Graphical Representation

Temperature vs. Energy Added Diagram

All liquid at T_{BP}

All gas at T_{BP}

All liquid at T_{MP}

Gas phase

All solid at T_{MP}

T_{BP}

Mixed phase

T_{MP}

Liquid phase

Solid phase

Mixed phase

Energy Added or Removed (at constant pressure)

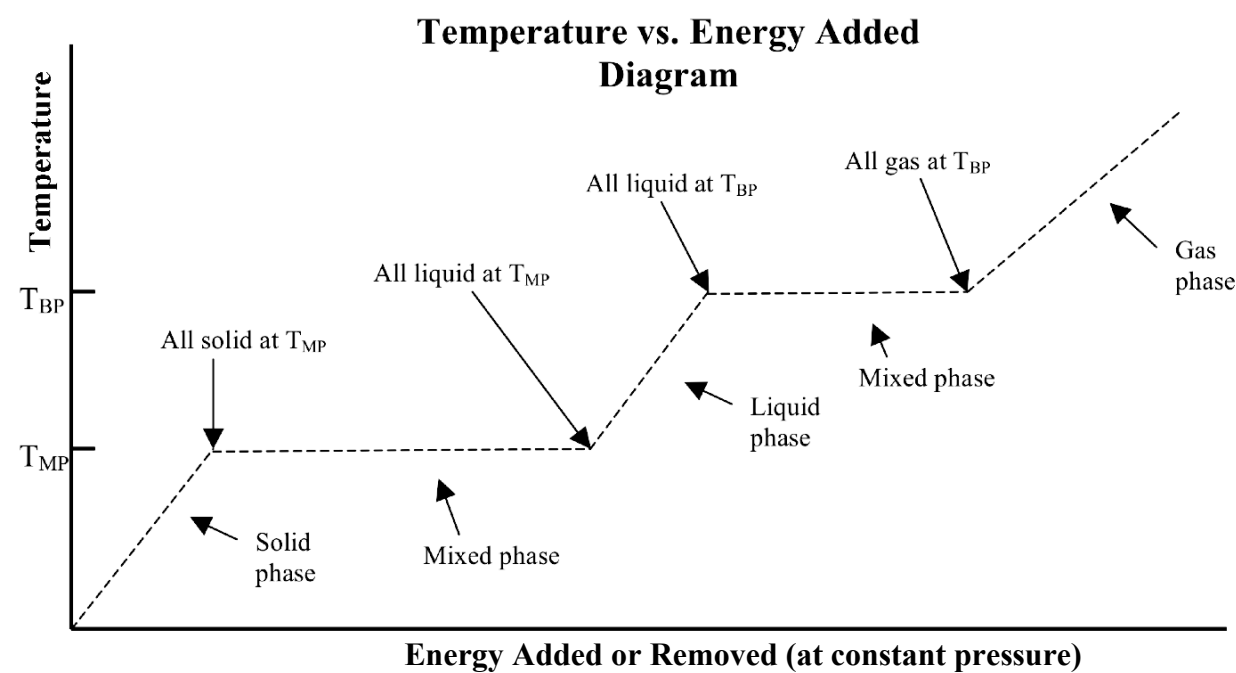Temperature

Algebraic Representations

Change in temperature of a substance when heat is added or removed:

$$\Delta T = Q/C$$

Amount of a substance that changes phase when heat is added or removed:

$$|\Delta m| = Q/\Delta H$$

Three-Phase Model of Matter

Constructs	Relationships
Pure substances Three phases Solid, Liquid, Gas Temperature Energy Energy added as heat or work	1) *Pure substances* exist in one of three phases, depending on the temperature and pressure: solid, liquid, and gas. *Non-pure* substances, e.g., solutions and composites, require more complex models for analysis.
	2) In order to change either the temperature or phase of a substance, energy must be added or removed. Often this energy is transferred to or from the substance as heat, Q, but can also be transferred as work, W.
Phase change temperature Change of phase Pressure	3) At constant pressure changes of *phase* (solid⇔liquid and liquid⇔gas or at some values of pressure, solid⇔gas (sublimation)) occur at *specific* temperatures, the phase change temperatures (T_{MP}, T_{BP}, and T_{SP}), that have particular values for each pure substance. The values of these temperatures are the same "going through" the phase change in "both directions." Phase change temperatures are, however, dependent on the pressure.
Heat of melting, Heat of vaporization, Heat of sublimation	The amount of energy added or removed at a phase change (usually written as ΔH signifying a constant pressure process) is unique to each substance and has been measured and tabulated for most substances.
Thermal equilibrium Mixed phase	If the substance is in thermal equilibrium (i.e., if the entire substance is at the same temperature) *at* the phase change temperature, both phases will *remain* at the phase change temperature as the phase change occurs. Mixed phases can exist in thermal equilibrium *only* when the temperature has the value of the phase-change temperature.
	4) Changes of *temperature* of a substance occur when energy is added or removed whenever the substance is not at a phase-change temperature.
Heat capacity Specific heat	When the energy added is in the form of heat, the change in temperature, ΔT, is related to the amount of energy added by a property of the substance called heat capacity, C. The specific heat has a particular value for each substance. Specific heats have been measured and tabulated for most substances.

1. Three-Phase Model of Matter

Energy-Interaction Model

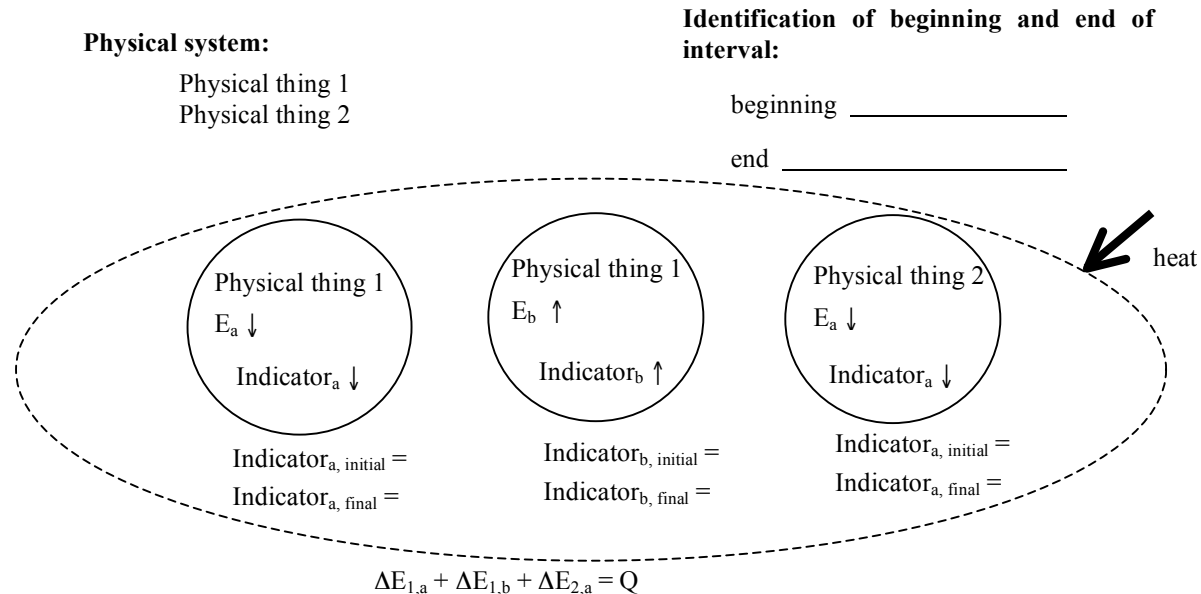## Algebraic Representations

Closed system: $\Delta E_{total} = \Sigma \Delta E_i = \Delta E_1 + \Delta E_2 + \Delta E_3 + \ldots = 0$

Open system: $\Delta E_{total} = \Sigma \Delta E_i = \Delta E_1 + \Delta E_2 + \Delta E_3 + \ldots = Q + W$

Diagrammatic Representation

Generic Example involving two physical systems, three energy systems, and with Heat Input

Physical system:
Physical thing 1
Physical thing 2

Identification of beginning and end of interval:

beginning _____

end _____

Physical thing 1
$E_a \downarrow$
Indicator$_a \downarrow$
Indicator$_{a, initial} =$
Indicator$_{a, final} =$

Physical thing 1
$E_b \uparrow$
Indicator$_b \uparrow$
Indicator$_{b, initial} =$
Indicator$_{b, final} =$

Physical thing 2
$E_a \downarrow$
Indicator$_a \downarrow$
Indicator$_{a, initial} =$
Indicator$_{a, final} =$

heat

$\Delta E_{1,a} + \Delta E_{1,b} + \Delta E_{2,a} = Q$

Commonly Used Energy Systems in Part 1

Energy system	Indicator	Algebraic Expression
Thermal energy	temperature, T	$\Delta E_{th} = C \, \Delta T$ (assuming C is constant; ΔE_{th} will change at a phase change if C changes, but we will ignore this until we get to the Model of Thermodynamics)
Bond energy	mass of a particular phase	$\Delta E_{bond} = \pm|\Delta m \times$ (heat of the particular phase change, ΔH)|
Gravitational PE	height	$\Delta PE_g = mg_E \, \Delta y$ (positive direction of y coordinate is up)
Translational KE	speed	$\Delta KE = 1/2 \, m \, \Delta(v^2)$
Rotational KE	rotational speed	
Elastic PE	displacement from equilibrium	$\Delta PE_{elastic} = 1/2 \, k \, \Delta(x^2)$ (x is measured from equilibrium position)
Spring-mass PE	displacement from equilibrium *with* mass attached	$\Delta PE_{spring-mass} = 1/2 \, k \, \Delta(x^2)$ (works for both hanging and horizontal spring-mass systems. x is measured from equilibrium with mass attached)

Useful Groupings of Energy Systems

Mechanical Energy	Sum of kinetic and potential energies associated with the physical "objects."
Internal Energy, U	Sum of kinetic and potential energies associated with the individual molecules/atoms comprising a substance, as well as the energies associated with their atomic and nuclear energies. We will mostly deal only with *changes in the energies* associated with thermal and bond energies (chemical energies).

Constructs

energy
- conservation of energy
- internal energy (U)
- mechanical energy
- energy transfers
- change in energy (ΔE)
- energy units
- relation of energy to power

energy system
- indicator

energy transfer
- heat, Q
- work, W

physical system
- closed (wrt energy transfers)
- open (wrt energy transfers

process or interaction
- interval
- initial or beginning time of interval
- final or end time of interval
- Delta prefix (Δ)

energy systems related to thermal & chemical processes
- $E_{thermal}$
- E_{bond}

Relationships

1) The heart of the energy-interaction model is energy conservation, one of a small number of powerful conservation principles used throughout science. One way of expressing a conservation principle is that for an isolated physical system there are certain physical properties that do not change during an interaction or process. A process or interaction is determined by explicitly expressing the beginning and ending times of the interval characterizing the process.

2) The total energy of every *physical system* can be expressed as a sum of the energies of separately identifiable *energy systems*. This division of the energy into energy systems can be carried out in multiple ways. The energy associated with a particular energy system can be expressed in terms of an observable and measurable property of the physical system, which we call *indicators*. The change in energy of each energy system can be determined from the observed change in the *indicator* that occurs from the beginning to the end of the interval characterizing the interaction or process.

3) Conservation of energy in a *closed physical system* (isolated with respect to energy transfers from other physical systems): The **total energy** of that physical system must remain constant during the interaction or process. When internal interactions occur this conservation principle can be expressed in terms of changes of energy systems: the changes of the energies of *all energy systems* associated with that *physical system* must sum to zero.

4) Conservation of energy in an *open physical system*: During an interaction or process during which energy is added or removed from the physical system as heat or work, the changes in energy of *all energy systems* associated with that physical system must sum to the net energy added (or removed) as heat and/or work. Equivalently, the change in the *total energy* of that physical system must equal the net energy added (or removed) as heat and/or work.

2. Energy-Interaction Model

Intro Spring-Mass Oscillator Model

Algebraic Representations

The restoring force, whose source comes from within an elastic object (including a spring) is given by the following expression:

$$| F_{\text{from within the spring}} | = k\, y$$

where k is referred to as the elastic (or spring) constant and y is the distance a specified point on the elastic has moved from its equilibrium position. The force is always in the direction that returns the object to its original shape or position, prior to being forced out of that shape or position by an external force.

The same expression as above applies to a mass hanging on a spring.

$$| F_{\text{spring-mass}} | = k\, y$$

where k is referred to as the spring constant and y is the distance a specified point on the mass has moved from the equilibrium position of the hanging mass. The force is always in the direction that returns the mass to its original shape or position, prior to being forced out of that shape or position by an external force, but not including the force of the earth. The force of the earth is already accounted for, by measuring y from the equilibrium position of the mass already hanging on the spring.

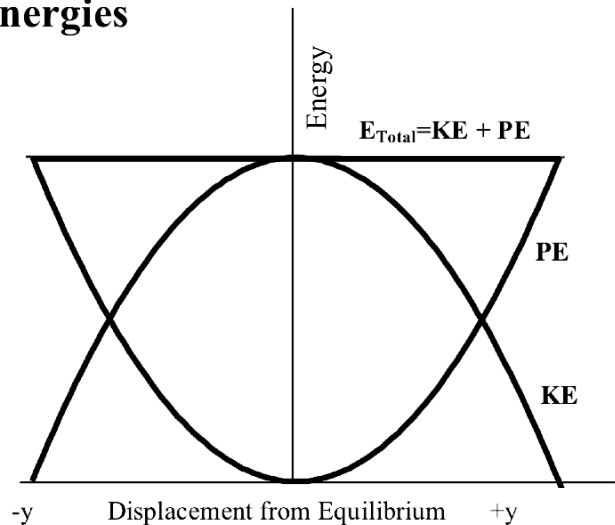The PE and KE of a spring-mass system are given by the expressions:

$$KE_{\text{spring-mass}} = \tfrac{1}{2} m v^2$$

where m is typically approximated to be simply the mass of the extra "weight" hung on a spring.

$$PE_{\text{spring-mass}} = \tfrac{1}{2} k y^2$$

where y is the distance a specified point on the mass has moved from the equilibrium position of the hanging mass. The gravitational PE of the earth-mass-spring system is already accounted for, by measuring y from the equilibrium position of the mass already hanging on the spring.

The total energy of a spring-mass system with no other energy systems involved (such as a thermal system) is given by the expression:

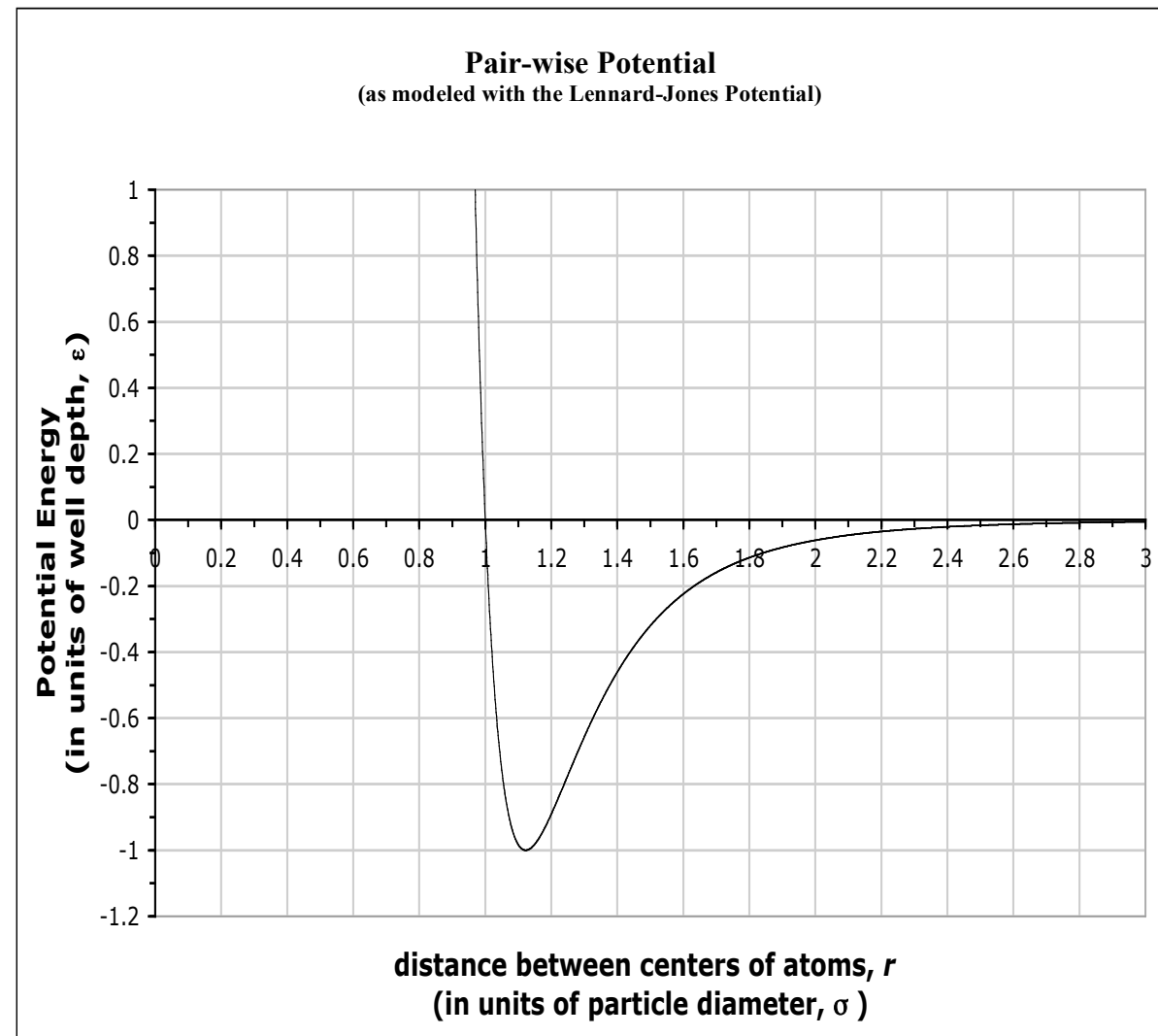$$KE_{\text{tot}} = KE_{\text{spring-mass}} + PE_{\text{spring-mass}}$$

Graphical Representation of Energies
of a spring-mass system

Constructs

Elastic object

Spring

Spring-mass

Hanging Spring-mass
- equilibrium position without mass
- equilibrium position with mass

Force
- spring force, force constant
- force exerted by external agent

Work (see Energy-Interaction Model)
- Work done on spring-mass system by an external agent

Oscillatory motion

Energy systems in Oscillatory Motion
- Oscillation about the equilibrium position
- Spring-mass Energy system indicators

PE_{elastic}
- PE_{spring}
- $PE_{\text{spring-mass}}$

$KE_{\text{spring-mass}}$

$Etotal_{\text{spring-mass}}$

Relationships

1) A spring is an example of an elastic object that has the property that if compressed by some external object (perhaps your fingers) and then the force from the external object is removed, the elastic object returns to its original shape or position. Likewise, if stretched and then released, the elastic object also returns to its original shape or position. It will typically move back and forth when this happens.

2) It is customary to pick some point on the elastic object while the object is at rest with no external objects acting on it. The location in space of that point is then defined as the fixed origin in space. The amount of stretch or compression is then measured as the distance from the fixed origin in space to the point on the elastic object.

3) A mass hanging on a stretched spring is an example of an elastic object that we will frequently use.

4) A hanging mass in the earth's gravitational field acts exactly like a horizontal mass (or a mass in outer space), *as long as the equilibrium point is determined when the mass is stationary and hanging on the spring, rather than from the equilibrium point of the spring alone without the mass.* That is, the expression for the potential energy, $PE_{\text{spring-mass}}$, has exactly the same form whether the spring is horizontal or vertical. The earth is *not* considered to be an external object acting on the spring-mass object, as long as the equilibrium point is determined as just described.

5) A stretched or compressed object (e.g., a spring-mass system) is characterized by an elastic constant or spring constant that is unique to the particular object or spring. Both the force and the PE depend linearly on this constant. The spring constant for a spring is the same whether there is a mass hanging on it or not. (Note: we assume in all this that we don't deform the elastic object by compressing or stretching it too far.)

6) The spring force with which the spring pulls back when stretched or pushes back when compressed is directly proportional to the spring constant and the distance moved from equilibrium.

7) The PE of the spring-mass system is directly proportional to the spring constant and the *square* of the distance moved from the equilibrium position.

8) In one dimension the magnitude of the spring force is related to the potential energy by $|F| = |d(PE)/dr|$. The force is always in the direction that lowers the potential energy. (Note: This is the same as Relation (2) that appears in Intro Particle Model of Matter.)

9) For an isolated elastic object (e.g., spring-mass system) the energy transfers back and forth between KE and PE. At the extremes of the oscillation, the KE is zero, and when the PE is zero at the point where the system is passing through its equilibrium point, the KE is at its maximum value. The instantaneous values of the spring mass PE and KE add to a constant E_{total}.

3. Intro Spring-Mass Oscillator Model

Graphical Representation

Pair-wise Potential
(as modeled with the Lennard-Jones Potential)

y-axis: **Potential Energy (in units of well depth, ε)**

x-axis: **distance between centers of atoms, *r* (in units of particle diameter, σ)**

Algebraic Representation

The magnitude of the attractive or repelling force between two particles is:

$$|F| = |d(PE)/dr|.$$

Constructs	Relationships

Force
• attractive force
• repulsive force
 	
Particle (atom or molecule)
 	
Particle spatial characterizations
• Center-to-center separation (*r*)
• Equilibrium position
• Equilibrium separation for two particles (r_0)
 	
Potential energy, PE(*r*)
• pair-wise potential energy, $PE_{pair-wise}$
   General shape of curve
   Well-depth (ε)
• single-particle potential energy
	1. All "normal" matter is comprised of tiny particles (atoms and molecules) that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. (paraphrased, Feynman)
	2) The attractive or repelling force is related to the shape of the potential energy curve characterizing the particle interaction. In one-dimension, the magnitude of the force is equal to the derivative of the potential energy with respect to the particle separation. The force is always in the direction that lowers the potential energy.
	3) The pair-wise potential energy for particles has the general shape shown in the graph. Important features of the force acting between two particles are revealed by applying the relationship listed in (2) above to the graph.
	   • strongly repulsive when the two particles are separated by a distance less than that corresponding to the minimum of the potential.
	   • attractive when the particle separation is greater than that corresponding to the minimum of the potential.
	   • attractive force is "short range," quickly approaching zero as the particle separation increases.
	   The particular curve shown is known as the Lennard-Jones potential, and is an excellent approximation for noble gas atoms. *All pair-wise potential energies* (except for like-charged ions) have this general shape with these features (*this includes all types of chemical bonds*).
	4) When there are *many* particles, the phase (s, l, g) of those particles depends on their total energy. At sufficiently high total energy, the particles are unbound and in the gas phase. At sufficiently low energy the particles are in the liquid or solid state and are bound. The average particle-particle separation in the bound state is approximately equal to the separation corresponding to the minimum of the pair-wise PE. In the unbound state it is much greater than the separation corresponding to the minimum PE.
	5) The interactions of one particle in a liquid or solid with *all* of its neighbors add together to form one three-dimensional potential energy *for a particular particle* with a minimum that defines the *equilibrium position* of that particle (where the *net* force due to all of the pair-wise interactions is zero). We refer to this potential as the *single-particle potential energy* to emphasize its distinction from the pair-wise potential energy.
	6) Each particle in a solid or liquid oscillates in three dimensions about its *equilibrium position* as determined by its *single-particle potential*.

4. Intro Particle Model of Matter

Algebraic Representations

Particle Model of Bond Energy

Note: The number of the algebraic Representation listed below corresponds to the number of the Relationship in the Boxed Summary on the right side of the page.

Relationship (3) $\quad E_{bond} = \Sigma_{all\ pairs} (PE_{pair\text{-}wise})$ (calculated with all particles at their equilibrium positions)

Relationship (5) $\quad$ Intermolecular $E_{bond} \approx - $ (total number of n-n pairs) $\times \varepsilon$

Relationship (6) $\quad |\Delta E_{bond}| \approx |\Delta H \Delta m|_{at\ a\ phase\ change}$

Constructs   Relationships

Energy
- Internal energy
- Thermal energy
- Bond energy
- Binding energy

Particle (atom or molecule)
- equilibrium positions

Pair-wise potential energy
- General shape of curve
- Well-depth (ε)

Nearest neighbors
- Nearest neighbor (n-n) pair
- Number of nearest neighbors
- Non-nearest neighbor pairs
- Total number of n-n pairs
- Total number of pair-wise potential energy pairs

Empirically determined values
- heats of melting
- heats of vaporization
- heats of formation

1) From a macroscopic perspective, the total internal energy of a substance, excluding nuclear and atomic energies, is comprised of thermal energy and bond energy. ($E_{internal} = E_{thermal} + E_{bond}$) Excluding atomic and nuclear energies, the bond energy is often referred to as the "chemical energy," because it is the changes in this part of the internal energy that result from changes in chemical bonds.

2) In terms of energy added to separate all the particles, if all of the particles of a substance were sitting *at rest* at their equilibrium positions, the *magnitude* of the bond energy would be the amount of energy that would have to be added to completely separate all of the particles, *still at rest*. This *positive* quantity is customarily referred to as "binding energy."

3) In terms of particle potential energies, the bond energy of a substance is the sum of *all* of the pair-wise potential energies of the particles comprising the substance calculated when all of the particles are *at* their equilibrium positions corresponding to a particular physical and chemical state. In molecular substances there will be both inter- and intra-molecular contributions to the bond energy.

4) By convention, all pair-wise potentials are defined to be zero when the particles are separated sufficiently so that the force acting between the particles is zero. Therefore, the *bond energy* of any condensed substance is *always negative*. The maximum value of the bond energy is zero when the particles that comprised the substance are all completely separated to large distances.

5) For molecular substances that don't disassociate, the total number of nearest-neighbor *pairs* times the well-depth of the pair-wise potential energy (ε) between molecules is a *rough approximation* for the sum of all *intermolecular* pair-wise potential energies of a substance. This approximation underestimates the *binding energy*.

6) The empirically determined heats of melting and heats of vaporization are reasonable *approximations* to the *changes* in bond energy at the respective physical phase changes.

7) The empirically determined heats of formation of various chemical species can be used to calculate changes in bond energy when chemical reactions occur.

5. Particle Model of Bond Energy

Algebraic Representations

Note: The number of the algebraic Representation listed below corresponds to the number of the Relationship in the Boxed Summary on the right side of the page.

**Relationship (6)** $E_{thermal}/mode = (1/2)k_BT$

This is the Big One!

Relationship (7) $E_{thermal}$ (total) = (total number of active modes) × $(1/2)k_BT$

Relationship (8) $C_V = dE_{thermal}/dT$,   (only if Q = ΔE$_{thermal}$)

Diagrammatic Representation

Corresponding to Relationship (2) in the Boxed Summary

The important point to remember here, is that, regardless of the actual kind of chemical bonding (types of bonds and the geometrical configuration of the bonds) the thermal energy due to the oscillation of the atoms or molecules (treated as rigid particles) is modeled as if they are connected by three independent springs (corresponding to the three independent spatial dimensions in a 3-D universe). This diagram helps us to remember this aspect of the model. Note, however, that the springs in each of the different directions can have different spring constants, which does not, however, have any affect on the this model for thermal energy. It simply doesn't matter.
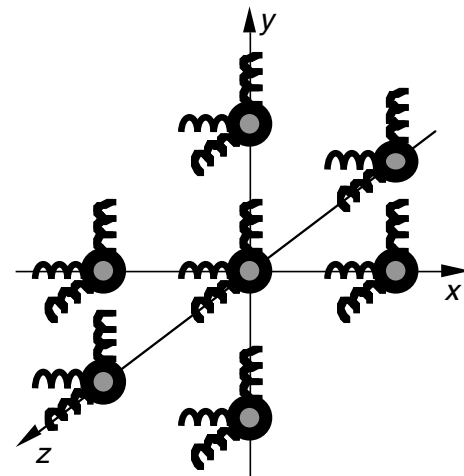
Qualifying Note mentioned in Relationship (4)
In the model of thermal energy we describe here, we consider only the contributions to the thermal energy (and heat capacity at constant volume) that arise from the motions of the atoms and molecules. It was historically the failure of this model to account for some interesting empirical deviations from the model that led to its extension and the discovery and understanding of the role of energies associated with electrons, magnetic entities, etc. in many solids, especially at low temperatures. This is a classic example of how models have been and continue to be used in science.

Particle Model of Thermal Energy

Constructs	Relationships

Energy modes
• Common modes:
  mass-spring,
  translational KE,
  rotational KE.
• Freezing out of modes
• Active modes
	1) In gases, the translational kinetic energy of each particle can be divided into three independent modes, each one corresponding to one of the three independent spatial dimensions; each particle in a gas has *at least* these three independent modes due to its kinetic energy.

Thermal Energy	**2)** In liquids and solids, the oscillations of each particle in its single-particle potential can be modeled as a mass held in place by three perpendicular springs, regardless of the actual bonding arrangement with surrounding particles. The potential and kinetic energies that are associated with each spring act independently of those of the other springs. Each particle in a liquid or solid has *at least* these six independent modes corresponding to the PE and KE of the three springs.
Thermal Equilibrium	**3)** In all phases (s, l, g) polyatomic molecules *may have* additional energies associated with rotations and/or internal vibrations of the molecule. These *might* contribute additional modes, depending on whether they are *active* or not at a particular temperature. See (6) below.
Equipartition of energy	**4)** All of the energies described above are given the label "mode." The *thermal energy* of a substance is the total energy in all the active modes of all the particles (see qualifying note on left page of this summary) comprising the substance.
Heat capacity	**5)** In thermal equilibrium all active modes (of the type considered here) have, *on average*, the same amount of energy. This principle is referred to as "*equipartition* of energy."
Single-particle potential	**6)** The amount of energy, on average, in an active mode is directly proportional to the temperature. The proportionality constant, for historical reasons, is written $k_B/2$, where k_B is the Boltzmann constant. ($k_B = 1.38 \times 10^{-23}$ J/K)
Empirically determined values • Heat capacity at constant volume	• Since energy is quantized, some modes may not be *active*, and thus not contribute to the thermal energy at "lower" temperatures. This occurs when k_BT is not considerably greater than the spacing of the quantized energy levels. This is often referred to as "*freezing out of modes*."
	7) The total thermal energy of a substance in thermal equilibrium is equal to the product of [the total number of active modes] and [the average energy per mode].
	8) When the change in thermal energy is due solely to the addition or removal of energy as heat, the heat capacity (C_V) is given by the derivative of thermal energy with respect to temperature.

6. Particle Model of Thermal Energy

Algebraic Representations

Relationships 1-3

$\Delta E = \Delta E_{mechanical} + \Delta U$

$\Delta E_{physical\ system} = Q_{in\ to\ physical\ system} + W_{done\ on\ physical\ system}$ or simply $\Delta E = Q + W$

$\Delta U = \Delta E_{bond} + \Delta E_{thermal} + \Delta E_{atomic} + \Delta E_{nuclear}$

The 1st Law of Thermodynamics

$\Delta U = Q + W$ in differential form: $dU = dQ + dW$ and for simple fluids: $dU = dQ - PdV$

and for fluid processes along reversible paths: $dU = TdS - PdV$

Because $dU = TdS - PdV$ involves only functions of state (Q's and W's have been replaced by state functions), it is true for all processes, whether they are reversible or not. Evaluations of TdS must, however, be carried out along a reversible path.

Expression for work done on a fluid

$$W = -\int_{V_i}^{V_f} P(V)\ dV \quad \text{or in differential form:} \quad dW = -P(V)\ dV$$

Relations 4-6

The Second Law of Thermodynamics

In a closed system, $\Delta S \geq 0$

Relation of S to Q: $dS = dQ/T$; in a reversible process, Q can be expressed as function of S: $dQ = TdS$

Extension of the concept of heat capacity

Heat Capacity

$C = dQ/dT$

Heat Capacity at Constant Volume and Constant Pressure (with $\Delta E_{Bond} = 0$)

$C_v = dE_{th}/dT \qquad C_p = C_v + P\ dV/dT$

Relations 7-10

Enthalpy

$H = U + PV$, At constant pressure, $\Delta H = Q$

Gibbs Energy

$G = H - TS$, At constant pressure and temperature, $\Delta G = \Delta H - T\ \Delta S$
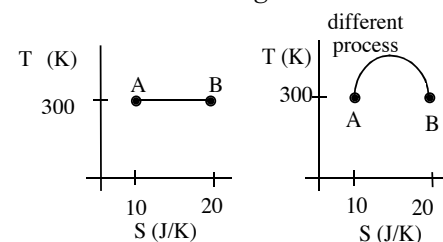
If $\Delta G < 0$, the process is spontaneous

If $\Delta G > 0$, the process is not spontaneous

If $\Delta G = 0$, the forward and reverse directions are in equilibrium
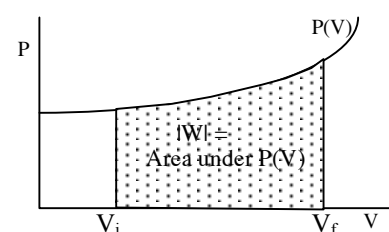
State Functions: Ideal Gas Law: $PV = nRT$ or $PV = N\ k_B T$

Graphical Representations

Two *identical states*, A & B shown on both *State Diagrams*, but the *processes* that take the physical system from A to B are *different* in the two *State Diagrams*.

Graphical representation of PdV work

Intro Model of Thermodynamics

Constructs	Relationships
Conservation of Energy	1) It is useful to divide energy into *mechanical* and *internal* pieces.
Mechanical and Internal Energies	2) Change in total energy of a system is equal to the energy added to the system. Energy added can be separated into heat, Q, and work, W.
	3) When changes in energy are restricted to only the *internal* energies, conservation of energy reduces to the statement: **the change in internal energy is equal to the energy added as heat and work. This statement is referred to as the First Law of Thermodynamics.**
Work done on a fluid	
State of a physical system	4) The entropy, S, of a closed system can never decrease in any process (the closed system could be a combined open system and the surroundings with which it interacts). If the process is reversible, the entropy of the closed system remains constant. If the process is irreversible. the entropy of the closed system increases. These relationships are referred to as the **Second Law of Thermodynamics.**
Equilibrium State	
State Function	
Extensive and Intensive state functions	
State Diagrams	5) When a small amount of heat, dQ, is added to a system, the differential change in entropy, dS, varies in direct proportion to dQ. The constant of proportionality is the reciprocal temperature, 1/T .
path on a state diagram	
State variables independence of path	6) For processes that are *reversible*, the heat added to or removed from the system can be expressed in terms of the change in entropy using the previous relationship (dQ = T dS).
reversible path	
PV Diagram	7) New energy state functions can be formed from combinations of other state functions. Two common examples are enthalpy, H, and Gibbs energy, G. (H = U + PV; G = H – TS)
ST Diagram	
other State Diagrams	8) At *constant pressure*, the energy added to a system can be expressed as a change in enthalpy.
Heat capacity	9) At *constant pressure and temperature*, the change in the Gibbs energy expresses a system's ability to satisfy both the conservation of energy and the tendency of entropy increase, i.e., satisfaction of both the 1st and 2nd law of thermodynamics. $\Delta G = \Delta H - T\ \Delta S$. ΔG represents the amount of energy available to do useful work in a reaction or process.
Heat capacity at constant volume	
Heat capacity at constant pressure	
Specific heats	10) The direction in which a reaction or process proceeds is determined by the sign of ΔG for the process: If $\Delta G < 0$, the reaction is spontaneous. If $\Delta G > 0$, the reaction is not spontaneous
Enthalpy, H	
Entropy, S	11) The *values* of a *small number of State Functions* completely *define the state* of a thermodynamic system. These values are *independent* of the *path* that took the system to that state.
Reversible and irreversible processes	12) The amounts of *heat and work* involved in going from State A to State B *will depend* on the *particular path taken*.
Gibbs Energy, G	13) Values of state functions at state B can be readily calculated, if they are known at state A and a reversible path is used for the calculation to get from A to B, even if the actual path the physical system takes, is irreversible.
Spontaneous reaction	
Endothermic	

7. Intro Model of Thermodynamics

Algebraic Representations

Ideal Gas Model

Ideal Gas Law:

$$PV = nRT \quad \text{AND} \quad PV = N\,k_B T$$

$$k_B = 1.381 \times 10^{-23} \text{ J/K}$$

$$R = 8.314 \text{ J / K} \cdot \text{mol}$$

Relationships that are connected by the thermodynamic temperature, T

$$PV = nRT \quad \text{and} \quad PV = N\,k_B T$$

$$dU = TdS - PdV$$

$$C_v = dE_{th}/dT$$

$$c_{pm} = c_{vm} + R \quad \textit{(true only in the ideal gas model)}$$

$$E_{thermal}/\text{mode} = (1/2)k_B T$$

$$E_{thermal} \text{ (total)} = \text{(total number of active modes)} \times (1/2)k_B T$$

Constructs	Relationships
Fundamental Properties of gases	1) The *Ideal Gas Model* is the entire *set of ideas* related to gases that scientists regularly use as whenever they reason about phenomena involving gases. Whether gases involved in the particular phenomenon "obey" the ideal gas law or not, the starting point for thinking about gases is the *Ideal Gas Model*.
Equation of State	
Microscopic	2) At the macroscopic level it embodies the ideas that the macroscopic variables that describe a gas (P, V, T, n) are totally independent of the kind of gas. That is, the relationships of these variables are the same for all gases.
Macroscopic	
Pressure	
Temperature	3) At the microscopic level it embodies the ideas that gases are composed of extremely small particles with a lot of space between them that interact only like perfect billiard balls when they happen to collide with each other.
Volume	
Gas Constant	4) As represented in terms of the "ideal gas law" it is an explicit way for connecting the *microscopic* way of thinking about gases to the *macroscopic* way of thinking about gases. This is strikingly seen in the two equivalent ways the model is written:
Number of moles	
Particles	$$PV = nRT \quad \text{and} \quad PV = Nk_B T,$$
Number of particles	where n is the number of moles and R is the gas constant (both macroscopic constructs) and N is the number of molecules and k_B is the Boltzmann's constant (both microscopic constructs).
Boltzmann's constant	
Energy of an Ideal Gas	5) The temperature term forms a bridge between the particle model of thermal energy and macroscopic thermodynamics. The temperature connects directly to the meaning of thermal energy through the fundamental relationship of temperature as a measure of the random thermal motion in any energy mode in thermal equilibrium at temperature T: $E_{thermal}/\text{mode} = (1/2)k_B T$, while at the same time, temperature is seen to be directly proportional to the pressure of a gas.
• monatomic	
• non-monatomic ideal gases	
Heat capacity at constant pressure	6) When combined with the particle model of thermal energy, $E_{thermal}$ (total) = (total number of active modes) × $(1/2)k_B T$, the *Ideal Gas Model* provides substantial insight into what the fundamental properties of an ideal gas are from a PV perspective and how they differ from an internal energy perspective, as well as providing a bridge between the two.
	7) The basic concept of heat capacity at constant pressure ($C_p = C_v + P\,dV/dT$), when applied to an ideal gas gives the fundamental result that the molar heat capacity at constant pressure of any ideal gas is greater than the heat capacity at constant volume simply by the additive factor R.

8. Ideal Gas Model

Algebraic Representations

Relationship (2)

P(state i) = (# of microstates in state i) / Ω

Relationship (4)

$S = k_B \ln\Omega$, where k_B is known as Boltzmann's constant

$k_B = 1.381 \times 10^{-23}$ J/K

Intro Statistical Model of Thermodynamics

Constructs	Relationships
Physical system	1) Given an isolated (thermodynamic) system in equilibrium, it will be found with equal probability in each of its accessible microstates.
State of a Physical System State Functions Equilibrium Equilibrium State of a physical system	2) The probability of finding a physical system in a particular state (not necessarily an equilibrium state) is equal to the ratio of the number of microstates in that state to the total number of microstates accessible to the physical system.
Microstates of a physical system Accessible Microstate States of a physical system Number of microstates in a particular state (not necessarily in an equilibrium state) Total number of (accessible) microstates of a physical system, Ω	3) When a constraint is removed or when systems interact, they evolve in such a way that the total number of microstates, Ω, always increases (or stays the same). This is an expression of the 2nd Law of Thermodynamics in terms of microstates and probabilities.
Entropy Energy Microstates Location Microstates Mixing Microstates	4) The total number of accessible microstates, Ω, in an isolated physical system is related to the thermodynamic state function entropy, S. The entropy, S, is directly proportional to the natural logarithm of the number of microstates, Ω.

9. Intro Statistical Model of Thermodynamics