MSE-204 Thermodynamics for Materials Science

L1. THERMODYNAMICS LAWS & THEIR MEANING

DEFINITION OF THE SYSTEM | THERMODYNAMIC VARIABLES | 0TH, 1ST LAW | HEAT, WORK | 2ND LAW, ENTROPY, 3RD LAW

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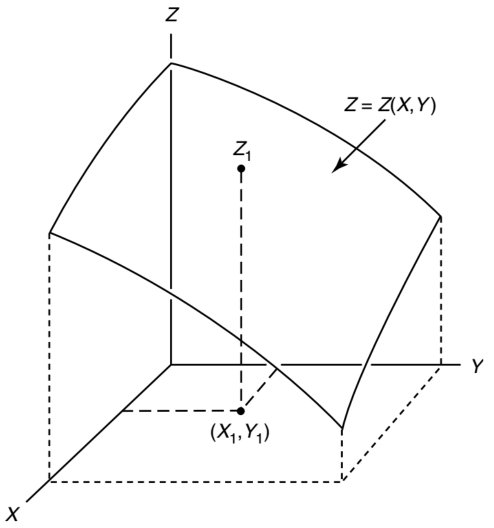
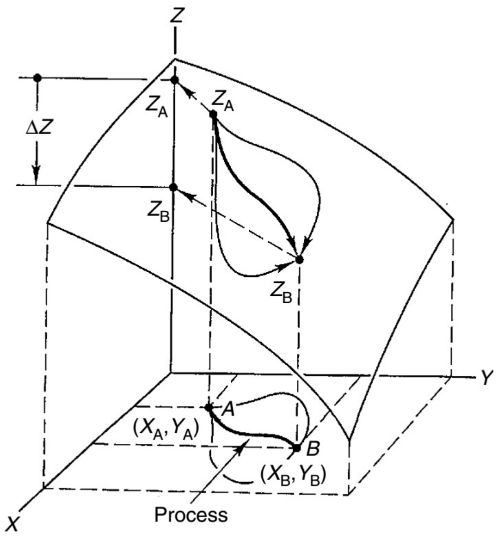
LET'S DEFINE THE SYSTEM

System	**Exchange with the environment**		

THERMODYNAMIC VARIABLES: STATE FUNCTIONS

A state function is a property of a system that has a value that depends upon the current condition of the system and not upon how the system arrived at that condition.

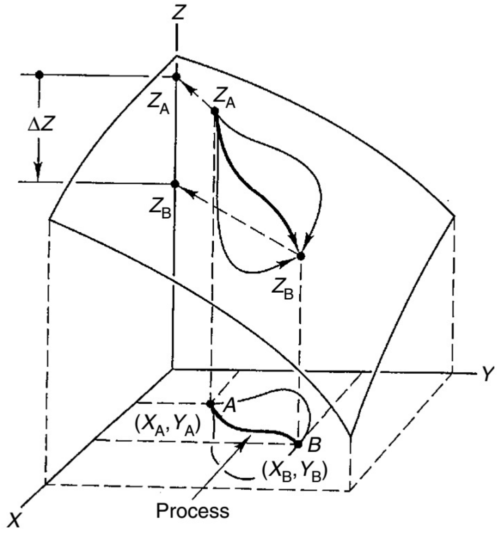




The fact that such state functions exist makes thermodynamic analysis powerful. The change in any state function for any process is always simply its value for the final state minus its value for the initial state. Thus, the change in any state function must be the same for every process that converts the system from the same initial state A to the same final state B

THERMODYNAMIC VARIABLES: PROCESS FUNCTIONS

In contrast to the notion of state functions, process variables are quantities that only have meaning for changing systems. Their values for a process depend explicitly upon the path, the specific sequence of states transversed, that takes the system from state A to state B.



EXTENSIVE PROPERTIES

Extensive properties depend upon the size or extent of the system when it is divided without changing its equilibrium state.

INTENSIVE PROPERTIES

An intensive property has the same value in different subdivisions of the system.

In a comparison of two systems, which have identical intensive properties, doubling the quantity of matter doubles all extensive properties.

Type of Processes That Can Happen to a System

A process is a succession of changes of the state of the system. Common processes are given special names, mainly based on the Greek isos (ίσος) meaning equal.

Possible system processes	

CLASSICAL THERMODYNAMICS OBEY THE FOLLOWING LAWS

Law	**Function of State**	**Characteristic**

The foundations of thermodynamics are three facts of ordinary experience:

1. bodies are at equilibrium with each other only when they have the same degree of hotness
2. the impossibility of perpetual motion
3. the impossibility of reversing any natural process in its entity

TEMPERATURE & THE ZEROTH LAW

It is a fact of experience that if bodies A and B are in thermal equilibrium with a third body C, they are also in thermal equilibrium with each other.

Microscopically the material particles will continue their complex motion, but MACROSCOPICALLY the thermal equilibrium state is reached and if the system is isolated, the final state cannot change.

INTERNAL ENERGY & THE FIRST LAW

Three broad categories of energy have been identified in scientific experience:

1. Kinetic energy, which is associated with the motion, translation or rotation, of a particle or body and nothing else.
2. Potential energy, which is associated with the position of a particle or body in a potential field and nothing else.
3. Internal energy, which is associated with the internal condition of the body and **does not otherwise depend upon its motion or position in space**.

Let U be a thermodynamic state function called the internal energy of the system. For any process, define ΔU to be the change in the internal energy of the system, given by:

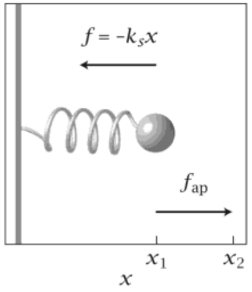
HEAT

The change of internal energy can be obtained without performing work. Therefore, there is a mode of energy transfer between bodies different from work.

The amount of heat transferred to a body can be determined in mechanical units only by measuring the amount of work which causes the same change of state.

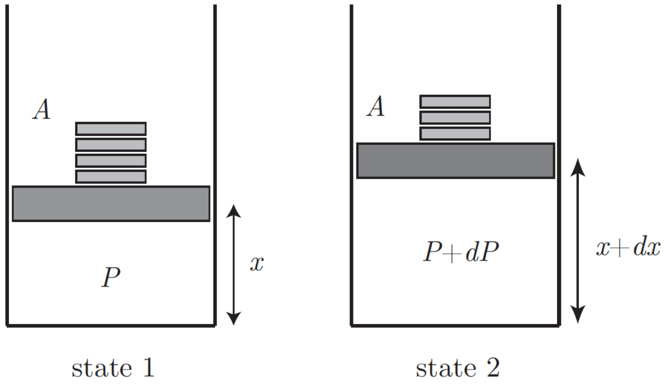
WORK

Based on Newtonian physics, the work is done by a force *F* moving through a distance *x* is:



WORK | Example: Work for a compressive substance

Consider the process in the schematic. In state 1 we have a material at pressure p confined in a cylinder of cross-sectional area A. The height of the piston in the cylinder is x. The pressure force of the material on the piston is just balanced by weights on top of the piston. Now remove one of the weights and wait so the system comes to rest at its new equilibrium. Let us calculate how much work was done.



WHAT TYPES OF WORK ARE POSSIBLE?

Types of Work	Thermodynamic ”Force”	Change in system’s Extent ”dx” in to this ”Force”

REVERSIBLE VS IRREVERSIBLE PROCESSES

Changes that can take place in a system spontaneously are called natural processes. This includes all processes which can occur spontaneously within an adiabatic enclosure.
Such changes cannot be reversed in their entirely because we know from experience that the system can be restored to its original condition ONLY by transferring a quantity of heat (or work) elsewhere.

Therefore, natural processes are…

Let’s consider a cycle:

QUASI-STATIC, REVERSIBLE PROCESSES

Let’s consider the following process:

ADIABATICALLY IMPOSSIBLE PROCESSES

It is impossible to make a heat transfer from a cooler body to a warmer body. We never observe this as a spontaneous event.

State A	**State B**
Two equal blocks of copper are connected by a wire. One block is at 20ºC and the other at 30ºC	Two blocks are at 25C
A dilute gas occupies ½ of an adiabatically enclosed vessel & another dilute gas occupies the other half. Both are at a temperature T	The gases are uniformly mixed throughout the vessel and the temperature has the same value
An adiabatically enclosed vessel contains hydrogen and oxygen and a catalyst. The volume is V and the temperature is T	The vessel contains the same amount of hydrogen and oxygen, combined as water, together with the catalyst. The volume is V and the temperature exceeds T by an amount corresponding to the heat of reaction

SECOND LAW

Under a given set of conditions, a system can be imagined to undergo several processes in which the energy is conserved (first law). However, it is common experience to observe that the only processes which occur are those which bring the system to a state of rest, i.e. to a state of equilibrium. By considering that this state of equilibrium is a property of the system, thus this state can be described by a function, the second law of thermodynamics determines the direction and extent of such processes. **It affirms the existence of a state function, the entropy S, which for all reversible processes is defined by:**

and for all irreversible processes is such that:

Specifically stated, in every volume element of every system and surroundings that may be experience change, the entropy production is positive. HOWEVER, this does not imply that the entropy of a system can only increase.

RELATIONSHIP BETWEEN ENTROPY TRANSFERRED AND HEAT ABSORBED

A quantitative treatment of entropy transfer for reversible processes establishes a connection between the reversible heat flow across the boundary of the system and its change in entropy. The argument applies to any system that is taken through a reversible process.

Let δq_{rev} be the heat absorbed by the system during an infinitesimal step in the reversible process. The system is at temperature T. The differential form $\frac{\delta q_{rev}}{T}$ has units J/K. The sum of the values of this differential form is the sequence of states traversed for the process. The sum has the mathematical form of a line integral along the path:

$$\oint \frac{\delta q}{T}$$

The consequence is that although δq_{rev} is a path-dependent variable ,$\frac{\delta q_{rev}}{T}$ is the differential of a state function.

The state function is then defined to be the entropy of the system:

$$\delta q_{rev} = T dS_{syst} \text{ and } q_{rev} = \oint T dS_{syst}$$

which permits the computation of the heat absorbed for any reversible process by integration of the combinations of the state functions of temperature and entropy

EQUIVALENT STATEMENTS OF THE SECOND LAW

Clausius:

Heat never spontaneously flows from an object of lower temperature to one of higher temperature

Kelvin:

It is impossible to continuously perform work by cooling a body to a temperature below that of the lowest temperature of its surrounding

Kelvin:

Using a system which undergoes a cyclic thermodynamic process, it is impossible to obtain usable work if globally heat is only exchanged with one thermal reservoir

Ostwald:

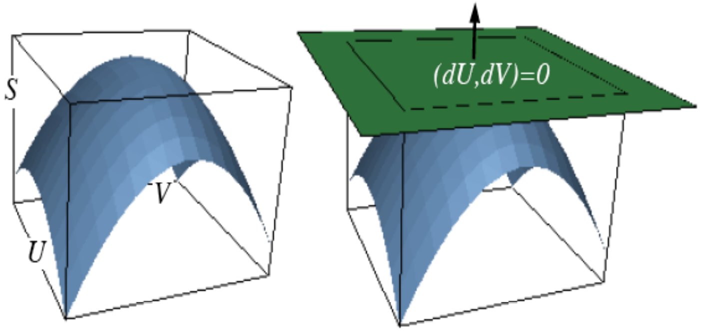
A perpetual motion machine “of the second type” has never been observed

Caretheodory:

In the neighborhood of every thermodynamic state that can be reached by a reversible path, there exists states which cannot be reached along a reversible adiabatic path (isentropic), or which can be reached either irreversibly or not at all

ENTROPY CONDITION FOR EQUILIBRIUM

In the equilibrium state of a process, the entropy is a maximum. Any variation about the equilibrium state can only decrease the entropy.

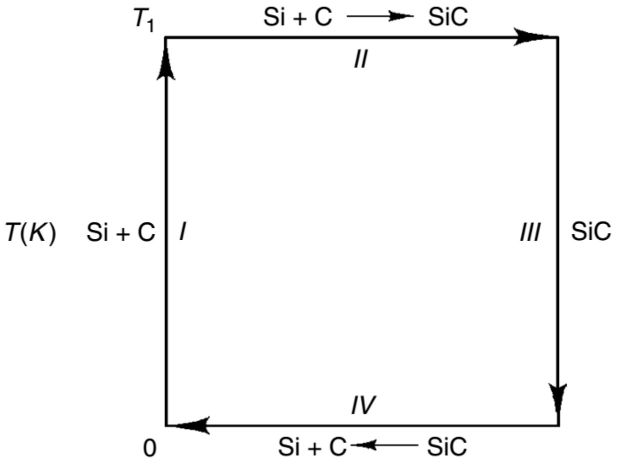


In general for systems of constant internal energy and volume, the condition of equilibrium is the attainment of the maximum entropy.

THIRD LAW

Near the turn of the last century, experiments studying the behavior of matter at very low temperatures established that there is a lower limit to the temperature that matter can exhibit.

To illustrate the principle, consider the following cyclic process. A system consisting of one mole of pure silicon and one mole of carbon is initially at temperature zero, and is then heated from 0 to 1500 K.



The third law of thermodynamics states:

> There exists a lower limit to the temperature that can be attained by matter, called the absolute zero of temperature and the entropy of all substances is the same at that temperature.

ENTROPY | Example: Hot bodies in contact

Consider the passage of heat from a hot body to a cold one, with no other work being performed. Consider two very large bodies, one at T=400K and the other at T=300K.

Case 1: Suppose 400 Joules of heat are transferred from hot object A to the cooler body B

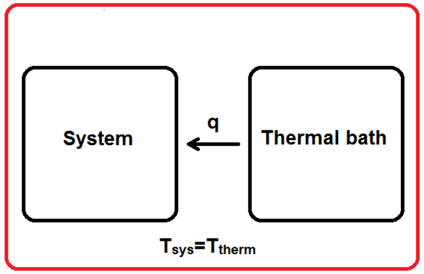
Case 2: Suppose 400 Joules of heat are transferred from cold object B to the hotter body A

ENTROPY IMPLICATIONS: SPONTANEITY

We now consider a closed adiabatic system. We assume this system evolves spontaneously and adiabatically from initial state I to final state F. Let us know imagine a reversible, isothermal process that brings the system back from state F to state I. During this part of the process, the system can eventually exchange heat with a thermal reservoir. The first law for the total process states:

HEAT ABSORBED IN REVERSIBLE VS IRREVERSIBLE PROCESSES

We investigate next an infinitesimal process of a closed system. This system can exchange heat with only one thermal reservoir at temperature T_{therm}. The global system is a closed adiabatic system. The system receives an amount of heat and since the global system is adiabatic, the amount of heat received by the thermal reservoir is:



Closed, adiabatic boundary