MSE-204 Thermodynamics for Materials Science

L1. THERMODYNAMICS LAWS & THEIR MEANING (CONT'D)

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

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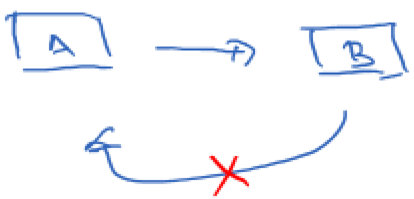
REVERSIBLE VS IRREVERSIBLE PROCESSES

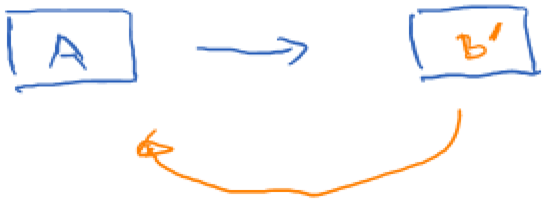
Changes that can take place in a system spontaneously are called natural processes. This includes all processes which can occur spontaneously within an adiabatic enclosure.
Such changes cannot be reversed in their entirely because we know from experience that the system can be restored to its original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

Therefore, natural processes are… irreversible

Let's consider a cycle:



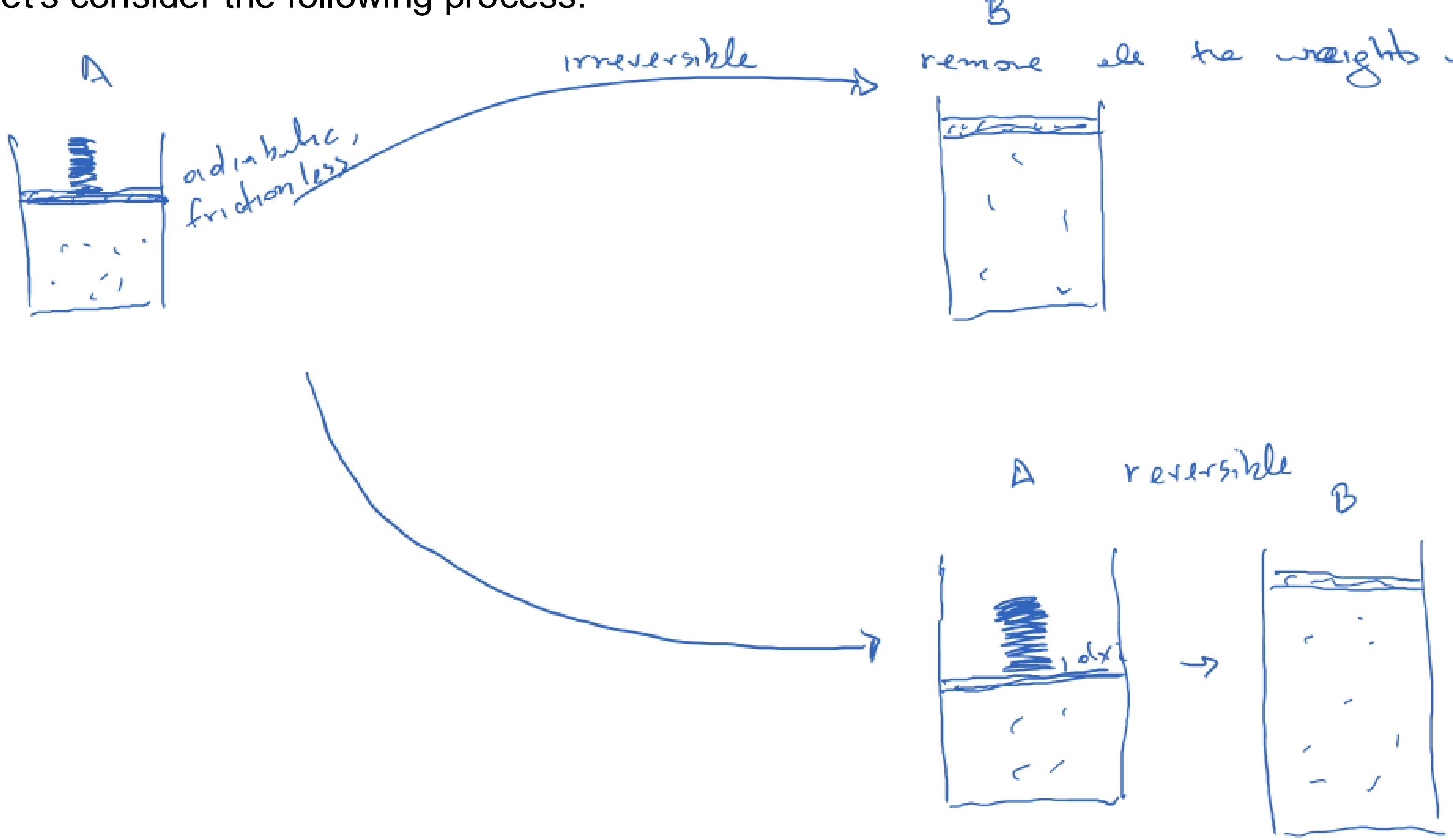
if the process is irreversible
we cannot close the cycle
unless there is a change
somewhere else



reversible process

QUASI-STATIC, REVERSIBLE PROCESSES

Let's consider the following process:



remove all the weight at once

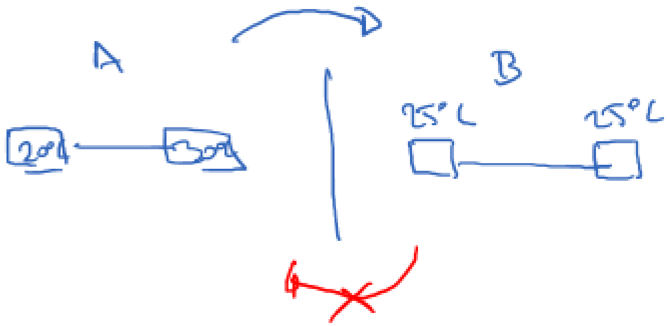
quasistatically
where equilibrium is
kept at all times
where removing
dx_i parts of the weight

yields the max work

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, 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 the change in entropy is defined by:**

$$dS \equiv \frac{\delta q_{rev}}{T}$$

when we have an adiabatically enclosed system

$$(\Delta S_{glob})_{rev} = 0$$

and for all irreversible processes is such that:

$$dS > \frac{\delta q_{irr}}{T}$$

$$(\Delta S_{glob})_{irr} > 0$$

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:

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

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:

$$\boxed{\underline{\delta q_{rev}}} = \underleftarrow{T dS_{syst}} \text{ and } q_{rev} = \int T dS_{syst}$$

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:

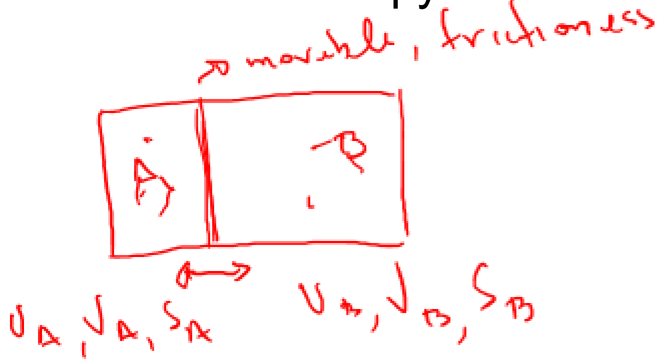
A perpetual motion machine “of the second type” has never been observed

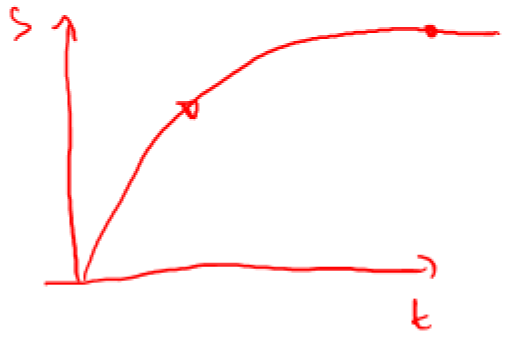
Caretheodory:

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

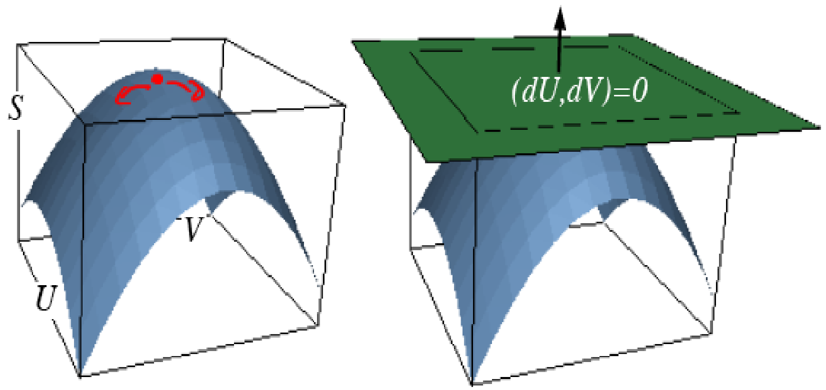
ENTROPY CONDITION FOR EQUILIBRIUM

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





any spontaneous process moves uphill on the entropy surface



$\delta S_{\delta U=\delta V=0} \leq 0$ criterium for equilibrium according to the second law

small changes

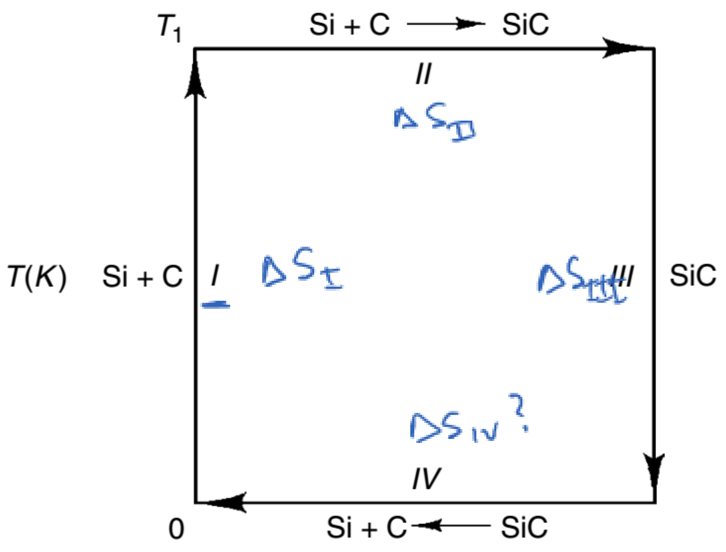
In general, for systems of constant internal energy and volume, the condition of equilibrium is the attainment of the maximum entropy.

$0 K = - 273.15 C$

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.



$$\Delta S_{tot} \overset{cycle}{=} 0$$

$$\underbrace{\Delta S_I + \Delta S_{II} + \Delta S_{III}}_{\substack{known \\ \| \\ 0}} + \Delta S_{IV} = 0$$

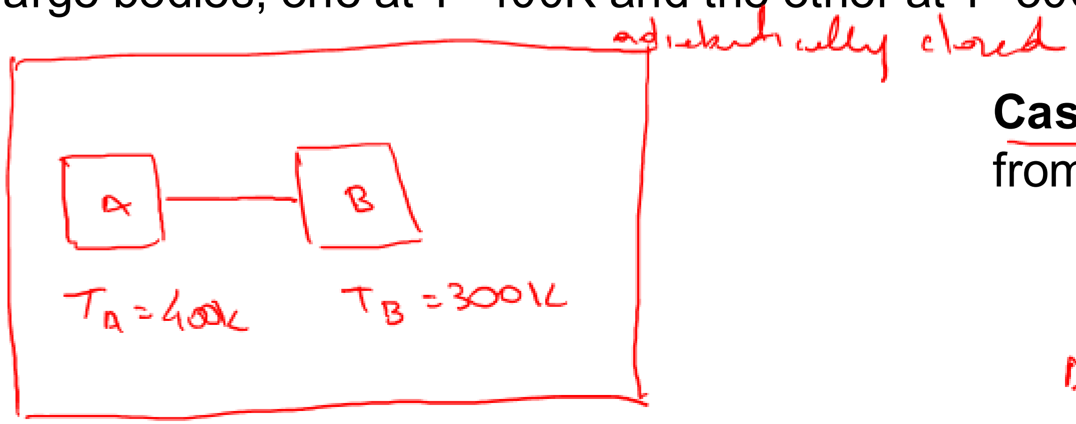
$$\Rightarrow \Delta S_{IV} = 0$$

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

$q_A = -400J$ $\qquad$ $q_B = 400J$

$$\Delta S_{glob} = \Delta S_A + \Delta S_B = \frac{q_A}{T_A} + \frac{q_B}{T_B} = -1 + \frac{4}{3} \Rightarrow$$

$$\Delta S_{glob} = +\frac{1}{3} J/K$$

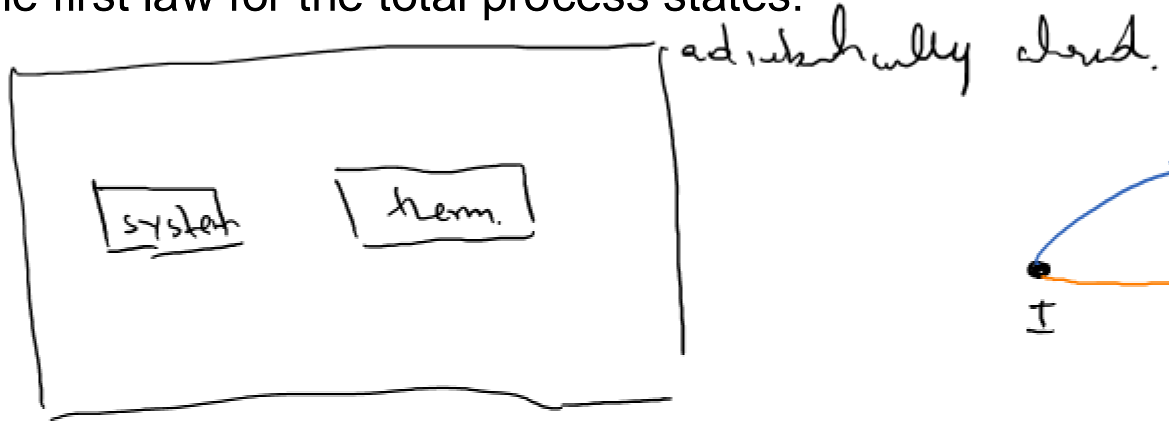
Case 2: Suppose 400 Joules of heat are transferred from cold object B to the hotter body A

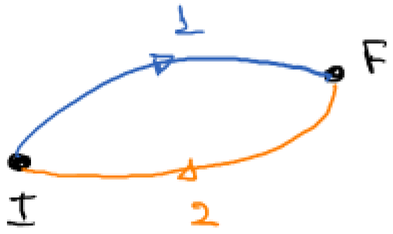
$q_A = 400J$ & $q_B = -400J$

$$\Rightarrow \cancel{\Delta S_{glob} = -\frac{1}{3} J/K}$$

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:





process 1 : irreversible, adiabatic $q_1 = 0$

process 2 : reversible, isothermal $\boxed{q_2 <}$

Total process, cyclic, irreversible

II Law (Kelvin) : $w > 0$

I Law : $\Delta U_{tot} = q + w \overset{cycle}{=} 0$

$$\Delta S_2 = \frac{q_2}{T} < 0$$

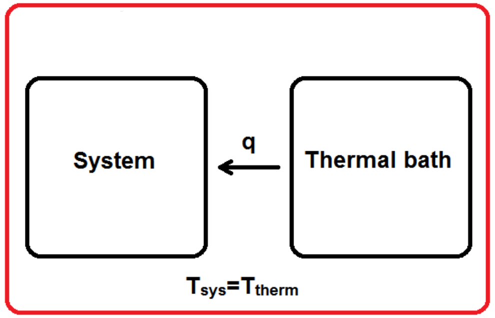
$$\Delta S_{tot} = \Delta S_1 + \Delta S_2 \overset{cycle}{=} 0$$

$$\Rightarrow \underline{(\Delta S_1)_{\text{irreversible process}} > 0}$$

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:

$$\delta q_{ther} = -\delta q_{sys}$$



Closed, adiabatic boundary

Thermal reservoir: $dS_{therm} = \dfrac{\delta q_{therm}}{T_{therm}} \overset{(1)}{=} -\dfrac{\delta q_{sys}}{T_{therm}}$

Globally: $dS_{glob} = dS_{sys} + dS_{therm} \overset{(1)}{=} dS_{sys} - \dfrac{\delta q_{sys}}{T_{therm}}$

$$\Rightarrow \boxed{\delta q_{sys} = T_{thermal}\, dS_{sys} - T_{thermal}\, dS_{glob}}$$

If the process is reversible $\Rightarrow dS_{glob} = 0 \Rightarrow (\delta q_{sys})_{rev} = T_{thermal}\, dS_{sys}$.

If the process is irreversible $\Rightarrow dS_{glob} > 0 \Rightarrow (\delta q_{sys})_{irr} < T_{thermal}\, dS_{sys}$

$$\Rightarrow (\delta q_{sys})_{irr} < (\delta q_{sys})_{rev}.$$