

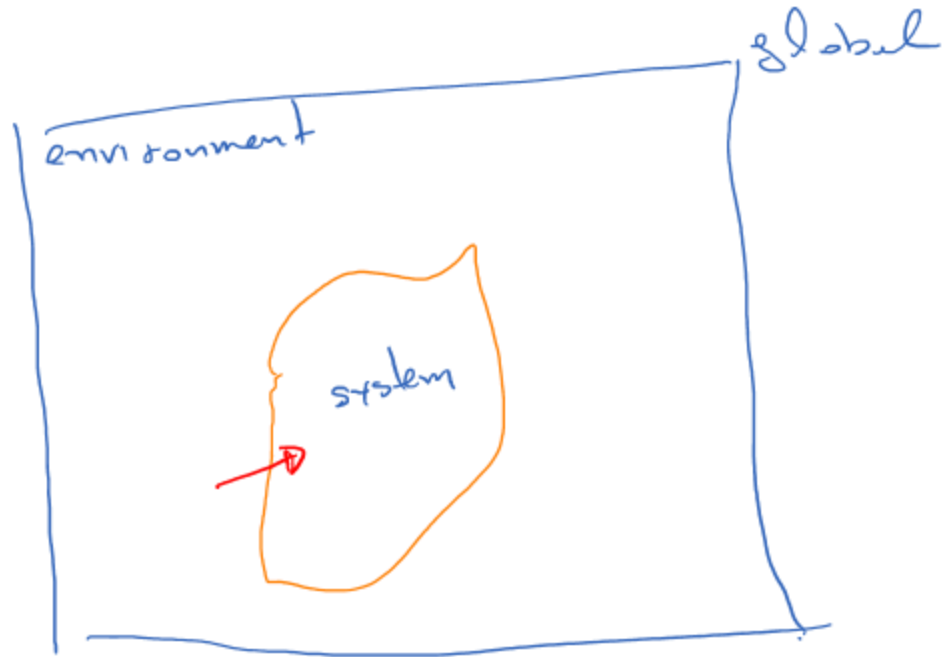
MSE-204 Thermodynamics for Materials Science

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: TD system: a quantity that has a mass
environment: everything external to the TD system

universe: environment + TD system

interface / boundary: separates env. with TD system

maybe: yes: interface is diathermal

no: " is adiabatic

System	Exchange with the environment		
	Mass	Heat	Work
Isolated	x	x	x
Closed	x	Maybe	✓
Open	✓	✓	✓

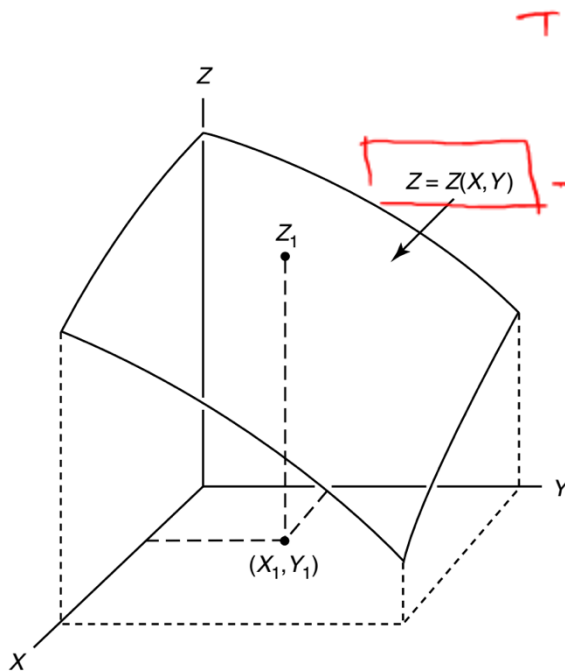
Sign Convention:

if I put work into the system $w > 0$

if I put heat into the system $q > 0$

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.



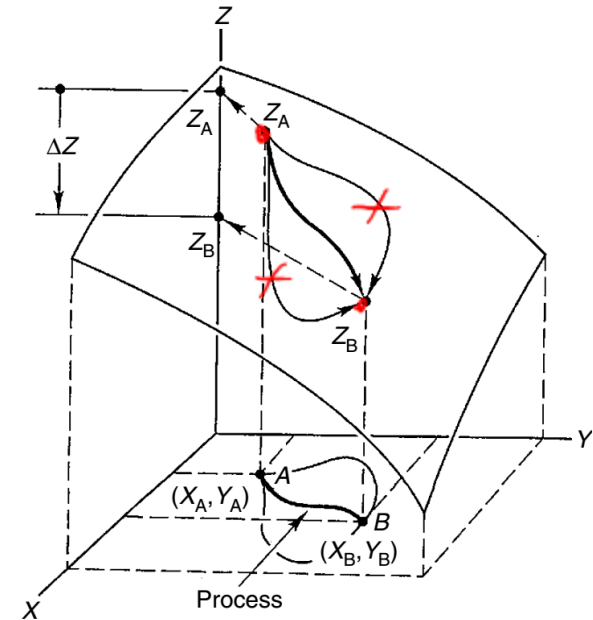
T, P, S, U, V

$z = z(x, y) \rightarrow$ all three are state functions

$$\Delta z = z_B - z_A$$

$A \rightarrow B \rightarrow A$ (cyclic process)

$$\oint dz = \int_A^B dz + \int_B^A dz = 0$$



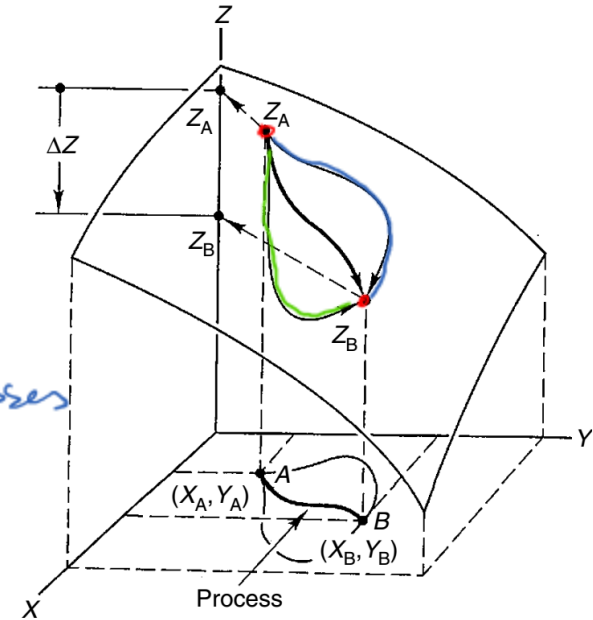
The fact that such state functions exist makes thermodynamic analysis powerful. The change in any state function for any process is always simply its value for the final state minus its value for the initial state. Thus, the change in any state function must be the same for every process that converts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

w, q

$\int dw$: change of work } inexact differentials
 $\int dq$: change of heat } path-dependent processes



EXTENSIVE PROPERTIES

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

$$S, V, U$$



$$T_A, P_A, V_A$$

$$\Rightarrow T_A = T_B = T_C \text{ : intensive}$$

$$P_A = P_B = P_C \text{ : intensive}$$

INTENSIVE PROPERTIES

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

$$T, P$$



$$T_B, P_B, V_B \quad T_C, P_C, V_C$$

divide in the middle by a non-permeable membrane

$$V_B = V_C = \frac{1}{2} V_A \text{ extensive}$$

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

$$[\text{intensive}] [\text{extensive}] = \text{work (energy)}$$

$$P \cdot V$$

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 (ἴσος) meaning equal.

Possible system processes	
isothermal	$dT = 0$ or $T = \text{constant}$
isochoric	$dV = 0$ or $V = \text{constant}$
isobaric	$dp = 0$
isobarochoric	$dV = 0$ & $dp = 0$
adiabatic	$\delta q = 0$ or $q = \text{const.}$
isentropic	$dS = 0$ or $S = \text{constant}$

CLASSICAL THERMODYNAMICS OBEY THE FOLLOWING LAWS

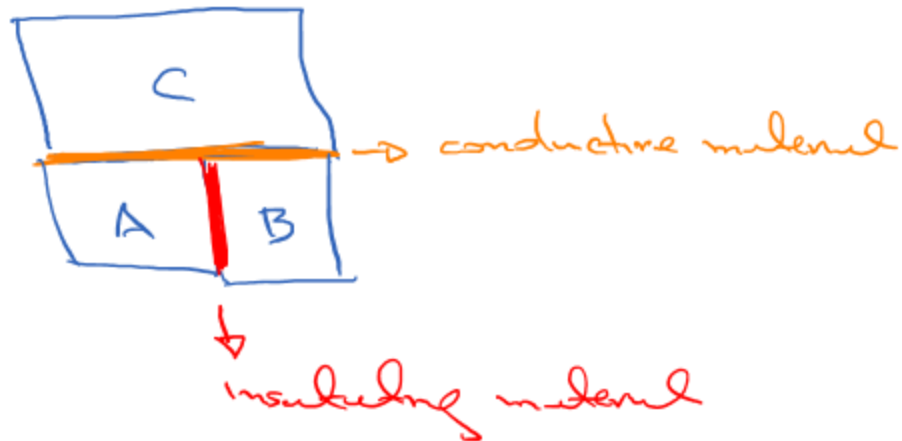
Law	Function of State	Characteristic
0th	T	defines the thermal equilibrium
1st	U (internal en.)	conservation of energy
2nd	S (entropy)	determines the spontaneity of the process
3rd	T	defines the absolute T range, absolute 0, or T is always positive

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 entirety

TEMPERATURE & THE ZEROETH 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.



$$\left. \begin{array}{l} T_A = T_C \\ T_C = T_B \end{array} \right\} T_A = T_B$$

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:

$$\Delta U = w + q$$

Sign Convention

if an adiabatic process $q = 0$

if $\Delta U > 0$ $w > 0$

$$dU = \delta w + \delta q \quad \Rightarrow \quad \underline{\text{1st Law}}$$

if we have a workless process $\delta w = 0$

if $dU > 0 \Rightarrow \delta q > 0$

HEAT

workless transfer of energy

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

$$q = -k \nabla T$$

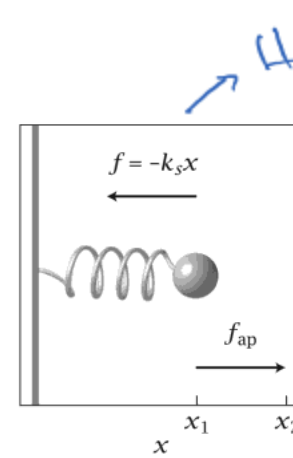
↘ gradient of T
↘ thermal conductivity

heat flows from high T to low T

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:

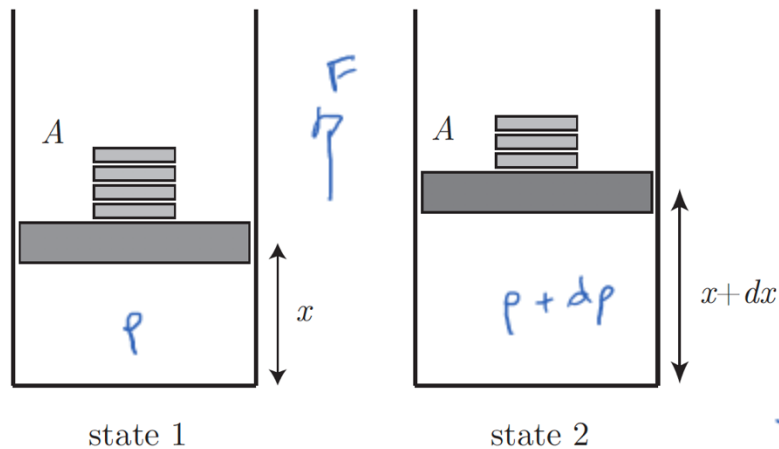


$$f_{ap} = -f$$

$$S_w = f_{ap} dx = -f dx$$

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.



$$S_w = -F dx$$

$$\text{state 1: } \underline{F_1} x$$

$$\text{state 2: } F_2 (x + dx)$$

$$F_1 = p A$$

$$F_2 = (p + dp) A$$

$$\text{approximately: } F = \frac{1}{2} (F_1 + F_2) = p A + \frac{1}{2} dp A$$

$$S_w = -F dx = -\left(p A + \frac{1}{2} dp A\right) dx$$

$$S_w = -\underline{p A} dx = -p dV$$

WHAT TYPES OF WORK ARE POSSIBLE?

Types of Work	Thermodynamic "Force"	Change in system's Extent "dx" in to this "Force"
Pressure work	P	dV
Electric work	\vec{E}	$d\vec{D} \rightarrow$ displacements
Magnetic work	\vec{H}	$d\vec{B} \rightarrow$ induction
Surface energy work	γ	$dA \rightarrow$ surface / Area
Chemical work	μ	$dn \rightarrow$ moles

μ
↑
chemical potential