Introduction to Thermodynamics

Thermodynamics:

→ Describes macroscopic properties of equilibrium systems

→ Entirely Empirical

→ Built on 4 Laws and "simple" mathematics

0th Law ⇒ Defines Temperature (T)

1st Law ⇒ Defines Energy (U)

2nd Law ⇒ Defines Entropy (S)

3rd Law ⇒ Gives Numerical Value to Entropy

These laws are UNIVERSALLY VALID, they cannot be circumvented.

Definitions:

- System: The part of the Universe that we choose to study

- Surroundings: The rest of the Universe
- Boundary: The surface dividing the System from the Surroundings

Systems can be:

- Open: Mass and Energy can transfer between the System and the Surroundings
- Closed: Energy can transfer between the System and the Surroundings, but NOT mass
- Isolated: Neither Mass nor Energy can transfer between the System and the Surroundings

Describing systems requires:

- A few macroscopic properties: p, T, V, n, m, …
- Knowledge if System is Homogeneous or Heterogeneous
- Knowledge if System is in Equilibrium State
- Knowledge of the number of components

Two classes of Properties:

- Extensive: Depend on the size of the system (n,m,V,...)
- Intensive: Independent of the size of the system ($T, p, \overline{V} = \frac{V}{n}, \ldots$)

The State of a System at Equilibrium:

- Defined by the collection of all macroscopic properties that are described by State variables (p,n,T,V,...) [INDEPENDENT of the HISTORY of the SYSTEM]
- For a one-component System, all that is required is “n” and 2 variables. All other properties then follow.

$$V = f(n, p, T) \qquad \text{or} \qquad p = g(n, V, T)$$

These are Equations of States

E.g. The Ideal gas law: $pV = nRT$

The Virial expansion: $\frac{p\overline{V}}{RT} = 1 + \frac{B(T)}{\overline{V}} + \frac{C(T)}{\overline{V}^2} + \cdots$

The van der Waals equation of state:

$$\left(p + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT$$

- Notation:

$$\underset{\substack{\uparrow\\ \text{3 moles}\\ (n=3)}}{3}\ H_2\ (\underset{\substack{\uparrow\\ \text{gas}}}{g},\ \underset{\substack{\uparrow\\ p=1\text{ bar}}}{1\text{ bar}},\ \underset{\substack{\uparrow\\ T=100\ ^\circ C}}{100\ ^\circ C})$$

$2\ Cl_2\ (g,\ 5\ L,\ 50\ ^\circ C)$, $5\ Ar\ (s,\ 5\text{ bar},\ 50\ K)$

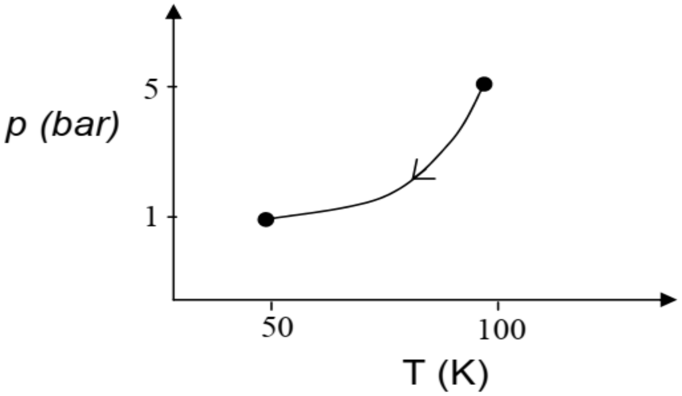
<u>Change of State:</u> (Transformations)

- Notation:

$$\underbrace{3\ H_2\ (g,\ 5\text{ bar},\ 100\ ^\circ C)}_{\text{initial state}} = \underbrace{3\ H_2\ (g,\ 1\text{ bar},\ 50\ ^\circ C)}_{\text{final state}}$$

$$\underbrace{2\ H_2O\ (\ell,\ 1\text{ bar},\ 50\ ^\circ C)}_{\text{initial state}} = \underbrace{3\ H_2O\ (g,\ 1\text{ bar},\ 150\ ^\circ C)}_{\text{final state}}$$

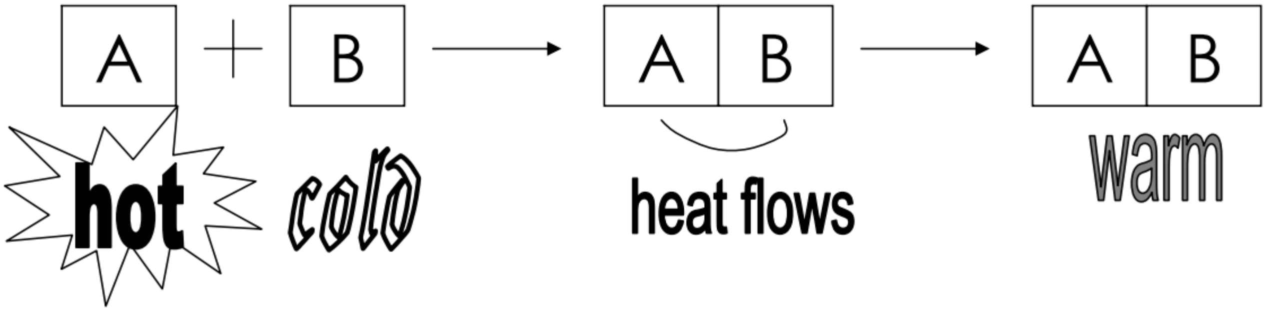
- Path: Sequence of intermediate states



- Process: Describes the Path

- Reversible	(always in Equilibrium)
- Irreversible	(defines direction of time)
- Adiabatic	(no heat transfer between sys. and surr.)
- Isobaric	(constant pressure)
- Isothermal	(constant temperature)
- Constant Volume	
- ...	

Thermal Equilibrium (Heat stops flowing)



When a hot object is placed in thermal contact with a cold object, heat flows from the warmer to the cooler object. This continues until they are in thermal equilibrium (the heat flow stops). At this point, both bodies are said to have the same "temperature".

This intuitively straightforward idea is formalized in the **0^{th} Law of thermodynamics** and is made practical through the development of thermometers and temperature scales.

===== ZERO'th LAW of Thermodynamics =====

If $\boxed{A}$ and $\boxed{B}$ are in thermal equilibrium and
$\boxed{B}$ and $\boxed{C}$ are in thermal equilibrium,
then $\boxed{A}$ and $\boxed{C}$ are in thermal equilibrium.

Consequence of the zero'th law:

$\boxed{B}$ acts like a thermometer, and $\boxed{A}$, $\boxed{B}$, and $\boxed{C}$ are all at the same "temperature".

Operational definition of temperature (t)

Need:
(1) substance
(2) property that depends on t
(3) reference points
(4) interpolation scheme between ref. pts.

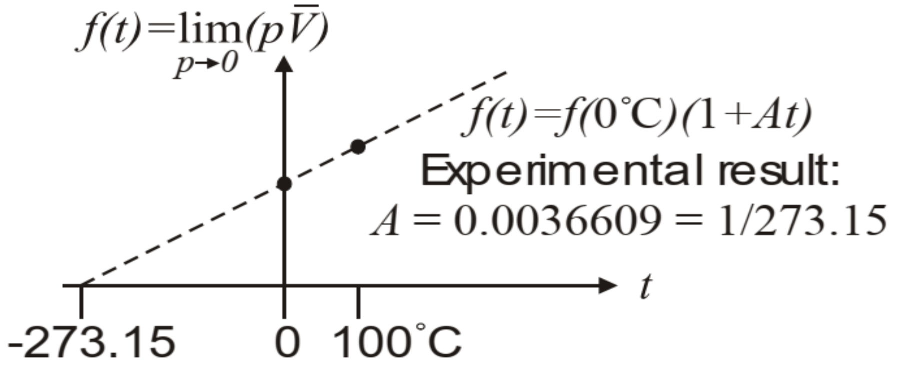
Example: Ideal Gas Thermometer with the Celsius scale.

Based on Boyle's Law

$$\lim_{p\to 0}\left(p\bar{V}\right)_t = \text{constant} = f(t)$$

for fixed t depends on t

- the substance is a gas
- $f(t)$ is the property
- the boiling point $(t_b = 100°C)$ and freezing point $(t_f = 0°C)$ of water are the reference points
- the interpolation is linear



<u>Note:</u> $(t = -273.15°C)$ is special

$t = -273.15°C$ is called the absolute zero,

This suggests defining a new temperature scale (Kelvin)

$$T(K) = t(°C) + 273.15$$

T = 0K corresponds to absolute zero $(t = -273.15°C)$

Better reference points used for the Kelvin scale today are

T = 0K (absolute zero) and T_{tp} = 273.16K (triple point of H_2O)

<u>Ideal Gases</u>

Boyle's Law and the Kelvin scale

$$\lim_{p\to 0}\left(p\bar{V}\right)_T = \left[\frac{\lim_{p\to 0}\left(p\bar{V}\right)_{tp}}{273.16}\right] T \underset{\text{define}}{\equiv} \underset{\text{the “gas constant”}}{R}T$$ valid for all gases for $p \to 0$

An ideal gas obeys the expression $p\bar{V} = RT$ at all pressures
(⇒ the gas molecules do not interact)

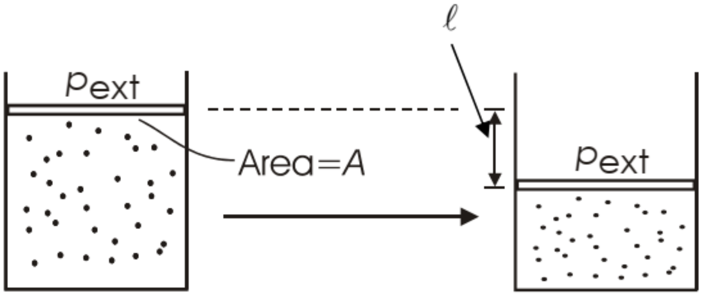
$$R = \left[\frac{\lim_{p\to 0}\left(p\bar{V}\right)_{tp}}{273.16}\right] = 8.31451\frac{J}{K-mol}$$ (gas constant)

- Work: “w”

$$w = \underset{\text{applied force}}{F} \cdot \underset{\text{distance}}{\ell}$$

Expansion work

$F = p_{ext} A$



$$w = \underset{\text{convention}}{-}\left(p_{ext} A\right)\ell = -p_{ext}\Delta V$$

convention: Having a “-“ sign here implies $w > 0$ if $\Delta V < 0$, that is, positive work means that the surroundings do work to the system. If the system does work on the surroundings $(\Delta V > 0)$ then $w < 0$.

- Heat: "q"

That quantity flowing between the system and the surroundings that can be used to change the temperature of the system and/or the surroundings.

Sign convention: If heat enters the system, then it is positive.

Work, Heat, and the First Law

- Work:

Epansion work: $w = -(p_{ext}A)\ell = -p_{ext}\Delta V$

If p_{ext} is not constant, then we have to look at infinitesimal changes

$đw = -p_{ext}dV$ đ means this is not an exact differential

Integral $w = -\int_1^2 p_{ext}dV$ depends on the path!!!

Other kinds of work

Surface work: $đw = \gamma_{ext}dA$ ... where γ_{ext} is the surface tension (J/m^2) and dA is the differential change in area. This is the work to change surface area.

Elongation work: $đw = fd\ell$ where f is the force per unit length and $d\ell$ is the length differential. This is important for discussing changing the length of polymers or DNA.

Electrostatic work: $đw = Vde$ where V is a fixed potential and de is the change in charge.

- Path dependence of w

Example: assume a reversible process so that $p_{ext} = p$

$$Ar\,(g, p_1, V_1) \quad = \quad Ar\,(g, p_2, V_2)$$

Compression $V_1 > V_2$ and $p_1 < p_2$

Two paths:

(1) First $V_1 \rightarrow V_2$ at $p = p_1$
then $p_1 \rightarrow p_2$ at $V = V_2$

(2) First $p_1 \rightarrow p_2$ at $V = V_1$
then $V_1 \rightarrow V_2$ at $p = p_2$

r(g, p_1, V_1) = Ar(g, p_1, V_2) = Ar(g, p_2, V_2)

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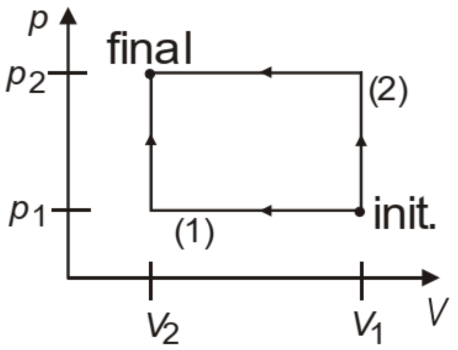


$$w_{(1)} = -\int_{V_1}^{V_2} p_{ext}\,dV - \cancel{\int_{V_2}^{V_2} p_{ext}\,dV}$$
$$= -\int_{V_1}^{V_2} p_1\,dV = -p_1(V_2 - V_1)$$

$$\boxed{w_{(1)} = p_1(V_1 - V_2)}$$

$$w_{(2)} = -\cancel{\int_{V_1}^{V_1} p_{ext}\,dV} - \int_{V_1}^{V_2} p_{ext}\,dV$$
$$= -\int_{V_1}^{V_2} p_2\,dV = -p_2(V_2 - V_1)$$

$$\boxed{w_{(2)} = p_2(V_1 - V_2)}$$

(Note w > 0, work done to system to compress it)

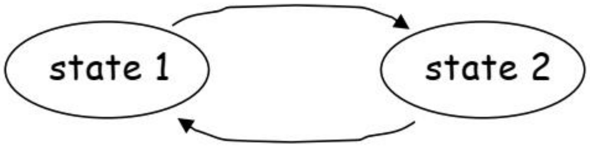
$$\boxed{w_{(1)} \neq w_{(2)}\ !!!}$$

Note for the closed cycle [path (1)] - [path (2)], $\oint đw \neq 0$

closed cycle

w is not a state function   cannot write w = f(p,V)

WORK Work (w) is not a function of state.
For a cyclic process, it is possible for $\oint đw \neq 0$



HEAT Heat (q), like w, is a function of path. Not a state function

It is possible to have a change of state

$$(p_1, V_1, T_1) \quad = \quad (p_2, V_2, T_2)$$

adiabatically (without heat transferred)
or nonadiabatically.

Historically measured in calories
[1 cal = heat needed to raise 1 g H_2O 1°C,
from 14.5°C to 15.5°C]

The modern unit of heat (and work) is the Joule.

1 cal = 4.184 J

Heat Capacity $\underline{\underline{C}}$ - connects heat with temperature

$$đq = C_{path}dT \qquad \text{or} \qquad C_{path} = \left(\frac{đq}{dT}\right)_{path}$$

heat capacity is path dependent

Constant volume: C_V

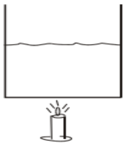
Constant pressure: C_p

$$\therefore \quad q = \int_{\text{path}} C_{\text{path}} dT$$

$\boxed{\text{Equivalence of work and heat}}$ [Joule (1840's)]

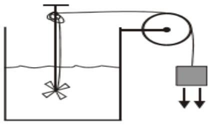
Joule showed that it's possible to raise the temperature of H_2O

(a) with only heat



$T_1 \rightarrow T_2$

(b) with only work
(weight falls &
churns propeller)



$T_1 \rightarrow T_2$

<u>Experimentally</u> it was found that

$$\oint (\text{đ}w + \text{đ}q) = 0$$

$\Rightarrow$ The sum (w + q) is <u>independent of path</u>

$\Rightarrow$ This implies that there is a <u>state function</u> whose differential is $\text{đ}w + \text{đ}q$

We define it as U, the "internal energy" or just "energy"

$$\therefore \quad dU = \text{đ}w + \text{đ}q$$

For a cyclic process $\oint dU = 0$

For a change from state 1 to state 2,

$$\Delta U = \int_1^2 dU = U_2 - U_1 = \underbrace{q}_{\nwarrow} + \underbrace{w}_{\nearrow} \quad \text{does not depend on path}$$

each depends on path individually, but not the sum

For fixed n, we just need to know 2 properties, e.g. (T, V), to fully describe the system.

So $U = U(T, V))$

U is an extensive function (scales with system size).

$\bar{U} = \frac{U}{n}$ is molar energy (intensive function)

THE FIRST LAW

Mathematical statement:

$$dU = \text{đ}q + \text{đ}w$$

or

$$\Delta U = q + w$$

or

$$-\oint \text{đ}q = \oint \text{đ}w$$

Corollary: Conservation of energy

$$\Delta U_{system} = q + w \qquad \Delta U_{surroundings} = -q - w$$

$$\Rightarrow \quad \Delta U_{universe} = \Delta U_{system} + \Delta U_{surroundings} = 0$$

Clausius statement of 1st Law:

The energy of the universe is conserved.