First Law

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First Law of Thermodynamics

- **Postulate: internal energy is both**
  - **Extensive广延性** $E = E_1 + E_2$
  - **Conserved: If the energy of a system changes, it must be a result doing something to the system— that is allowing some form of energy to flow into or out the system**
- **This directly lead to the definition of heat**

$$dE = đQ + đW$$

- **This is the first law !**

- **EXTENSIVE**
- **A property is called extensive if its value for an overall system is the sum of its values for the parts into which the system is divided. Mass, volume, energy, and several other proper- ties introduced later are extensive. Extensive properties depend on the size or extent of a system.**

This equation is usually referred to as the first law. In it, $đW$ is the differential work done *on* the system (manipulating mechanical constraints), and $đQ$ is the differential heat flow into the system. The work term has the general form

$$đW = \mathbf{f} \cdot d\mathbf{X},$$

where $\mathbf{f}$ is the applied "force," and $\mathbf{X}$ stands for a mechanical extensive variable. A familiar example is

$$đW = -p_{\text{ext}}\, dV,$$

where V is the volume of a bulk system, and p_{ext} is the external pressure. As another example,

$$đW = f\, dL,$$

where here f is the tension applied to a rubber band and L is the length of that rubber band. In general, there are many mechanical extensive variables, and their changes involve work. The abbreviated vector notation, $\mathbf{f} \cdot d\mathbf{X}$, is used to indicate all the associated work terms, $f_1\, dX_1 + f_2\, dX_2 + \cdots$.

First Law of Thermodynamics

- **Work was well defined scientific term and was first used in the scientific sense by Coriolis in 1829. See Science 173,118(1971)**
- **Work has many different faces—electrical, chemical, mechanical and so on.**

  - **Push-pull work**
  - **pV work**
  - **Electrical work**
  - **Surface tension work**
  - **Elastic work**
  - **Other forms of work**

First Law of Thermodynamics

- **Push-pull work** $W = Fx$

- **pV work**

$$W = \int F dx$$

$$= \int \frac{F}{A} d(xA) \qquad \left[Pa \cdot m^3 = \frac{N}{m^2} m^3 = J \right]$$

$$= \int_{V_1}^{V_2} p dV$$

# Thermodynamics (axiomatic approach)

- **In the axiomatic approach, work is assumed to be a well-defined mechanical concept but heat has yet to be defined. The goal is to define all thermal properties in terms of mechanical variables. This can be accomplished by appealing to certain observations, such as the Joule experiment**

Joule Experiment

- Extract from Joule's notebook showing the paddlewheel experiment demonstrating that mechanical energy causes friction and a rise in water temperature.
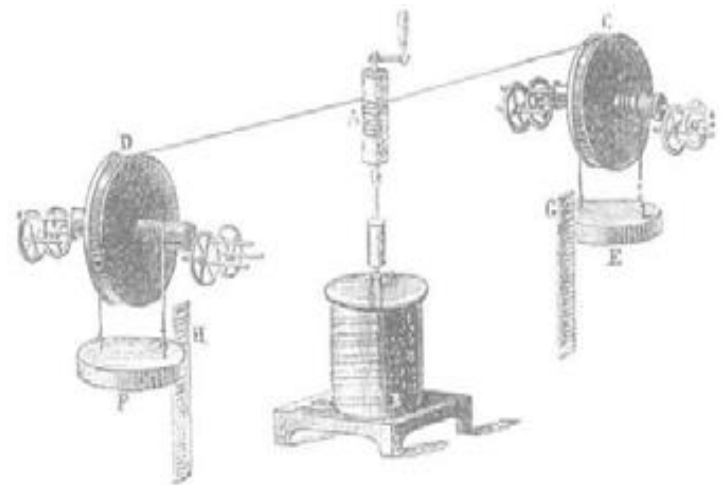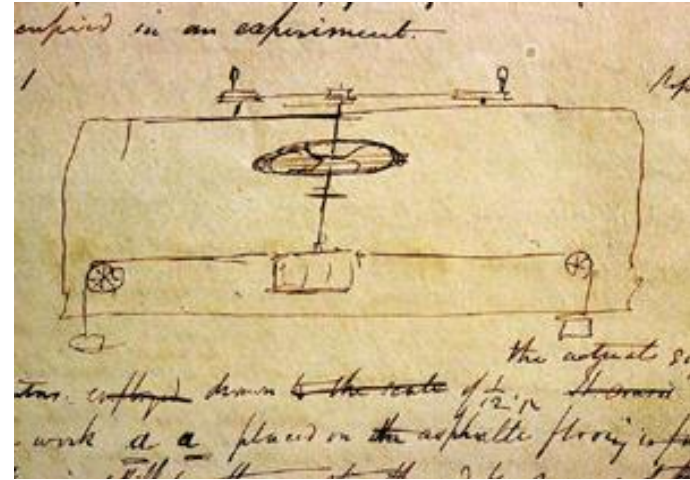
Why Joule ?
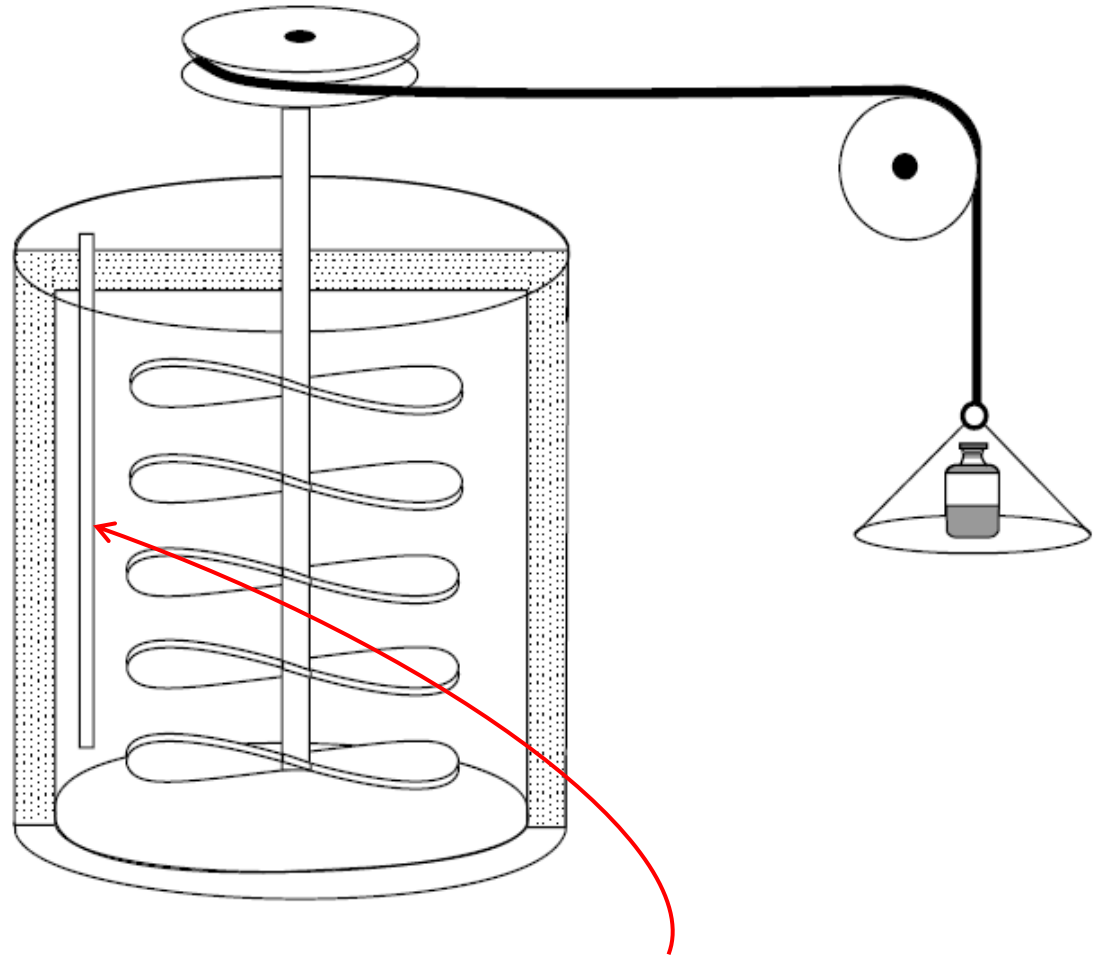
Joule was a wine brewer

First Law of Thermodynamics

- **Adiabatic walls**: are the constraints that prohibit the passage of heat into the system.
- One state A, of the system can be reached from another, B, by some mechanical process while the system is enclosed by an adiabatic wall, it is possible to measure the energy difference, $E_A - E_B$, by determining the work required to pass between these states by an adiabatic process

First Law of Thermodynamics

- **Work and heat are forms of energy transfer. Once energy is transferred (dQ or dW) it is indistinguishable from energy that might have been transferred differently. There is a quantity *E*, there are no quantities *W* and *Q***

- dQ and dW **are inexact differentials (path dependent) , and the strokes are used to indicate this fact**

Exact and inexact differentials

- **Consider the purely mathematical problem**

  $F(x, y)$ **where is some general function of two independent variables x and y. Consider the change in F in going from the point (x,y), in the x-y plane to the neighboring point (x+dx, y+dy). This is given by**

$$dF = F(x + dx, y + dy) - F(x, y)$$

- **which can also be written**

-
$$dF = \frac{\partial F}{\partial x} dx - \frac{\partial F}{\partial y} dy$$

- **This is an *exact differential***

- **If we move in the x-y plane from an initial point i = (xi, yi), to a final point f = (xf,yf), then the corresponding change in is given by**

$$\Delta F = F_f - F_i = \int_i^f dF = \int_i^f \left(\frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy \right)$$

- **Since the difference on the left hand side depends only on the initial and final points, the integral on the righthand side can only depend on these points as well. Therefore, it is path independent.**

- **and**

$$\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x}$$

- **Assume** $\:đG = Xdx + Ydz$

- **Recall** $\quad \dfrac{\partial^2 F}{\partial x \partial y} = \dfrac{\partial^2 F}{\partial y \partial x}$

- **If** $\quad \dfrac{\partial X}{\partial y} \neq \dfrac{\partial Y}{\partial x}$

- **Then** $đG$ **cannot be an *exact differential***

Energy Balance for Closed Systems

- **Since no streams enter or leave a closed system, no internal energy is _transported_ across the boundary of the system. All energy exchange between a closed system and its surroundings then appears as heat and work, and the total energy change of the surroundings equals the net energy transferred to or from it as heat and work.**

$$\Delta\textbf{(Energy of surroundings)} = \pm\ Q \pm\ W$$

Thermodynamic state and state functions

- **The internal-energy terms on the left reflect _changes_ in the internal state or the _thermodynamic state_ of the system.**

- **It is this state that is reflected by its _thermodynamic properties,_ among which are temperature, pressure, and density.**

- **Such properties do not depend on the past history of the substance nor on the means by which it reaches a given state. They depend only on present conditions, however reached. Such quantities are known as _state functions_.**

- **The differential of a state function represents an infinitesimal _change_ in its value. Integration of such a differential results in a finite difference between two of its values.**

$$\int_{p_1}^{p_2} dp = p_2 - p_1 = \Delta p$$

$$\int_{V_1}^{V_2} dV = V_2 - V_1 = \Delta V$$

cross many states (lift an object with a pulley)

Thermodynamic state and state functions

- **On the other hand, the terms on the right sides representing heat and work quantities, are not properties; they account for the energy changes that occur in the surroundings and appear only when changes occur in a system. They depend on the nature of the process causing the change.**

- **The differentials of heat and work are not _changes_, but are infinitesimal _amounts_. When integrated, these differentials give not finite changes, but finite amounts.**

$$\int dQ = Q$$
$$\int dW = W$$

length of rope

- **For a closed system undergoing the same change in state by several processes, experiment shows that the amounts of heat and work required differ for different processes, but that**

  the sum Q + *W is the same for all processes.*

  This is the basis for identification of internal energy as a state function.

- **In thermodynamics, we often reserve the term _system_ for a closed of batch system and we reserve the term _control volume_ for the open system or the section of space that we are considering**

Experimentally we know that isolated systems tend to evolve spontaneously toward simple terminal states. These states are called *equilibrium states*. By "simple" we mean that *macroscopically* they can be characterized by a small number of variables. In particular, the equilibrium state of a system is completely characterized macroscopically by specifying E and $\mathbf{X}$. For a system in which the relevant mechanical extensive variables are the volume and the numbers of molecules, the variables that characterize the system are

$$E, V, n_1, \ldots, n_j, \ldots, n_r \lesssim r \text{ components.}$$

volume ↑

└──── number of moles of species j

Equilibrium

- *<u>Equilibrium</u>* **is a word denoting a static condition, the absence of change. In thermodynamics it means not only the absence of change but the absence of any** *tendency* **toward change on a macroscopic scale. Thus a system at equilibrium exists under conditions such that no change in state can occur.**

Center limit theorem
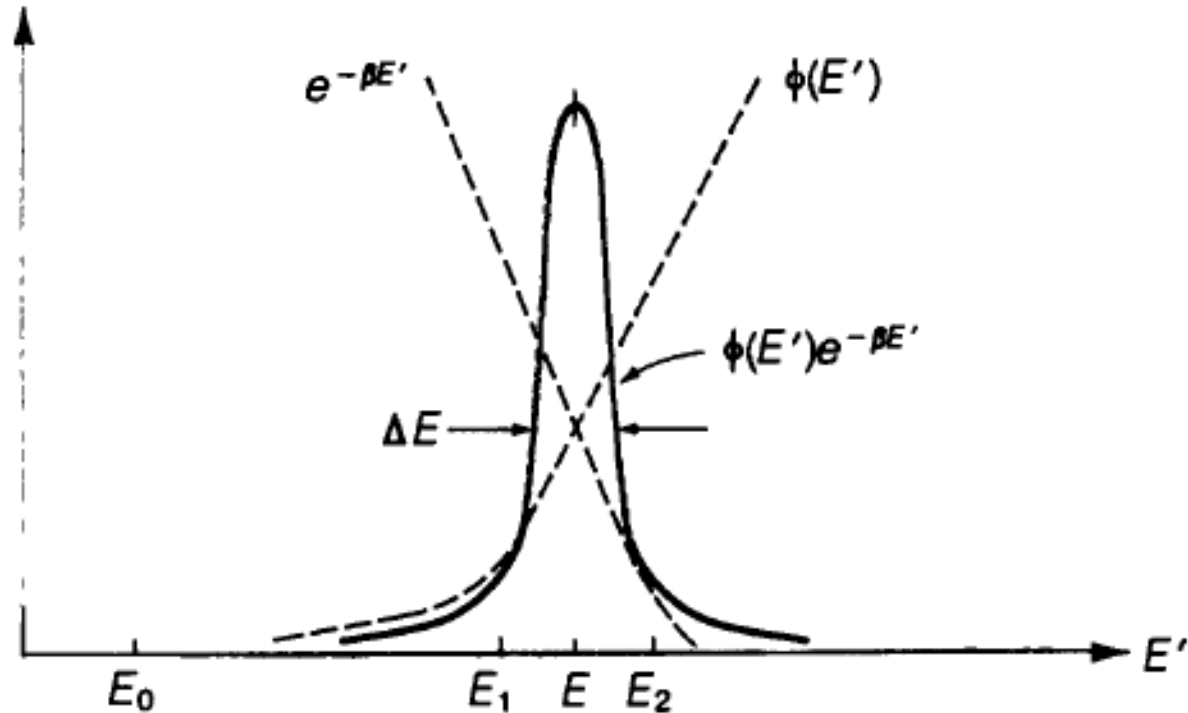
- **Phase extension and probability distribution**

Macro-micro

- **Now the thermodynamic energy is to be identified with the mean value taken over the canonical ensemble**

$$E = \frac{\int E' \phi(E') e^{-\beta E'} dE'}{\int \phi(E') e^{-\beta E'} dE'}$$

- **Since it was stated early that for a very large N, the macroscopic system, the distribution must be a sharp narrow one, may be given by the position of the maximum of the peak.**

Reversible Process

- **Reversible Expansion of a Gas**
  - **Is frictionless**
  - **Is never more than differentially removed from equilibrium**
  - **Traverses a succession of equilibrium states**
  - **Is driven by forces whose imbalance is differential in magnitude**
  - **Can be reversed at any point by a differential change in external conditions**
  - **When reversed, retraces its forward path, and restores the initial state of system and surroundings**

Reversible Process

- **The first requirement is that the system be no more than infinitesimally displaced from a state of _internal_ equilibrium characterized by uniformity of temperature and pressure. The system then always has an identifiable set of properties, including pressure _P._ The second requirement is that the system be no more than infinitesimally displaced from mechanical equilibrium with its surroundings. In this event, the internal pressure _P_ is never more than minutely out of balance with the external force, Processes for which these requirements are met are said to be _mechanically reversible,_**

$$W = \int_{V_1}^{V_2} pdV$$

Reversible Process

- **The reversible process is ideal in that it can never be fully realized; it represents a limit to the performance of actual processes. In thermodynamics, the calculation of work is usually made for reversible processes, because of their tractability to mathematical analysis. The choice is between these calculations and no calculations at all. Results for reversible processes in combination with appropriate _efficiencies_ yield reasonable approximations of the work for actual processes.**

Constant V and Constant P Processes

- **Constant-Volume Process**

    $Q = n \, \Delta U$ **(const V)**

- **Constant-Pressure Process**

    $dQ = d(nU) + d(nPV) = d[n(U + PV)]$

- **The appearance of the group U+ P V, both here and in other applications, suggests the definition for convenience of a new thermodynamic property. Thus, the mathematical (and only) definition of _enthalpy_**

Enthalpy

- **When the energy of an object is to be evaluated, the volume, V, the object had to push the surroundings out of the way to make room for itself, must be added**

$$W = \int_0^V p\,dV = pV$$

- **The total energy of a body is its internal energy plus the extra energy it is credited with having volume V at pressure p.**

- **This total energy is called enthalpy**

$$H = U + pV$$

Standard states for U and H

- **The absolute value of the internal energy of any material at rest is given by Einstein's special theory of relativity,**

$$U_0 = E_0 = \frac{m_0 C^2}{g_c}$$

- **This expression says that if you heat an object it gets heavier; cool it and it gets lighter**

Hamilton's Equations

- Special relativity

$$\mathbf{p} = \gamma m_0 \mathbf{v}\,, \qquad \gamma = \frac{1}{\sqrt{1 - (v/c)^2}}\,, \quad \textbf{\textit{γ} is the Lorentz factor}$$

$$\mathbf{v} = \frac{c^2\mathbf{p}}{\sqrt{(pc)^2 + (m_0 c^2)^2}} = \frac{c^2\mathbf{p}}{E}\,,$$

$$T = c(\mathbf{p}^2 + \mathbf{m}_0^2 c^2)^{1/2} - \mathbf{m}_0 c^2$$

$$= c\left(\sum_{i=1}^{3} p_i^2 + m_0^2 c^2\right)^{1/2} - m_0 c^2$$

$$\frac{dq_i}{dt} = \frac{\partial T}{\partial p_i} = cp_i\left(\sum_{i=1}^{3} p_i^2 + m_0^2 c^2\right)^{-1/2} \qquad ; \; i = 1,\, 2,\, 3$$

Hamilton's Equations

- Since

$$\mathbf{v} = \frac{c\mathbf{p}}{\sqrt{\mathbf{p}^2 + m_0^2 c^2}}$$

$$\mathbf{p}^2 = \frac{m_0^2 \mathbf{v}^2}{1 - \mathbf{v}^2/c^2}$$

- Take square root

$$p = \frac{m_0 v}{\sqrt{1 - \mathbf{v}^2/c^2}}$$

Hamilton's Equations

- Therefore,

$$m \equiv \frac{m_0}{\sqrt{1 - v^2/c^2}}$$

$$v^2 \equiv \mathbf{v}^2 = \sum_{i=1}^{3} \mathbf{v}_i^2$$

- When m0 = 0

$$T = cp$$

$$v = c$$

Standard states for U and H

- This expression is not practical, since when one ton of water is heated from 10°C to 90°C, the increase in the energy, in joules, would be enormous. However, the increase in mass would be so small as to be unmeasurable .

- Instead, we arbitrarily pick some convenient standard state, and let internal energy or enthalpy equal zero at that state