

# Thermodynamics

- Thermodynamics answers the following question:
- For any reaction - defined by a set of reactants and products set in exactly defined conditions (temperature, pressure, concentration, etc.) → will that reaction go forward spontaneously or not??
- It can address ANY geochemical reaction, if thermo says NO, rest assured the reaction will not proceed, if thermo says yes, then we can progress to the next question → how fast?

# Thermodynamics

- “the branch of science that deals with energy levels and the transfer of energy between systems and between different states of matter”

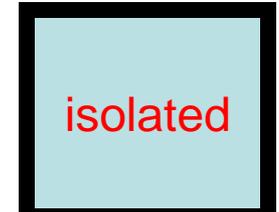
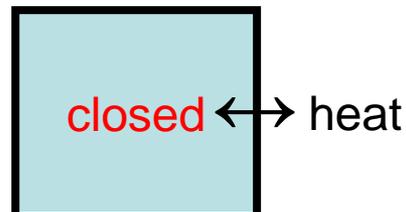
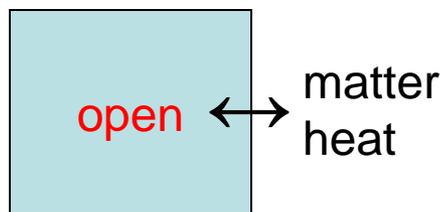
# What is Energy???

- **“It is important to realize that in physics today, we have no knowledge of what energy *is*. We do not have a picture that energy comes in little blobs of a definite amount. It is not that way.” –Richard Feynman**
- **HOWEVER → Feynman goes on to elaborate that energy has meaning as a way to define, and quantify, changes which bring about changes – between systems, energy levels, or states of matter – i.e. for any reaction**
- **“How seriously must we take the physical existence of this energy? No more and no less than any other bookkeeping practices.” –Richard Feynman**

- State - Refers to the energy content of a given system. The state is defined by specifying certain variables such as temperature, pressure, volume and composition.
- State Variables specifically refer to the change inherent if a reaction proceeds because of a change in state
- State variables are either extensive or intrinsic
- Extensive → variables which are proportional to the quantity of matter (such as volume)
- Intrinsic → variables which are independent of quantity, that instead describe the whole system (such as density, temperature, and concentration)

# Systems

- System – the PART of the universe that is under consideration. It is separated from the rest of the universe by it's boundaries
  - Open system → when matter CAN cross the boundary
  - Closed system → when matter CANNOT cross the boundary
  - Isolated → Boundary seals matter and heat from exchange with another system

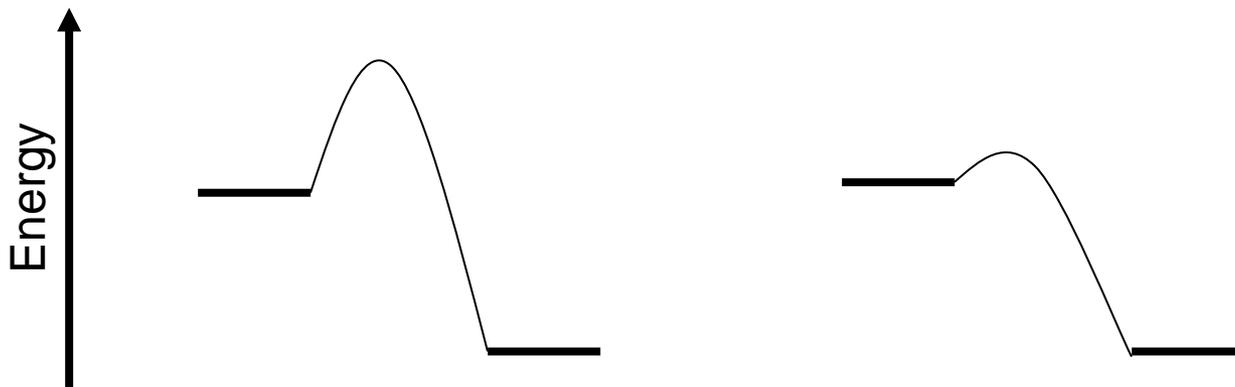


# Picking a system

- The investigator picks the system
- It can be as large or as small as you want it to be, proper definition of the system is important to address the reactions you want to
- Leaving out gases or sediments or melts or other can make a problem simpler/tractable or more inaccurate...

# Defining a system

- A system at equilibrium has measurable properties
- If the system changes from one equilibrium 'state' to another → these changes depend of the properties changed and not on the path (or exact process) the change went along



In thermodynamics, these 2 reactions are NOT different  
Example: Catalysis does not affect thermodynamic calculations!



# Processes

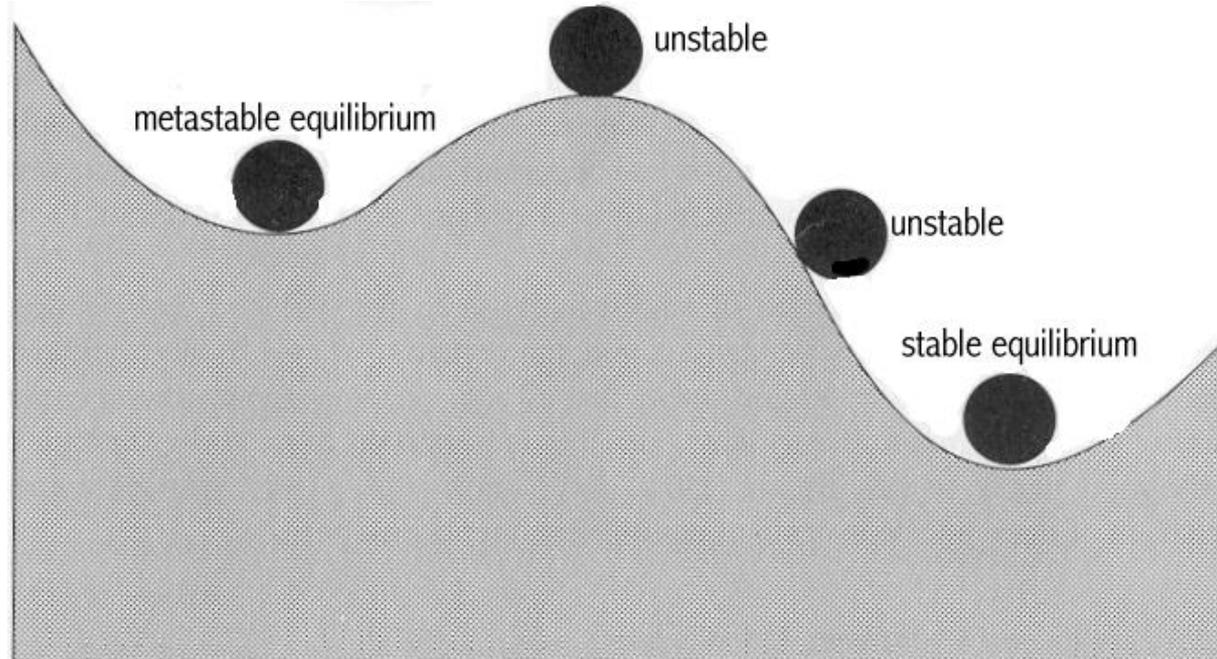
- The way a system changes states
  - Adiabatic → no heat exchange across boundaries of a system
  - Isobaric → constant pressure, but boundaries of the system can change (volume changes)

# Equilibrium/ Reversibility

- Anything at equilibrium is theoretically undergoing forward and reverse reactions:
- $A + B \leftrightarrow C$ 
  - $A + B \rightarrow C$  **AND**  $C \rightarrow A + B$
- Equilibrium has 2 criteria:
  - Reaction does not appreciably change in time
  - Perturbation of that equilibrium will result in a return to the equilibrium

# STABLE VS. METASTABLE EQUILIBRIUM

- Stable equilibrium - System is at its lowest possible energy level.
- Metastable equilibrium - System satisfies above two criteria, but is not at lowest possible energy.



# The historical perspective

- Benjamin Thompson, in 1798, proposed a link between work and heat generated from observing the boring of cannons
- Nicolas Carnot, in 1824, first proposed the concept of reversibility
- James Joule (a brewmaster), between 1840-1849 measured rising temperature from mechanical stirring – quantifying the relation between work and heat

# Heat

- The origin of thermodynamics dealt with heat
- Thermo considers heat, and really ANY energy as though it were an indivisible fluid, always flowing from higher to lower energies
- Ergo  $\rightarrow$  signs are + when energy flows from surroundings to the system and – when energy flows from system to surroundings

# Work

- Work is another kind of energy
- Different from heat
- Can flow in and out of a system and invoke changes
- Imagine the energy required to lift a book – that work changes the potential energy of the book, but is not related to heat...

# Internal Energy, $U$

- Changes in  $U$ ,  $dU$  or  $\Delta U$ , are + if energy of a system increases:
  - Energy here as heat  $\rightarrow$  heat added = +
  - Work done on the system  $\rightarrow$  +
  - Sometimes it has been formulated that work done BY a system is + in energy change  $\rightarrow$  not how we have it formulated above, difference in perspective..Be careful when reading other sources, this sign change confusion propagates through the rest of thermodynamics...

# Mechanical work description

- Work = force required to move a body x distance that body is moved

$$w = \int_{x_0}^x F dx$$

- Because  $F=PA$ , force= pressure per unit area

$$w = \int_{x_0}^x F dx = -(PA)(x - x_0) = -PdV$$

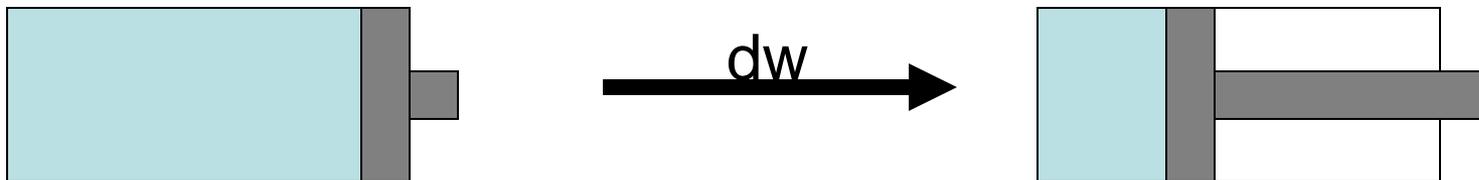
- This describes a piston's movement and potential 'energy'

# 1<sup>st</sup> Law of Thermodynamics

- Aka the Law of conservation of energy, Gibbs in 1873 stated energy cannot be created or destroyed, only transferred by any process
- The net change in energy is equal to the heat that flows across a boundary minus the work done BY the system
  - **$\Delta U = q + w$** 
    - Where q is heat and w is work
    - Some heat flowing into a system is converted to work and therefore does not augment the internal energy

# Work and the 1<sup>st</sup> Law...

- We can think about work as a function of pressure and volume
  - $dw = PdV$
- Where  $PdV$  is the incremental small change in volume at pressure associated with force x distance (dimensions of work)
- Restate the first law as:
  - **$dU = dq - PdV$**



# Energy change with volume and heat

- Taking  $dU = dq - PdV$  from state 1 to state 2:

$$\int_1^2 dU = \int_1^2 dq - P \int_1^2 dV$$

- Yields:  $U_2 - U_1 = (q_2 - q_1) - P(V_2 - V_1)$
- Make  $q_p = q_2 - q_1$ , multiply PV terms and rearrange:
- $q_p = (E_2 + PV_2) - (E_1 + PV_1)$
- $q_p$  is MEASURABLE – by measuring temperature changes resulting from energy changes (i.e. from a chemical reaction)

# Enthalpy (H)

- $H = U + PV$
- Total differential for Enthalpy is:
$$dH = dU + PdV + VdP$$
- For our integrated change in state previous:
- $H_1 = U_1 - PV_1$  and  $H_2 = U_2 - PV_2$ 
$$\Delta H = H_2 - H_1 = q_p \quad (\text{AT constant } P, V)$$
- Recall that energy is not known, only the change is meaningful
- Therefore change is measured from a reference state  $\rightarrow$  pure elements, 25°C, 1 bar pressure have an enthalpy of zero  $\rightarrow H_f^0$

# 2<sup>nd</sup> Law of Thermodynamics

- 2<sup>nd</sup> Law introduces entropy,  $S$

$$dS = \frac{dq}{T}$$

(reversible)

$$dS > \frac{dq}{T}$$

(irreversible)

- Some of the enthalpy in a system is not convertible into work (PdV work for instance) because it is consumed by an increase in entropy
- Which could be restated that it requires some amount of work to increase entropy

# NEED FOR THE SECOND LAW

- The First Law of Thermodynamics tells us that during any process, energy must be conserved.
- However, the First Law tells us nothing about in which direction a process will proceed spontaneously.
- It would not contradict the First Law if a book suddenly jumped off the table and maintained itself at some height above the table.
- It would not contradict the First Law if all the oxygen molecules in the air in this room suddenly entered a gas cylinder and stayed there while the valve was open.

# THE SECOND LAW IN WORDS

- However, experience tells us that certain processes only run spontaneously in one direction or the other. This allows us to deduce the Second Law.
- The Kelvin formulation - It is impossible to construct an engine that, working in cycles, shall produce no effect other than the extraction of heat from a reservoir and the production of work.
- The Clausius formulation - It is impossible to construct an engine that, working in cycles, shall produce no effect other than the transfer of heat from a colder to a hotter body.

# Directionality from the 2<sup>nd</sup> Law

- For any spontaneous irreversible process, entropy is always increasing

$$dS > \frac{dq}{T}$$

- How can a reaction ever proceed if order increases?? Why are minerals in the earth not falling apart as we speak??

# MEANING OF ENTROPY AND THE SECOND LAW

- Entropy is a measure of the disorder (randomness) of a system. The higher the entropy of the system, the more disordered it is.
- The second law states that the universe always becomes more disordered in any real process.
- The entropy (order) of a system can decrease, but in order for this to happen, the entropy (disorder) of the surroundings must increase to a greater extent, so that the total entropy of the universe always increases.

# Entropy quotes...

- "There is a great difference between energy and availability of energy...The availability of energy is always decreasing. This is... what is called the entropy law, which says the entropy is always increasing." – Richard Feynman
- "The thermodynamic sense of order decrease that is enshrined in the second law is at first sight in conflict with many of the complicated things that we see going on around us. We see complexity and order increasing with time in many situations: when we tidy up our office,... the evolution of complex life-forms from the simpler ones...

"In many of these cases, we must be careful to pay attention to all the order and disorder that is present in the problem. Thus the process of tidying the office requires physical effort on someone's part. This causes ordered biochemical energy stored in starches and sugars to be degraded into heat. If one counts this into the entropy budget, then the decrease in entropy or disorder associated with the tidied desk is more than compensated for by the other increases."

[Barrow](#) (1990)

- Combining the 1<sup>st</sup> and 2<sup>nd</sup> Laws of Thermodynamics:

$$dU = dq_{\text{rev}} + dw = TdS - PdV$$

- If a process is at constant volume,  $V$ , and entropy,  $S \rightarrow dU = 0 \rightarrow$  nothing happens, energy does not change in the system
- This is EQUILIBRIUM:
  - $dU > 0 \rightarrow$  spontaneous rxn products to reactants
  - $dU < 0 \rightarrow$  spontaneous rxn reactants to products

# Temperature

- In thermodynamics, temperature is **always** represented in Kelvins
- $K = ^\circ C + 273.15$

# The Fundamental Equation

- Combining the first and second laws yields:
  - **$dU = TdS - PdV$**
- This is a key step, but the next one is the cornerstone of most thermodynamic calculations...