

PREVIOUSLY ON

...*Thermodynamics*

State variables depend on the state only

Cannot be defined during irreversible processes

Changes can be calculated using ANY path

Partial derivatives: change in X due to change in Y with Z
constant

Equivalent processes - to calculate state variables

Calculate the final temperature when cold ice is dropped into hot water. Proceed by assuming a series of processes in which the energy goes into some unspecified storage reservoir

- The water cools to 0° .
- The ice warms to 0° .
- The ice melts.

Finally, the sum of these energies is put back into the system to warm the water back up from 0° to its final temperature, or refreeze some ice.

This is an example of using an *equivalent* process to make a thermodynamic problem mathematically tractable.

It is legitimate because temperature and internal energy are state variables.

What is Heat

Newton: 1690

The rate of heat loss of a body is proportional to the temperature difference between the body and its surroundings.

Lavoisier: 1790

Heat consists of a self-repellent fluid, caloric, that flows from hotter bodies to colder bodies.

Joule and Thomson: 1851

Heat is not a substance, but a dynamical form of mechanical effect

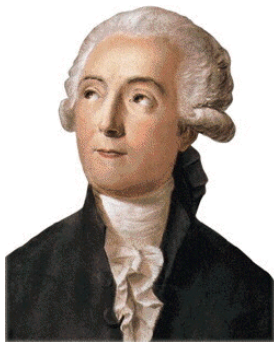
Google: 2018...

What is heat? (something to do with reversible processes)



What is heat?

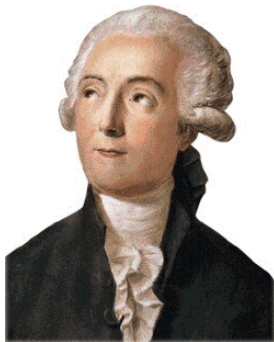
Lavoisier's Elements 1789



Arsenic. Molybdena. Tungstein. Manganese. Nickel. Cobalt. Bismuth.
Antimony. Zinc. Iron. Tin. Lead. Copper. Mercury. Silver. Platina. Gold.
"Metals"

Father of Chemistry

Lavoisier's Elements 1789



“Earths”

Lime, Magnesia, Barytes, Alumine, Silice

“Radicals”

Sulphur, Phosphore, Carbon, fluorique, boracique, muriatique (Chlorine),

What is heat?

and Caloric? Lavoisier's Elements 1789



“Gases”

nitrogen, oxygen hydrogen Heat Light

What is heat?



Lavoisier classified heat as an *element* because.

- 1 You could mix it with other things, and change them.
- 2 It wasn't made of other elements.
- 3 There's a finite amount in any fuel.
- 4 Diffuses and flows to equilibrium concentration
- 5 but then came the boring problem.

Boring

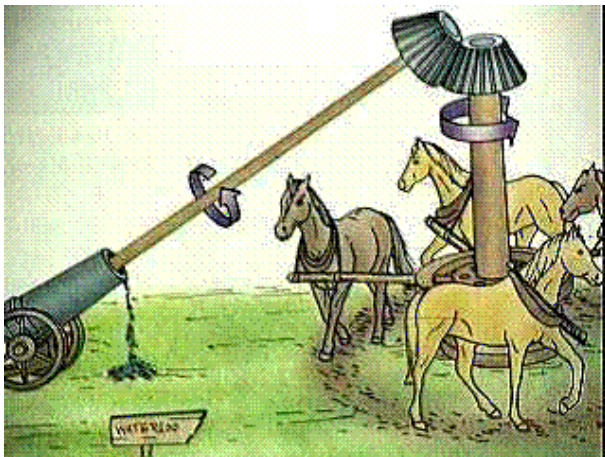


Yellow pages, (pre-1996).



Elon Musk's hyperloop, (2017)

Boring Cannons

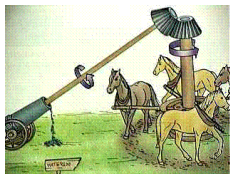


“An inexhaustible source of caloric”

Boring

Observation attributed to Sir Benjamin Thompson (Reichsgraf von Rumford).

“ ...we must not forget to consider that most remarkable circumstance, that the source of the Heat generated by Friction, in these Experiments, appeared evidently to be inexhaustible. It is hardly necessary to add, that anything which any insulated body, or system of bodies, can continue to furnish without limitation, cannot possibly be a material substance: and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of any thing, capable of being excited and communicated, in the manner the heat was excited and communicated in these Experiments, except it be MOTION. ”



Rumford 2 Lavoisier 0



Rumford: Colonel and Loyalist in US Revolution, Bavarian Army Minister, founded Englischer Garten in Munich and Royal Institution of London married Marie-Anne Lavoisier.

Lavoisier (50) Guillotined for selling dodgy fags.

Lavoisier, scientific genius and member of the Ferme Generale (privatised Royal tax collectors) accused by rival scientist and revolutionary Marat

{ *Lavoisier, guillotined at 50 via*

{ *Jean-Paul Marat, murdered at 50 by*

{ *Charlotte Corday, guillotined at 25 by*

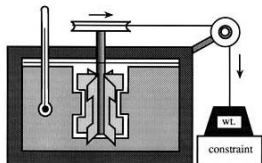
{ *by Charles Sanson, executioner dynasty for 150 years*

}}}



INTERNAL ENERGY - ANOTHER STATE FUNCTION

Joule used falling weights to turn paddles to heat water.



The same work (mgh) always produce the same rise in temperature.

The mechanical equivalent of heat: $4.2 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$.

The same value as using electric heating with a mechanical dynamo.

Joule had proved that heat could be produced by work alone.

If a thermally ISOLATED system is brought from one equilibrium state to another, the work necessary is independent of the process used.

If a THERMALLY ISOLATED system is brought from one equilibrium state to another, the work necessary is independent of the process used.

Joule's observation "*independent of the process used*" requires there is a **state function** U , which we call the internal energy.

$$\Delta U = U_2 - U_1 = W_{adiabatic}$$

- 1 Work done adiabatically equals the change in U .
- 2 Does not define absolute value ($U=0$)
- 3 This is a restricted form of the First Law of Thermodynamics.
- 4 It applied to the thermally isolated system, not the whole Universe.

First Law of Thermodynamics

Conservation of Energy



Clausius: In all cases in which work is produced by the agency of heat, a quantity of heat is consumed which is proportional to the work done; and conversely, by the expenditure of an equal quantity of work an equal quantity of heat is produced.

What about the thermally isolated constraint?

If system is not thermally isolated, $W \neq U_2 - U_1$

Can include heat $U_2 - U_1 = W + Q$,

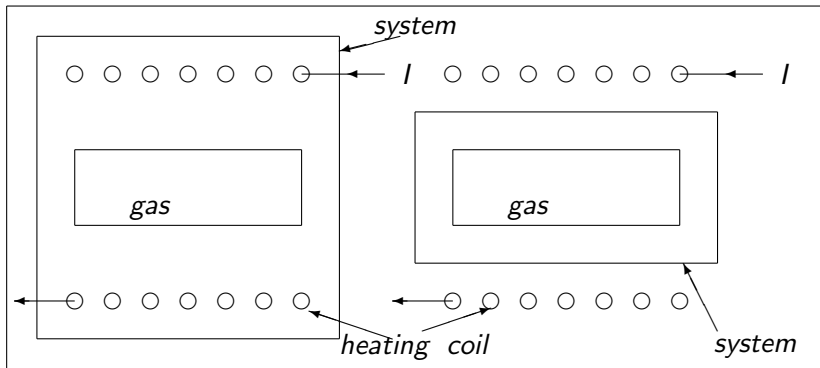
where Q is the energy transfer which cannot be accounted for as work,

Define Q as positive for heat going **INTO** the system:

Heat is the exchange of energy between the system and the surroundings that cannot be identified as work (eg mechanical work).

Illustration of the difference between W and Q

Same experiment, different definition of the system.



First Law of Thermodynamics

This leads to the general statement of the First Law of Thermodynamics, for infinitesimal changes:

$$dU = \delta W + \delta Q,$$

where both δW and δQ are path-dependent. For work done mechanically on a compressible fluid, First Law for infinitesimal reversible processes is:

$$dU = -PdV + \delta Q$$

Work: electrical, magnetic, gravitational etc.

Internal energy: kinetic and potential energy.

Potential energy includes chemical, nuclear, mass, gravitational.

The first law has time-reversal symmetry.

THE HEAT CAPACITY (C) OF A SYSTEM

“Heat needed to raise the temperature by 1 degree”

$$C = \lim_{\Delta T \rightarrow 0} \left(\frac{Q}{\Delta T} \right) = \frac{dQ}{dT}$$

Specific heat capacity is $c = C/m$, where m is the mass.

Molar heat capacity is $c = C/n$, where n is the number of moles.

(confusingly denoted by the same symbol)

Also, specify what is held constant. Using $dQ = dU + PdV$

$$C_V = \left(\frac{\partial Q_V}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_P = \frac{dQ_P}{dT} = \left(\frac{dU + PdV}{dT} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P$$

Introducing enthalpy, $H = U + PV$ a state function useful when the *pressure* is known.

Derive difference between heat capacities $C_p - C_V$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (1)$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

$$\Rightarrow \left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P = C_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

Substituting this in the equation for C_p ,

$$C_P - C_V = \left(P + \left(\frac{\partial U}{\partial V} \right)_T \right) \left(\frac{\partial V}{\partial T} \right)_P,$$

For Ideal gas $\left(\frac{\partial U}{\partial V} \right)_T = 0$ and so $(C_P - C_V) = P \left(\frac{\partial V}{\partial T} \right)_P = nR$.

Slow Ideal Gas Processes - Isothermal

Reversible Isothermal Expansion of an Ideal gas $\Delta T = 0$

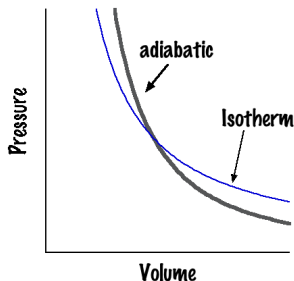
For isotherms, it is convenient to write the equation of state $P(V,T)$:

Isotherms are hyperbolae

$$P = nRT/V \propto 1/V$$

T is constant, P depends only on V .

Reversible means work done on system is equal and opposite to work done on surroundings



$$\int PdV_T = nRT \int dV/V = nRT \ln\left(\frac{V_2}{V_1}\right)$$

Fast Ideal Gas Process - Adiabats

Reversible Adiabatic Expansion (No heat transfer: $\Delta U = \text{work}$)

$$\text{First Law: } \delta Q = dU + PdV = C_v dT + PdV.$$

Adiabatic ($\delta Q = 0$), so $\int PdV = -\int C_v dT = -C_v \Delta T$

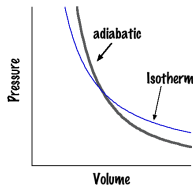
Substitute for $P = nRT/V$, replace nR by $C_p - C_v$ and put $\delta Q = 0$ (adiabatic).

$$-\frac{C_v dT}{T} = \frac{nR dV}{V}$$

$$-c_v \ln(T) = (c_p - c_v) \ln(V) + \ln(A)$$

$$T^{-c_v} = AV^{c_p - c_v}$$

$$A^{-1/c_v} = TV^{(c_p - c_v)/c_v}$$



$$\text{Define: } \gamma = C_p/C_v = c_p/c_v$$

$$TV^{\gamma-1} = \text{a constant, } A$$

$$\text{Equivalently: } PV^\gamma = \text{a different constant}$$

$$\text{And also: } TP^{(\gamma-1)/\gamma} = \text{yet another constant}$$

Irreversible Free Expansion and Joule Coefficient

Rigid adiabatic contained, partitioned into equal volumes: gas & vacuum

System: All gas inside the container.

Irreversible Process: Partition breaks.

On system:

no work, no heat, so $U_i = U_f$

So we can write $T = T(U, V)$,

$$\begin{aligned}dT &= \left(\frac{\partial T}{\partial V}\right)_U dV + \left(\frac{\partial T}{\partial U}\right)_V dU \\&= \left(\frac{\partial T}{\partial V}\right)_U dV \\&= \mu_J dV;\end{aligned}$$

This defines the “Joule coefficient” μ_J
(For Ideal gas, $U = U(T)$ so $T_f = T_i$, so $\mu_J = 0$)

