}^{-1} \text{ mol}^{-1}) + (69.91 \text{ J K}^{-1} \text{ mol}^{-1})\}$$
$$= -96.3 \text{ J K}^{-1} \text{ mol}^{-1} \quad \blacksquare$$

- **Self exercise:** Calculate the entropy change associated with the complete oxidation of solid sucrose, $C_{12}H_{22}O_{11}(s)$, by O_2 gas to CO_2 gas and liquid H_2O at 25°C.

The Spontaneity of Reactions

- A process may be spontaneous even though the entropy change that accompanies it is negative.
- Consider the binding of oxidized nicotinamide adenine dinucleotide (NAD), an important electron carrier in metabolism, to the enzyme lactate dehydrogenase, which plays a role in catabolism and anabolism of carbohydrates.

Pyruvate → Lactic Acid (Lactate Dehydrogenase, NADH + H⁺ → NAD⁺)
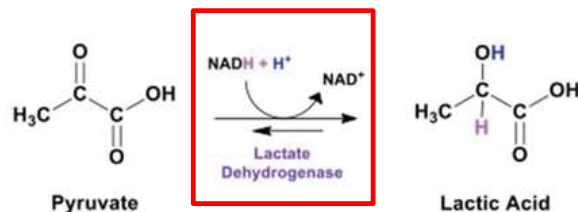
- Experiments show that $\Delta_r S^\ominus$ = - 16.8 J / K mol for binding at 25°C and pH 7.0.
- The negative sign of the entropy change is expected because the association of two reactants gives rise to a more compact structure.
- The reaction results in less dispersal of matter, yet it is spontaneous!

- It is essential to consider the entropy of both the system and its surroundings when deciding whether a process is spontaneous or not.
- The reduction in entropy by 16.8 J / K mol relates only to the system, the reaction mixture.
- To apply the Second Law correctly, we need to calculate the total entropy, the sum of the changes in the system and the surroundings that jointly compose the "isolated system" referred to in the Second Law.
- It may well be the case that the entropy of the system decreases when a change takes place, but there may be a more than compensating increase in entropy of the surroundings, so that overall entropy change is positive.
- The opposite may also be true: a large decrease in entropy of the surroundings may occur when the entropy of the system increases.

- To calculate the entropy change in the surroundings when a reaction takes place at constant pressure, we use ΔH in that expression as the reaction enthalpy.
- For example, for the formation of the NAD-enzyme complex, discussed above, with $\Delta_r H^{\ominus} = - 24.2$ kJ/mol, the change in entropy of the surroundings (which are maintained at 25°C, the same temperature as the reaction mixture) is

$$\Delta_r S_{sur} = -\frac{\Delta_r H}{T} = -\frac{(-24.2 \text{ kJ mol}^{-1})}{298 \text{ K}} = +81.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

- Then the total entropy change is:

$$\Delta_r S_{total} = (-16.8 \text{ J K}^{-1} \text{ mol}^{-1}) + (81.2 \text{ J K}^{-1} \text{ mol}^{-1}) = +4.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

the reaction is spontaneous.

Gibbs Energy

- One of the problems with entropy calculations is already apparent: we have to work out two entropy changes, the change in the system and the change in the surroundings, and then consider the sign of their sum.

- The great American theoretician J.W. Gibbs (1839–1903), who laid the foundations of chemical thermodynamics toward the end of the nineteenth century, discovered how to combine the two calculations into one.

- The combination of the two procedures in fact turns out to be of much greater relevance than just saving a little labor.

Gibbs Energy

- The total entropy change that accompanies a process is:

$$\Delta S_{total} = \Delta S + \Delta S_{sur}$$

- At constant pressure and temperature:

$$\Delta S_{total} = \Delta S - \frac{\Delta H}{T}$$

- the **Gibbs energy**, *G*, is defined as:

$$G = H - TS$$

- A change in Gibbs energy, *G*, at constant temperature arises from changes in enthalpy and entropy and is

$$\Delta G = \Delta H - T\Delta S$$

- At constant pressure and temperature Gibbs Energy is:

$$\Delta G = -T\Delta S_{total}$$

- The difference in sign between ΔG and ΔS_{total} implies that the condition for a process being spontaneous changes from $\Delta S_{total} > 0$ in terms of the total entropy (which is universally true) to $\Delta G < 0$ in terms of the Gibbs energy (for processes occurring at constant temperature and pressure).

- Thus, in a spontaneous change at constant temperature and pressure, the Gibbs energy decreases.

- A system tends to fall toward lower Gibbs energy.
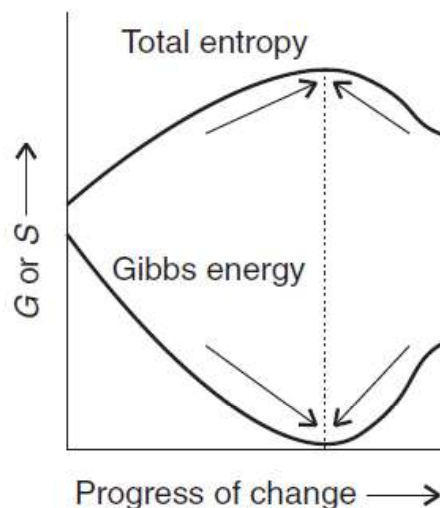
Spontaneity of Life

- Every chemical reaction that is spontaneous under conditions of constant temperature and pressure, including those that drive the processes of growth, learning, and reproduction, is a reaction that changes in the direction of lower Gibbs energy, or—another way of expressing the same thing—results in the overall entropy of the system and its surroundings becoming greater.

- With these ideas in mind, it is easy to explain why life, which can be regarded as a collection of biological processes, proceeds in accord with the Second Law of thermodynamics.

- It is not difficult to imagine conditions in the cell that may render spontaneous many of the reactions of catabolism. After all, the breakdown of large molecules, such as sugars and lipids, into smaller molecules leads to the dispersal of matter in the cell.

- Energy is also dispersed, as it is released upon reorganization of bonds in foods.

Gibbs free energy of Life

- More difficult to rationalize is life's requirement of organization of a very large number of molecules into biological cells, which in turn assemble into organisms.

- The entropy of the system—the organism—is very low because matter becomes less dispersed when molecules assemble to form cells, tissues, organs, and so on. However, the lowering of the system's entropy comes at the expense of an increase in the entropy of the surroundings.

- Cells grow by converting energy from the Sun or oxidation of foods partially into work. The remaining energy is released as heat into the surroundings, so $q_{sur} > 0$ and $\Delta S_{sur} > 0$.

- As with any process, life is spontaneous and organisms thrive as long as the increase in the entropy of the organism's environment compensates for decreases in the entropy arising from the assembly of the organism. Alternatively, we may say that $\Delta G < 0$ for the overall sum of physical and chemical changes that we call life.

$$\Delta S_{sys} + \Delta S_{surr} > 0$$
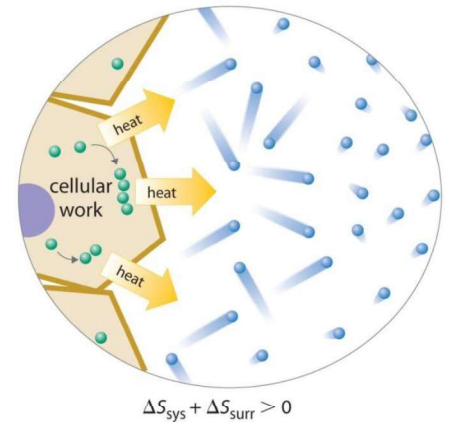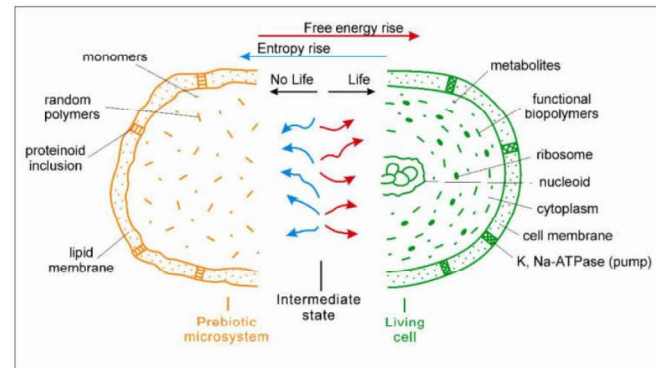
$$\Delta G_{life} < 0$$

Work and Gibbs Energy Relationship

- An important feature of the Gibbs energy is that the value of ΔG for a process gives the maximum non-expansion work that can be extracted from the process at constant temperature and pressure.

- By **non-expansion work**, w', we mean any work other than that arising from the expansion of the system.

- It may include electrical work, if the process takes place inside an electrochemical or biological cell, or other kinds of mechanical work, such as the winding of a spring or the contraction of a muscle.

- The relation between the infinitesimal change in Gibbs energy, dG, accompanying a process and the maximum amount of non-expansion work that the process can do, dw'.

$$\text{At constant temperature: } dG = dH - TdS$$

- The change in enthalpy at constant pressure is:

$$dH = dU + pdV$$

- *Thus:*

$$\text{At constant temperature and pressure: } dG = dU + pdV - TdS$$

- Then we replace dU in terms of infinitesimal contributions from work and heat:

$$dU = dw + dq$$

$$dG = dw + dq + pdV - TdS$$

- The work done on the system consists of expansion work, $p_{ex}dV$, and nonexpansion work, dw'. Therefore,

$$dG = -p_{ex}dV + dw' + dq + pdV - TdS$$

- For reversible expansion work, $p = p_{ex}$ and because the transfer of energy as heat is also reversible, we can replace dq by TdS:

$$\text{At constant temperature and pressure, for a reversible process: } dG = dw_{rev}'$$

- Maximum work is done during a reversible change:

$$\text{At constant temperature and pressure: } dG = dw_{max}' \qquad \Delta G = w_{max}'$$

- Suppose a certain small bird has a mass of 30 g. What is the minimum mass of glucose that it must consume to fly up to a branch 10 m above the ground? The change in Gibbs energy that accompanies the oxidation of 1.0 mol $C_6H_{12}O_6(s)$ to carbon dioxide gas and liquid water at 25°C is 2828 kJ.

  - The non-expansion work to be done is $w' = mgh$

$$w' = (30 \times 10^{-3}\ kg) \times (9.81\ m\ s^{-2}) \times (10\ m) = 3.0 \times 9.81 \times 1.0 \times 10^{-1}\ J$$

- The amount, n, of glucose molecules required for oxidation to give a change in Gibbs energy of this value given that 1 mol provides 2828 kJ is

$$n = \frac{3.0 \times 9.81 \times 1.0 \times 10^{-1}\ J}{2.828 \times 10^6\ J\ mol^{-1}} = \frac{3.0 \times 9.81 \times 1.0 \times 10^{-7}}{2.828}\ mol$$

- Therefore, because the molar mass, M, of glucose is 180 g/mol, the mass, m, of glucose that must be oxidized is

$$m = nM = \left(\frac{3.0 \times 9.81 \times 1.0 \times 10^{-7}}{2.828}\ mol \right) \times (180\ g\ mol^{-1})$$
$$= 1.9 \times 10^{-4}\ g$$

That is, the bird must consume at least 0.19 mg of glucose for the mechanical effort (and more if it thinks about it).

- The great importance of the Gibbs energy in chemistry is becoming apparent.

- It is a measure of the non-expansion work resources of chemical reactions: if we know ΔG, then we know the maximum non-expansion work that we can obtain by harnessing the reaction in some way.

- In some cases, the non-expansion work is extracted as electrical energy. This is the case when electrons are transferred across cell membranes in some key reactions of photosynthesis and respiration.
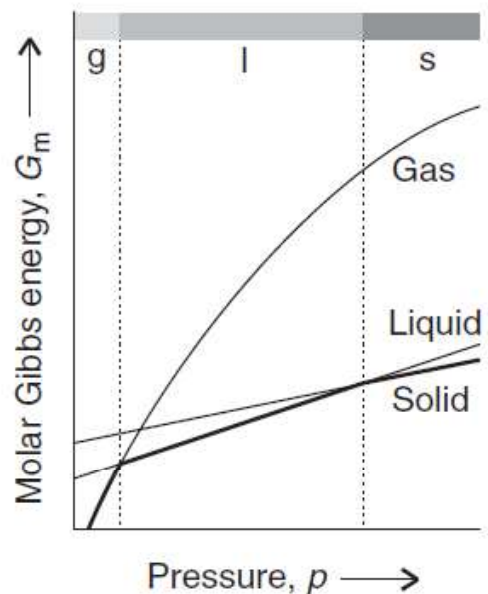
The variation of Gibbs Energy with pressure

- When the temperature is held constant and the pressure is changed by a small amount p, the molar Gibbs energy of a substance changes by

$$\Delta G_m = V_m \Delta p$$

- where Vm is the molar volume of the substance. This expression is valid when the molar volume is constant in the pressure range of interest.
- Acc. To this equation, because all molar volumes are positive, *the molar Gibbs energy increases* ($\Delta G_m > 0$) *when the pressure increases* ($\Delta p > 0$).
- We also see that, for a given change in pressure, the resulting change in molar Gibbs energy is greatest for substances with large molar volumes.
- Therefore, because the molar volume of a gas is much larger than that of a condensed phase (a liquid or a solid), the dependence of G_m on p is much greater for a gas than for a condensed phase.
- For most substances (water is an important exception), the molar volume of the liquid phase is greater than that of the solid phase. Therefore, for most substances, the slope of a graph of G_m against p is greater for a liquid than for a solid.

- When we increase the pressure on a substance, the molar Gibbs energy of the gas phase rises above that of the liquid, then the molar Gibbs energy of the liquid rises above that of the solid.
- Because the system has a tendency to convert into the state of lowest molar Gibbs energy, the graphs show that at low pressures the gas phase is the most stable, then at higher pressures the liquid phase becomes the most stable, followed by solid phase.
- In other words, under pressure the substance condenses to a liquid, and then further pressure can resultin the formation of a solid.

The variation of Gibbs energy with temperature

- For small changes in temperature, the change in molar Gibbs energy at constant pressure is

$$\Delta G_m = -S_m \Delta T$$

- where $\Delta G_m = G_m(T_f) - G_m(T_i)$ and $\Delta T = T_f - T_i$.
- This expression is valid provided the entropy of the substance is unchanged over the range of temperatures of interest.
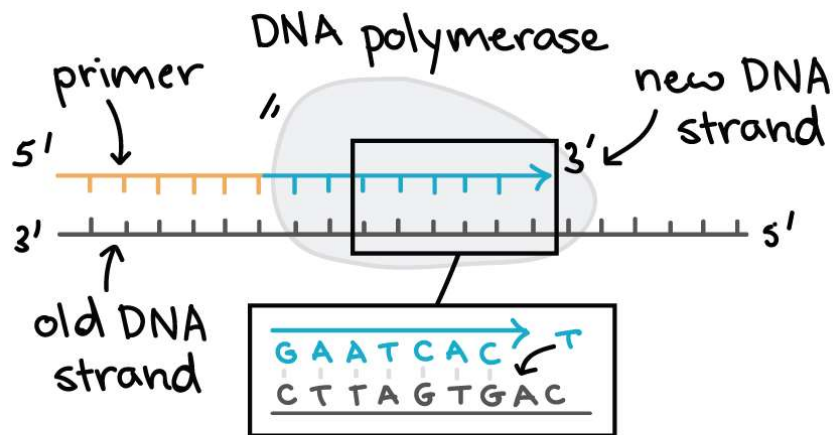
- Because molar entropy is positive, *an increase in temperature ($\Delta T > 0$) results in a decrease in G_m ($\Delta G_m < 0$).*
- We see that for a given change of temperature, the change in molar Gibbs energy is proportional to the molar entropy.
- For a given substance, matter and energy are more dispersed in the gas phase than in a condensed phase, so the molar entropy of the gas phase is greater than that for a condensed phase.
- It follows that the molar Gibbs energy falls more steeply with temperature for a gas than for a condensed phase.
- The molar entropy of the liquid phase of a substance is greater than that of its solid phase, so the slope is least steep for a solid.
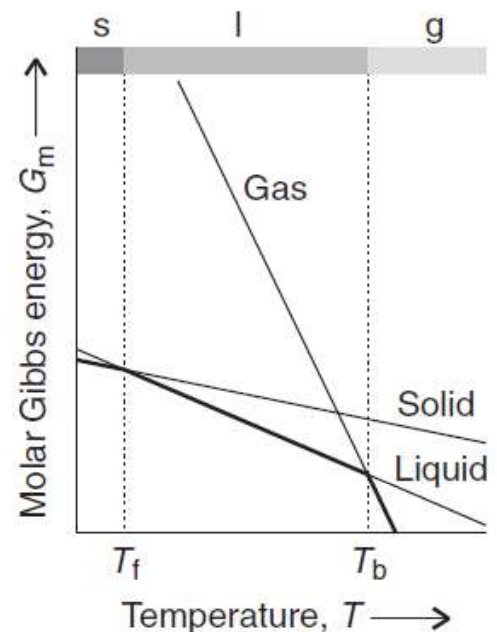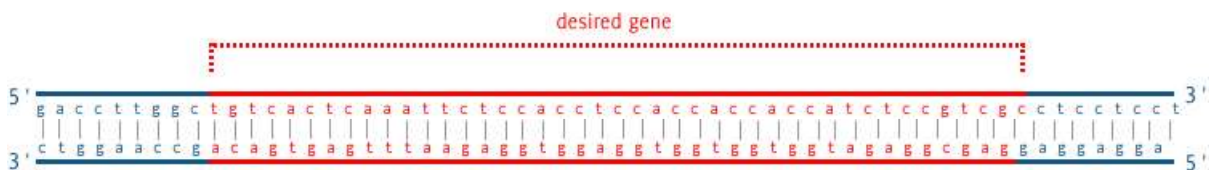
- This figure also reveals the thermodynamic reason why substances melt and vaporize as the temperature is raised.
- At low temperatures, the solid phase has the lowest molar Gibbs energy and is therefore the most stable.
- However, as the temperature is raised, the molar Gibbs energy of the liquid phase falls below that of the solid phase, and the substance melts.
- At even higher temperatures, the molar Gibbs energy of the gas phase plunges down below that of the liquid phase, and the gas becomes the most stable phase. In other words, above a certain temperature, then liquid vaporizes to a gas.
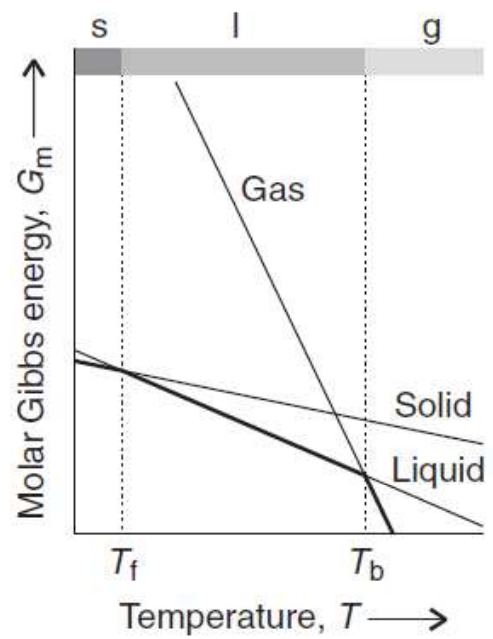
- The **transition temperature** between two phases, such as between liquid and solid or between conformations of a protein, is the temperature, at a given pressure, at which the molar Gibbs energies of the two phases are equal.

- For example, at 1 atm, the transition temperature for ice and liquid water is 0°C.

- At the transition temperature itself, the molar Gibbs energies of the two phases are identical and there is no tendency for either phase to change into the other. At this temperature, therefore, the two phases are in equilibrium.

- At 1 atm, ice and liquid water are in equilibrium at 0°C.

## Find the sequences just before and after the desired gene

desired gene

```
5'  g a c c t t g g c  t g t c a c t c a a a t t c t c c a c c t c c a c c a c c a c c a t c t c c g t c g c  c t c c t c c t  3'
    | | | | | | | | |  | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |  | | | | | | | |
3'  c t g g a a c c g  a c a g t g a g t t t a a g a g g t g g a g g t g g t g g t g g t a g a g g c g a g  g a g g a g g a  5'
```

Anneal primers to isolate that gene during extension

```
    g a c c t t g g c  t g t c a c t c a a a t t c t c c a c c t c c a c c a c c a c c a t c t c c g t c g c  c t c c t c c t
                                                                                                            | | | | | | | |
                                                                                                  3'  g a g g a g g a  5'
```

primer 1   extension of gene   ←   extension of gene   primer 2

```
5'  g a c c t t g g c  3'
    | | | | | | | | |
    c t g g a a c c g  a c a g t g a g t t t a a g a g g t g g a g g t g g t g g t g g t a g a g g c g a g  g a g g a g g a
```

Phase Diagram

- The **phase diagram** of a substance is a map showing the conditions of temperature and pressure at which its various phases are thermodynamically most stable.

- For example, at point A in the illustration, the vapor phase of the substance is thermodynamically the most stable, but at C the liquid phase is the most stable.

- The boundaries between regions in a phase diagram, which are called **phase boundaries**, show the values of p and T at which the two neighboring phases are in equilibrium.

- For example, if the system is arranged to have a pressure and temperature represented by point B, then the liquid and its vapor are in equilibrium (like liquid water and water vapor at 1 atm and 100°C).

- If the temperature is reduced at constant pressure, the system moves to point C, where the liquid is stable (like water at 1 atm and at temperatures between 0°C and 100°C).

- If the temperature is reduced still further to D, then the solid and the liquid phases are in equilibrium (like ice and water at 1 atm and 0°C).

- A further reduction in temperature takes the system into the region where the solid is the stable phase.
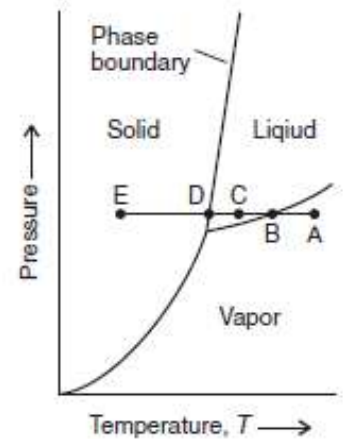
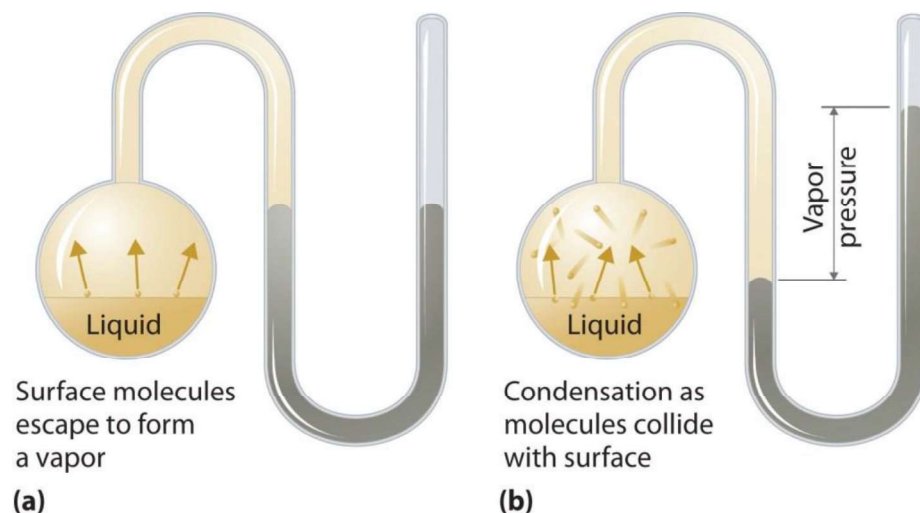# Thermal analysis determined the transition temperatures

- **Thermal analysis** takes advantage of the heat released during a transition.

- In a typical thermal analysis experiment, a sample is allowed to cool and its temperature is monitored.

- When the transition occurs, energy is released as heat and the cooling stops until the transition is complete.

- The transition temperature is obvious from the shape of the graph and is used to mark a point on the phase diagram.
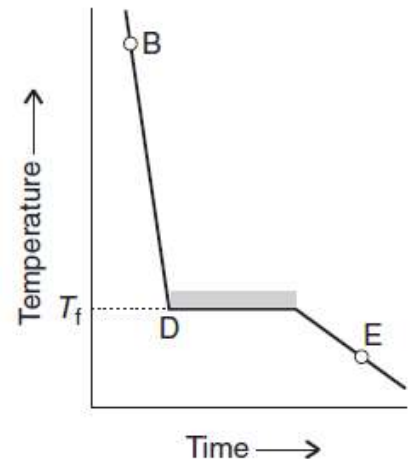
- Any point lying on a phase boundary represents a pressure and temperature at which there is a "dynamic equilibrium" between the two adjacent phases.
- A state of **dynamic equilibrium** is one in which a reverse process is taking place at the same rate as the forward process.
- Although there may be a great deal of activity at a molecular level, there is no net change in the bulk properties or appearance of the sample.
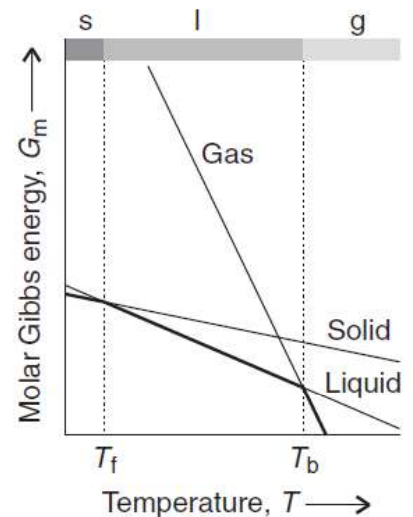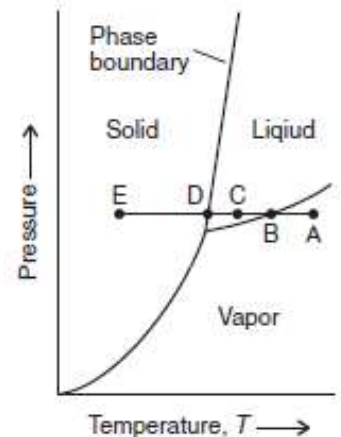
- The pressure of the vapor in equilibrium with its condensed phase is called the **vapor pressure** of the substance.

- Vapor pressure increases with temperature because, as the temperature is raised, more molecules have sufficient energy to leave their neighbors in the liquid.

- The liquid-vapor boundary in a phase diagram is a plot of the vapor pressure against temperature.

Liquid

Surface molecules escape to form a vapor

(a)

Vapor pressure

Liquid

Condensation as molecules collide with surface

(b)

- Now suppose we have a liquid in a cylinder fitted with a piston.
- If we apply a pressure greater than the vapor pressure of the liquid, the vapor is eliminated, the piston rests on the surface of the liquid, and the system moves to one of the points in the "liquid" region of the phase diagram. Only a single phase is present.
- If instead we reduce the pressure on the system to a value below the vapor pressure, the system moves to one of the points in the "vapor" region of the diagram. Reducing the pressure will involve pulling out the piston a long way so that all the liquid evaporates; while any liquid is present, the pressure in the system remains constant at the vapor pressure of the liquid.
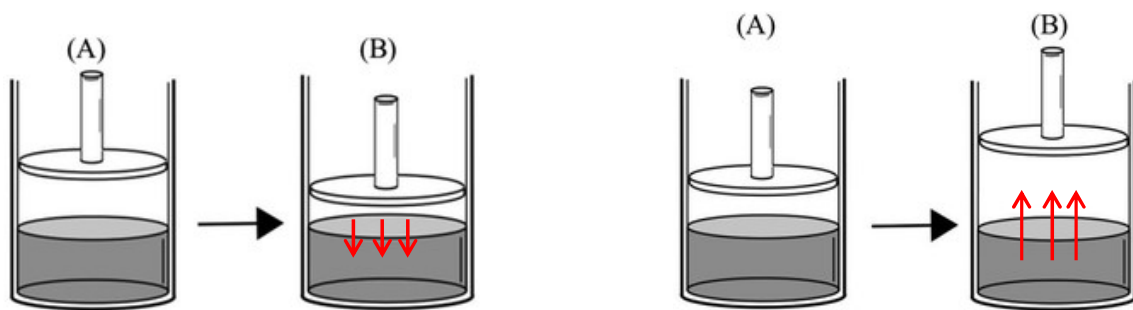
- What would be observed when a pressure of 50 kPa is applied to a sample of water in equilibrium with its vapor at 25°C, when its vapor pressure is 3.167 kPa?
 - The sample condenses entirely to liquid.
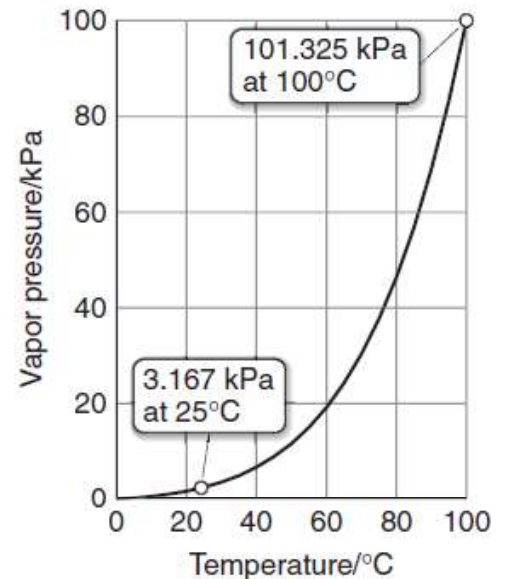
The experimental variation of the vapor pressure of water with temperature.

- We have seen that as the temperature of a liquid is raised, its vapor pressure increases.
- First, consider what we would observe when we heat a liquid in an open vessel. At a certain temperature, the vapor pressure becomes equal to the external pressure.
- At this temperature, the vapor can drive back the surrounding atmosphere and expand indefinitely. Moreover, because there is no constraint on expansion, bubbles of vapor can form throughout the body of the liquid, a condition known as **boiling**.
- The temperature at which the vapor pressure of a liquid is equal to the external pressure is called the **boiling temperature**.
- When the external pressure is 1 atm, the boiling temperature is called the **normal boiling point**, T_b.
- It follows that we can predict the normal boiling point of a liquid by noting the temperature on the phase diagram at which its vapor pressure is 1 atm.

- Now consider what happens when we heat the liquid in a closed vessel.
- Because the vapor cannot escape, its density increases as the vapor pressure rises and in due course the density of the vapor becomes equal to that of the remaining liquid.
- At this stage the surface between the two phases disappears.
- The temperature at which the surface disappears is the **critical temperature**, T_c.
- The vapor pressure at the critical temperature is called the **critical pressure**, p_c, and the critical temperature and critical pressure together identify the **critical point** of the substance.
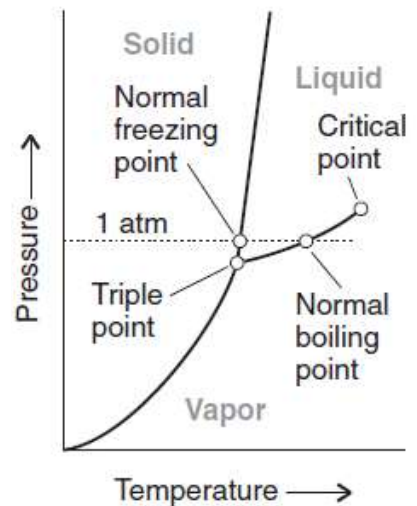
Increasing temperature ⟶
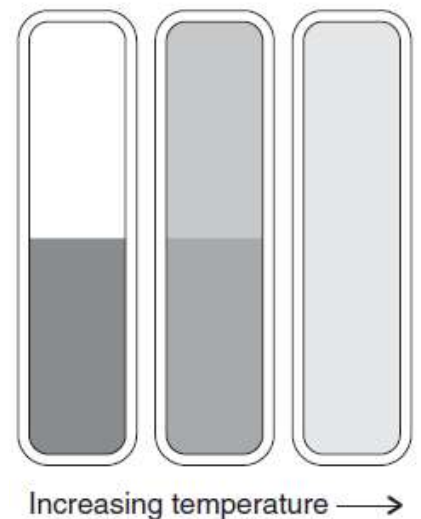
- If we exert pressure on a sample that is above its critical temperature, we produce a denser fluid. However, no surface appears to separate the two parts of the sample and a single uniform phase, a **supercritical fluid**, continues to fill the container.
- That is, we have to conclude that *a liquid cannot be produced by the application of pressure to a substance if it is at or above its critical temperature*.
- That is why the liquid-vapor boundary in a phase diagram terminates at the critical point.
- A supercritical fluid is not a true liquid, but it behaves like a liquid in many respects—it has a density similar to that of a liquid and can act as a solvent.
- For example, supercritical carbon dioxide is used to extract caffeine in the manufacture of decaffeinated coffee, where, unlike organic solvents, it does not result in the formation of an unpleasant and possibly toxic residue.
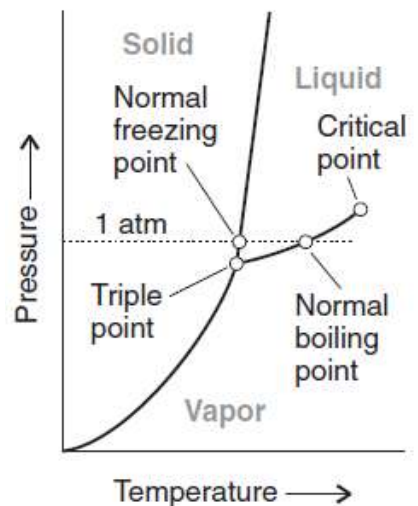
- The temperature at which the liquid and solid phases of a substance coexist in equilibrium at a specified pressure is called the **melting temperature** of the substance.
- Because a substance melts at the same temperature as it freezes, the melting temperature is the same as the **freezing temperature**.
- The solid-liquid boundary therefore shows how the melting temperature of a solid varies with pressure.
- The melting temperature when the pressure on the sample is 1 atm is called the **normal melting point** or the **normal freezing point**, Tf.
- A liquid freezes when the energy of the molecules in the liquid is so low that they cannot escape from the attractive forces of their neighbors and lose their mobility.

- There is a set of conditions under which three different phases (typically solid, liquid, and vapor) all simultaneously coexist in equilibrium.
- It is represented by the **triple point**, where the three phase boundaries meet. The triple point of a pure substance is a characteristic, unchangeable physical property of the substance.
- For water the triple point lies at 273.16 K and 611 Pa, and ice, liquid water, and water vapor coexist in equilibrium at no other combination of pressure and temperature.
- At the triple point, the rates of each forward and reverse process are equal (but the three individual rates are not necessarily the same).
  - **The triple point** marks the lowest temperature at which the liquid can exist.
  - **The critical point** marks the highest temperature at which the liquid can exist.