## Thermodynamic Materials - Systems composed of atoms and molecules are called materials.

**Two kinds of materials**:

* pure materials - composed of only one molecular species, and
* mixtures - composed of two or more molecular species.

ideal mixtures - mixtures where the volume and enthalpy of the mixture are simply the sums of the volumes and enthalpies of the pure components at the temperature and pressure of the mixture. Elementary thermodynamics deals only with ideal mixtures. Advanced thermodynamics is concerned with non-ideal mixtures, in phase equilibrium and reaction equilibrium.

**Four basic concepts of materials:**

(1) **Quantity**

 (a) mass (or weight in a known gravitational field)

 (b) number of objects (one gram mole = 6.025 x 1023 objects)

mean-molar-mass (molecular weight or atomic weight) is the mass of one mole of a particular collection of objects, and is the constant which allow conversion between these two measures of quantity.

(2) **Composition** of a mixture

 (a) fraction - quantity of a particular species per unit quantity of the mixture.

 (b) concentration - quantity of a particular species per unit volume of the mixture.

(3) **Phase** - a homogeneous quantity of material, characterized throughout by a single set of thermodynamic properties.

 (a) solids - materials which are capable of resisting shear stresses.

 (b) fluids - materials which exhibit continuous deformation under shear stress.

 (c) liquids - fluids which can conform to their containers without occupying them completely.

 (d) gases - fluids which conform to and completely occupy their containers.

 (e) vapors - gases at temperatures less than their critical temperature.

quality - ratio of quantity of vapor to the total quantity of material [vapor & liquid] or [vapor & solid] in a system.

(4) **State** - defined by the **properties** of a material.

 (a) subcooled liquid (or compressed liquid) - a liquid at a temperature below its saturation temperature or at a pressure above its saturation pressure.

 (b) superheated vapor - a vapor at a temperature above its saturation temperature or at a pressure below its saturation pressure.

 (c) saturated - if two or more phases exist within a system at **equilibrium**, the system is said to be saturated and all phases present are saturated. In particular, if vapor and liquid phases are both present within a system, the vapor is said to be **saturated vapor** and the liquid is said to be **saturated liquid**. Similarly, if two liquid phases exist within a system at equilibrium, both liquid phases are saturated.

saturation pressure (or vapor pressure) - the pressure at which a phase change will take place at a given temperature.

saturation temperature - the temperature at which a phase change will take place at a given pressure.

critical point - that state of a saturated system where the liquid and vapor phases become indistinguishable. The properties of a material at its critical point are the same for both vapor and liquid phases.

equilibrium - the condition of a system in which no net change in the properties of the system occur with time. A closed system is usually implied.

[steady state - no accumulations of matter or energy occur within the system. An open system is implied.]

**Gibbs Phase Rule**: **F = 2 + Ns - Np**

**F** - degrees of freedom of the system = the number of *independent*,

 *intensive* thermodynamic *variables* (properties or compositions) which

 must be specified to fix the *intensive* state of the system,

**Ns** - number of molecular species within the system, and

**Np** - the number of phases within the system.

The thermodynamic variables specified as degrees of freedom are normally temperature, pressure and compositions (mole fractions) of the phases. Note that only [Ns - 1] compositions of each phase are *independent*. To fix the *extensive* state of the system, an additional *extensive* variable must be specified (i.e. total moles of the system).

## Thermodynamic Data Presentation

Data, such as properties of pure materials, is generally acquired by experimentation and can be presented in three fundamentally different forms:

(1) **Tables** [i.e. the steam tables]

(2) **Graphs** [i.e. a T-s or P-h diagrams]

(3) **Equations** [i.e. the ideal gas equation]

Each of these forms of presentation has advantages and disadvantages.

(1) Tables are precise but discontinuous, so that interpolation is often required. In addition, they can be bulky and can be difficult to use when implicit variables are specified. They also can require large amounts of data storage when used with computer programs.

(2) Graphs are continuous in their explicit variables but suffer loss of precision when they are of convenient size. In addition, they are discontinuous for implicit variables, so that imprecise visual interpolation is often required. They also suffer in readability as the number of implicit variables displayed increases above three or four. Although they can give an excellent overall "feel" for the data, they are virtually useless for computer purposes.

(3) Equations are in many ways the best form of presentation for data. They allow mathematical manipulation, are easy to use with computer programs, and are as precise as the data used to generate their constants. However, equations that accurately represent significantly large ranges of data can be very complex and usually employ a number of constant terms. Complex equations are usually difficult to solve for their implicit variables and often require trial and error procedures in their use. They are most suited for use in computer programs.

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| **Introduction to Thermodynamics**Because we will be using a great deal of thermodynamics in discussing the generation and evolution of basaltic melts in the ocean crust, it seems like a good idea to review some of the basic thermodynamic relationships and definitions. **Definitions:**A **System** is any portion of the universe isolated for the purpose of considering experimental or natural changes in conditions within it. Examples include a beaker, and experimental charge, or an ocean basin. A **closed system** is one that changes only by receiving energy from the outside environment or by yielding energy to it. An **open system** may exchange both matter and energy with it surroundings. **Equilibrium** within a system is achieved when the system reaches its lowest energy state consistent with the imposed conditions. If temperature and pressure are specified, the equilibrium configuration possesses the lowest possible Gibbs Free energy (G). **Stability** is the condition of equilibrium (minimum G).**Phases** are physically separate regions of homogeneous chemistry. Possible phases include a liquid phase (multiple liquid phases if the liquids are immiscible), a gas phase, and multiple solid phases. Solid phases may exhibit solid solution, i.e., have a range of compositional variation.**Components** of a phase consist of the smallest number of chemically distinct substances needed to specify the bulk composition of the phase. **Phase diagrams** depict phase relationships within multi-component systems. **Heat Capacity**Heat capacity is defined as the heat added to the system divided by the rise in temperature. While the heat capacity is not strictly speaking constant, it remains a nearly constant material property over wide temperature ranges. Heat capacity is either considered at constant pressure:

|  |  |
| --- | --- |
| Image22 | (8) |

or constant volume

|  |  |
| --- | --- |
| Image23 | (9) |

Heat capacity normally has the units Wkg-1 C -1 and is physically defined as the amount of heat required to raise 1 kg of a material 1  C. Closely related is the **Specific Heat**, which has the same units, and is the ratio of the heat capacity of a substance to that of water at 15  C.**Second Law of Thermodynamics**A succinct statement of the second law: "Things break down", or "You can't even break even". Entropy, S is the measure of the disorder in the system and is a single-valued function of the state of the system. Like the internal energy, it is dependent on the mass of the system. Under equilibrium conditions:

|  |  |
| --- | --- |
| Image24 | (10) |

meaning that the process is reversible. for a spontaneous, disequilibrium process:

|  |  |
| --- | --- |
| Image25 | (11) |

That is, irreversible processes increase the entropy of the system. **Third Law of Thermodynamics**There is such a thing as absolute zero, a temperature below which there is no more entropy in the system. Knowing this entropy allows us to use the second law to calculate the isobaric entropy within a phase at any temperature. From Eq. 8, the definition of isobaric heat capacity, we have:

|  |  |
| --- | --- |
| *dQ = CPdT* | (12) |

which can be substituted into Eq. 10 to yield

|  |  |
| --- | --- |
| Image26 | (13) |

The entropy at some fixed pressure and any temperature T is then

|  |  |
| --- | --- |
| Image27 | (14) |

or

|  |  |
| --- | --- |
| Image28 | (15) |

where the second term accounts for the heat of transition for any phase transformation that may have occurred along the way. **Gibbs Free Energy**The energy available to drive reactions in a system is less than the total energy, because some is tied up in entropy and some is tied up in the PV term. The remaining energy is called the Gibbs free energy, and is defined as:

|  |  |
| --- | --- |
| *G = E + PV - TS = H - TS* | (16) |

at constant P and T:

|  |  |
| --- | --- |
|  G =  H - T S | (17) |

However, for the more general case, let us differentiate Eq. 16:

|  |  |
| --- | --- |
| *dG = dE + PdV + VdP - TdS - SdT* | (18) |

Substituting the expressions for the first and second laws (Eqs. 4 and ??) gives:

|  |  |
| --- | --- |
| *G = VdP - SdT* | (19). |

Two important relationships from this equation lie in its partial derivatives with respect to pressure and temperature:

|  |  |
| --- | --- |
| Image29 | (20) |

and

|  |  |
| --- | --- |
| Image30 | (21) |

Reversible equilibrium reactions take place with no change in G, whereas spontaneous reactions involve a decrease in G. **Chemical Potential**The Gibbs free energy is only a function of P, T and the quantities of phases in the system. It is necessary to extend G to also describe compositional changes in the phases. In phases showing chemical variation, it is useful to establish another quantity, the chemical potential  , which is the partial molar free energy of a component in a phase, and is defined as:

|  |  |
| --- | --- |
| Image31 | (22) |

where ni are the numbers of moles of each component in each phase in the system. The more general form of the Gibbs free energy equation then becomes:

|  |  |
| --- | --- |
| Image32 | (23) |

So not only must the Gibbs free energy of both reactant and product in a single component system be equal, at equilibrium (as we saw in the previous section) but the chemical potentials of each component must be equal between the phases. The chemical potentials will be different from each other within each given phase, of course. The minimization of the Gibbs free energy of a system is the basis of almost all petrology and geochemistry. **Gibbs Phase Rule**The variance or degrees of freedom in a system is denoted by F, and it is the number of independent parameters which must be fixed or determined arbitrarily in order to specify completely the state of the system. This includes both the physical conditions (P and T) of the system, but also the compositions of all the phases. Consider a closed system consisting of *p* phases and *c* components, the temperature and pressure are also free parameters. Suppose that all c components occur in each phase. The composition of a phase is then defined by *c*-1 composition variables (the last being the reminder). With *p* phases, the total number of unknowns in the system is *p*(*c* - 1). In addition there are pressure and temperature for a total of *p*(*c* - 1) + 2 unknowns. Obviously, P and T must be the same for all phases at equilibrium. However, we also know that the chemical potentials of all the components must be equal in each phase. So if we determine  i in one phase, we have determined it in all the other phases as well. Therefore there are (*p-1)* chemical restrictions for each component, for a total of *c*(*p* - 1) dependent relationships. The total number of independent variables can be found by subtracting the restrictions from the total unknowns we found above:

|  |  |
| --- | --- |
| *F* = *p*(*c* - 1) + 2 - *c*(*p* - 1) | (24) |

which reduces to

|  |  |
| --- | --- |
| *F* = *c* - *p* + 2 | (25). |

Equation 25 is known as the Gibbs Phase Rule, and holds for systems closed to gain or loss of mass. Where physical conditions are fixed, the number of independent variables is reduced. For an isobaric or isothermal system, the the expression becomes *c* - *p* + 1. Consider a system at constant pressure, where there is a reactant that undergoes a phase transformation to a product at Tm as the temperature rises. Before Tm is reached, there is one component, 1 phase and thus one degree of freedom -- the system is said to be **univariate**. As the temperature rises to Tm, a second phase appears, the product phase, and the number of degrees of freedom drops to 0. This is referred to as an **invariant** point, and the temperature of the system remains constant until the last of the product phase is consumed, and the number of degrees of freedom returns to 1. A pleasant fact of life on a hot summer day. **More Definitions****Thermal expansion coefficient ** is the ratio of the change of length per degree C to the length at 0  C. The coefficient of volume expansion for solids ( ) is approximately 3 times the linear expansion coefficient. It is a ratio, and so has no unit, and typical values are around 10-5.**Thermal conductivity k** is the time rate of transfer of heat by conduction, through unit thickness, across unit area for unit difference in temperature. It has units of Watts per meter per degree C (Wm-1 C-1). The thermal conductivity of solids varies widely, from 418 Wm-1 C-1 for silver to 2-3 Wm-1 C-1 for rock, to 0.1 Wm-1 C-1 for wood.**Thermal Diffusivity ** is a diffusion coefficient for heat. It is the ability heat to move through a material and is defined as k/ Cp**,** where  is the density and Cp is the heat capacity at constant pressure, defined above.  |

**Brief Review of Thermodynamics**

Discussion on statistical mechanics (SM) often begins with thermodynamics. Thermal energy (heat) transferred to a molecule does not change the nature of the available energy levels, but it does change which energy levels are occupied by the electrons:



* Within a macroscopic material sample (made up of Avogadro’s number of atoms), the total internal energy is still theoretically quantized, though the energy levels may be very close together (so close that we cannot really measure the quantization). At finite temperature, each atom’s electrons are excited to some distribution among the available energy levels; with increasing thermal energy in the system, the electrons are able to access higher and higher energy levels. One of the main objectives of statistical mechanics is to predict how the energy levels are occupied for a given model of how a system responds to thermal energy.

The reason is that SM provides a microscopic basis of thermodynamics and meaning to such terms as entropy and free energy which is otherwise rather hard to understand. Another important reason, not often emphasized enough, is that thermodynamics by itself is not very useful because it does not have the capacity to generate numbers needed to understand experiments. For example, the first two laws define all sorts of relations between thermodynamic variables and functions, but do not tell you how to calculate them. This deficiency partly the reason for the third law which tells that entropy of a perfectly crystalline solid is zero. Remember that this law is used to obtain entropy and enthalpy and then free energy, by integrating temperature dependent specific heat all the way from zero Kelvin.

Let us go through the three laws quickly. The *first law* has to do with conservation of energy. But in practical terms in gives a relation between energy, work and heat.

 

where work and heat are not exact differentials because they depend on path and are not state functions.

There are several nearly equivalent statements of *the second law* but ultimately all boil down to statements about entropy. The extensive state function entropy is an increasing function of energy. Entropy obeys Clausius Inequality in the form

 

where the equality is sign is for a reversible process. The success of second law of thermodynamics is of course in the introduction of free energies







**Internal Energy**



**Enthalpy**



 at constant *P* and *T* 

It is a state function.



 , 

and the important variational statement that for a system at equilibrium, the free energy of the system is minimum. That is, any change will increase the free energy of the system. It measures the useful work obtainable for a closed thermodynamic system at a constant temperature and volume.



 = 0 at constant *P* and *T* (e.g. in phase transition such as melting)







For different components



Where the chemical potential  is given by:



Students are encouraged to read the article by Frank Lambert in Chemical Education, available in a more recent form in the site

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<http://www.entropysite.com/students_approach.html> for a shorter approach to understanding the second law and entropy.

The *third law* is simple : Entropy of a perfectly crystalline substance is zero ate absolute zero.

However, it is the third law that allows calculation of entropy



We can find temperature dependence of the specific heat in the form of a series in T in many handbooks and these expansions are widely used by Geologists, Metallurgists and Chemical Thermodynamics researchers in the evaluation of free energy.

More discussions

Intensive and extensive quantities

Suppose we have a homogeneous macroscopic system in equilibrium, if we separate the system into parts, the thermodynamic quantities which remain unchanged after the partition are called intensive quantities. The temperature *T*, pressure *P*, and chemical potential μ are intensive quantities. In contrast, *U*, *S* , *V*, and *N* are extensive quantities which are proportional to the amount of matters in the system.

Note: When we put two identical systems together, the intensive quantities such as the total internal energy would be unchanged but the extensive quantities would be doubled. This is possible only when the surface energy of the system is neglected. Such condition is justified since we are considering a macroscopic system which can be assumed arbitrarily large and the surface effect can be made arbitrarily small. Since *U*, *S* , *V*, and *N* all scale linearly with the amount of the matter in the system while *P*, *T*, and μ are kept constant, the internal energy can be written as a homogeneous linear function of the other three extensive quantities as:









Statistical Mechanics

In contrast to thermodynamics it provides a link between microscopic and macroscopic physics, because it starts with a Hamiltonian H, which describes the microscopic interaction.

Canonical ensemble, the partition function:







**In Brief**:

 





.

**Helmholtz free energy** :



Use



Then







# Summary of Thermodynamics

* **Thermodynamics** - the science that is concerned with **energy**, particularly **‘energy-in-transit’** in the forms of **heat** and **work**, and those **properties** of **systems** that are related to energy.
* **Energy** – the ability to do work. **All energy is *relative*!** Energy-in-transit is not relative.

**Three kinds of energy**:

* potential - energy due to *relative* position,
* kinetic - energy due to *relative* velocity,
* internal - the sum of all potential and kinetic energies of constituent parts [atoms, molecules, etc.] of a system.

**Two kinds of ‘energy-in-transit’**:

* heat – energy transferred between system and surroundings because of a temperature difference, or gradient.
* work - energy transferred between system and surroundings because of a pressure difference, or gradient.

**Thermodynamic System**

* ***System*** is any portion of the universe isolated for the purpose of considering experimental or natural changes in conditions within it. Examples include: a beaker, and experimental charge, or an ocean basin.

**Three kinds of systems:**

* ***Isolated systems*** (micro-canonical ensemble) do not exchange energy or mater with the exterior, e.g. a thermos.
* ***Closed systems*** (canonical ensemble) exchange energy with the exterior but not matter, e.g. a sealed beaker. (System with a fixed amount of material.)
* ***Open systems*** (grand-canonical ensemble) exchange both energy and matter with the exterior, e.g. an open beaker.



* ***Universe*** It is system (interior) + surrounding (exterior).
* ***Ensembles*** I have a set of 1000 systems. I want to predict average values for this set. This is the right question for Stat Thermo! The set is called ensemble.
* ***Macroscopic state variables*** such as volume *V*, pressure *P*, temperature *T*, mole numbers *n*.

**Five of basic thermodynamic properties:**

* temperature [*T*] (thermal potential) - a measure of the relative hotness or coldness of a material.
* pressure [*P*] (mechanical potential) - the normal (perpendicular) component of force per unit area.
* volume [*V*] (mechanical displacement) - the quantity of space possessed by a material.
* entropy [*S*] (thermal displacement) - the quantity of disorder possessed by a material.
* internal energy [*U*] - the energy of a material which is due to the kinetic and potential energies of its constituent parts (atoms and molecules, usually).

**Two secondary thermodynamic properties**:

* enthalpy [*H*] - internal energy plus the pressure-volume product.
* heat capacity [ or ] (specific heat) - the amount of energy required to increase the temperature of one unit quantity of material by one degree, under specific conditions.

(a)    constant pressure 

(b)    constant volume 

Unlike gases, liquids and solids are nearly incompressible, and it is almost impossible to change their temperature while holding their volumes constant. The specific heats of liquids and solids almost always imply their constant pressure heat capacity (usually on a unit mass basis), so that, in general, for liquids and solids we used .

**Thermodynamic Properties** - any quantity (variables) that depends only on the state of a material and is independent of the process by which a material arrives at a given state.

**Two types of variables:**

* **Intensive variables**: do not depend on the amount of substance present. Examples include: the temperature *T*, pressure *P*, density (mass/volume) , chemical potential of type *i* , and the external magnetic field .
* **Extensive variables**: depend on the amount of matter in the system (e.g. mass). Examples include: particle number of typ type *i* , the volume *V*, internal energy *U*, enthalpy *H*, entropy *S*, and heat capacity *C*, total magnetic moment.

Notes:

1. When we put two identical systems together, the intensive quantities, such as the temperature, would be unchanged but the extensive quantities, such as the entropy, would be doubled. This is possible only when the surface energy of the system is neglected. Such condition is justified since we are considering a macroscopic system which can be assumed arbitrarily large and the surface effect can be made arbitrarily small.
2. Any extensive variable can be converted to an intensive variable by dividing it by the moles or the mass.
3. The usual extensive variables become infinite in the thermodynamic limit. We therefore use densities:



* Thermodynamic limit, i. e. in the limit where

 at fixed intensive variables

**Reasons:**

1. For finite systems the thermodynamic quantities are always analytic functions of their variables. In a finite system the partition function of any system is a finite sum of analytic functions of its parameters, and is therefore always analytic
2. Singular behavior as required for phase transitions does not occur. Because of the finite volume the correlation length is finite.
3. Spontaneous symmetry breaking exists only in the thermodynamic limit. In finite systems the breaking is explicit by an external field or by the boundary conditions.
4. In the thermodynamic limit the different ensembles are equivalent.
5. In the thermodynamic limit there is no boundary (surface) dependence.
* ***Equilibrium state*** is one in which the properties of the system are uniform throughout and do not change with time unless the system is acted upon by external influences (e.g. magnetic or electric fields). **Equilibrium** within a system is achieved when the system reaches its lowest energy state consistent with the imposed conditions. If temperature and pressure are specified, the equilibrium configuration possesses the lowest possible Gibbs Free energy (G). **Stability** is the condition of equilibrium (minimum G).

*A system is said to be in thermodynamic equilibrium if it attains*:

* Thermal equilibrium (Δ*T* = 0).
* Mechanical equilibrium (Δ*P* = 0), which means that all forces of interaction between the system and surroundings are in equilibrium.
* Chemical equilibrium (Δ = 0), i.e. no change in structure takes place.
* ***Non-Equilibrium*** characterizes a systemin which gradients exist and whose properties vary with time (e.g. the atmosphere and the oceans)
* ***Equation of state*** is a functional relationship among the state variables for a system in equilibrium, e.g. .
* ***State function*** depends only on the initial and final positions. For example: Energy, Entropy. Work and heat are not state functions because they are depending on their path.
* ***Exact differentials*** e.g. *dV*, *dP*, *dT*, and *dU*. Exact differentials may be integrated since we are only concerned with the initial and final states, not with the path taken as *dW*. Usually the state function is an exact differential.
* ***Inexact differentials*** e.g.  and *,* cannot integrated unless we know the path taken by the system in passing from state to another.
* ***Systems wall*** is the boundary between a system and its surroundings through which changes may be imposed.

**Two kinds of separation walls:**

1. ***Adiabatic wall*** is a boundary that permits no heat interaction between the system and its surroundings.
2. ***Diathermal wall*** is a boundary that freely allows heat to be exchanged.

## Thermodynamic Processes and Cycles

* ***Path*** is a series of states through which a system passes.
* ***A process*** any succession of events, i.e. a change of state expressed in terms of a path along the equation of state surface.
* ***A quasi-static process*** isa process in which, at each instant, the system is only departs infinitesimally from an equilibrium state.
* **chemical process** - a chemical or physical operation, or series of operations, which transforms raw materials into products.
* **thermodynamic process** - the path of succession of states through which the system passes in moving from an initial state to a final state.
* **polytropic process** - a thermodynamic process for which . These processes are usually associated only to systems for which the ideal gas assumption holds.

**Four special polytropic processes**:

1. isobaric process done at constant pressure, (Δ*P* = 0). []
2. isothermal process done at constant temperature , (Δ*T* = 0). []
3. isentropic process done at constant entropy []
4. isochoric (isometric) - process done at constant volume, (Δ*V* = 0). []

**Two other important processes**:

1. adiabatic - no heat transfer, (Δ*Q* = 0).
2. isenthalpic - constant enthalpy. This is the same as isothermal for an ideal gas system.
* ***A reversible process*** – an *idealized* process in which the deviation from thermodynamic equilibrium is infinitesimal at any particular instant during the process. All of the states through which a system passes during a reversible process may be considered to be equilibrium states. This is an *idealized* situation that would require infinite time and/or equipment size to be realized. The concept of a reversible process serves to set a maximum for the efficiency of a given process. Note that an *isentropic* process is an adiabatic-*reversible* process, so that real *isentropic* processes are not possible.
* ***Irreversible***: if the process cannot be reversed (like most processes).
* **Thermodynamic cycle:** a process for which the final and initial states are the same.

**Four common ‘*idealized*’ thermodynamic cycles**:

1. **Carnot cycle** - isothermal and isentropic compressions followed by isothermal and isentropic expansions.
2. **Rankine cycle** - isobaric and isentropic compressions followed by isobaric and isentropic expansions.
3. **Otto cycle** - isentropic and isochoric compressions followed by isentropic and isochoric expansions.
4. **Diesel cycle** - isentropic compression followed by isobaric, isentropic and isochoric expansions

**Thermodynamic Laws**

A physical law is a simple statement of an observable physical phenomenon that has no underlying, more-basic reason for being except that the most accurate observations have always proved it to be true.

**Laws of Thermodynamics**

**Zeroth**: Two bodies in thermal equilibrium with a third body are in thermal equilibrium with each other. (This Law? simply states that ‘thermometers work’.)

**First law**: has to do with conservation of energy; “The total energy of an isolated system must remain constant, although there may be changes from one form of energy to another”. If we designate the total or internal energy of an isolated or closed system as *U*, heat as *Q* and work as *W*, then the circular integral involving no change in net internal energy is:

 (1)

where work and heat are not exact differentials because they depend on path and are not state functions.

If the system is closed to the input of matter, but not of energy, then

  (2)

Mechanical work is, of course only the product of force x distance and force is pressure *P* x surface area, so mechanical work is simply the product of pressure x surface area x distance, or *PV*. At constant pressure:

(3)

Substituting in Eq. 2 yields the most common form of the first law of thermodynamics:

 (4)

In other words, you can't win -- energy cannot be created, only converted from one form to another.

**A Simple Statement**: Heat and work are both forms of energy in transit, and energy is always conserved. **or**

**A Classical Statement**: During any cyclic process on a closed system the cyclic integral of heat is always equal to the cyclic integral of work.

**Enthalpy**

The enthalpy or heat content is defined as:

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| --- | --- |
| *H = U + PV* | (5) |

It's clear from this relationship that enthalpy is the sum of two energy terms. Differentiating (5) at constant pressure:

|  |  |
| --- | --- |
| *dH = dU+PdV* | (6) |

and from (4) *,* we have

|  |  |
| --- | --- |
| *dH = dQ* | (7) |

which shows that at constant pressure, the change in enthalpy is governed by the added work performed on the system.

**Second law**: There are several nearly equivalent statements of *the second law* but ultimately all boil down to statements about entropy. The extensive state function entropy is an increasing function of energy. Entropy obeys Clausius Inequality in the form

 

where the equality sign is for a reversible process. The success of second law of thermodynamics is of course in the introduction of free energies

**Simple Statement #1**: Spontaneous fluxes always take place down their corresponding potential gradients. **or**

**Simple Statement #2**: Heat and work are both forms of energy in transit, but they are not qualitatively equal forms of energy because work can always be converted entirely into heat, but heat can never be converted entirely into work. **or**

**Kelvin-Plank Statement**: It is impossible to construct a device which operates in a cycle and produces no effect other than the raising of a weight and the exchange of heat with a single reservoir. **or**

**Clausius Statement**: It is impossible to construct a device which operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.

Albert Einstein considered the Second Law of Thermodynamics to be the **only** real physical law.







**Third law**: in simple statement “Entropy of a perfectly crystalline substance is zero ate absolute zero”.

However, it is the third law that allows calculation of entropy



We can find temperature dependence of the specific heat in the form of a series in *T* in many handbooks and these expansions are widely used by Geologists, Metallurgists and Chemical Thermodynamics researchers in the evaluation of free energy.

**Nerst’s** **statement**: *All reactions in a* ***pure******liquid or solid*** *in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero*.

 

where the subscripts 1 and 2 refer to the initial and final states, respectively.

**Planck’s** **statement**: *The entropy of a true equilibrium state of a system at absolute zero is zero*. It is applicable to all condensed phases, including solutions

 

**Unattainability** **statement**: *It is impossible to reduce the temperature of a system to absolute zero using a finite number of processes.*

**Important notes**:

1. As the entropy of a substance is a measure of randomness or disorder, *So = 0* implies a highly order (maximum order) state of matter.
2. This law applies to perfect crystalline substance only. Unfortunately, perfect crystalline substances are difficult to identify.
3. A glass or amorphous substance is not completely ordered even at the absolute zero of temperature. Therefore, any disorder remaining at the absolute zero of temperature gives a finite value of *So*.

**Consequences of the third law**:

1. For all known solids, the expansivity approaches zero as the temperature approaches absolute zero.

 .

1. The slope of the boundary between two phases is zero at absolute zero.

 .

1. The heat capacities approach zero as the temperature approaches absolute zero.

 .

**Other Laws of Importance in Thermodynamics**

**Conservation of Matter**: Matter can be neither created nor destroyed but only changed from one form to another. Note that Albert Einstein showed that matter could be ‘destroyed’ by converting it into energy.

**Joule's Law**: The internal energy of an ideal gas is a function of temperature only.

**Avagadro's Law**: Equal volumes of different ideal gases at the same temperature and pressure contain the same number of molecules.

**Thermodynamic potentials (summary)**

|  |  |  |  |
| --- | --- | --- | --- |
| Thermodynamic potential | Independent variables | Reciprocity relations | Maxwell relations |
| Internal energyU | *S,V**dU = TdS - PdV*  |  |   |
| Enthalpy*H =U+PV* | *S,P**dH = TdS + VdP*  |  |  |
| Helmholtz function*F =U – TS* | *T,V**dF = – SdT – PdV* |  |   |
| Gibbs function*G =U – TS+PV* *=H – TS*  *= F+PV* | *T,P**dG = – SdT + VdP* |  |   |
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| Adiabatic |  |  |  |

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| --- | --- | --- | --- |
| Theromdynamic functions | Notation | Independent variables | Differential |
| Internal energy |  |  |  |
| Heat function (enthalpy) |  |  |  |
| Helmholtz free energy |  |  |  |
| Gibbs free energy |  |  |  |
| Landau free energy |  |  |  |

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1. In thermodynamics, the **Helmholtz free energy** is a thermodynamic potential that measures the “useful” work obtainable from a closed thermodynamic system at a constant temperature.

**Gibbs Free Energy (G)** - The energy associated with a chemical reaction that can be used to do work.  The free energy of a system is the sum of its enthalpy (H) plus the product of the temperature (Kelvin) and the entropy (S) of the system:



The Gibbs free energy is defined as:



which is the same as:



where:

* *U* is the [internal energy](https://en.wikipedia.org/wiki/Internal_energy) (SI unit: [joule](https://en.wikipedia.org/wiki/Joule))
* *p* is [pressure](https://en.wikipedia.org/wiki/Pressure) (SI unit: [pascal](https://en.wikipedia.org/wiki/Pascal_%28unit%29%22%20%5Co%20%22Pascal%20%28unit%29))
* *V* is [volume](https://en.wikipedia.org/wiki/Volume_%28thermodynamics%29) (SI unit: m3)
* *T* is the [temperature](https://en.wikipedia.org/wiki/Temperature) (SI unit: [kelvin](https://en.wikipedia.org/wiki/Kelvin%22%20%5Co%20%22Kelvin))
* *S* is the [entropy](https://en.wikipedia.org/wiki/Entropy) (SI unit: joule per kelvin)
* *H* is the [enthalpy](https://en.wikipedia.org/wiki/Enthalpy) (SI unit: joule)

More relations (just for your information):

* , 
* ,

To Prove that ,

use  which implies ,

and use Maxwell’s equation, one can gets 

To Prove that , use  which implies , and use Maxwell’s equation, one can gets 

To Prove  use  which implies

,

then



To Prove  use  which implies



,

then



To calculate



To calculate



* *Postulate 1: For a system in equilibrium all microstates are equally probable.*
* *Postulate 2: The observed macrostate is the one with the most microstates.*