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5.60 Thermodynamics & Kinetics
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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:

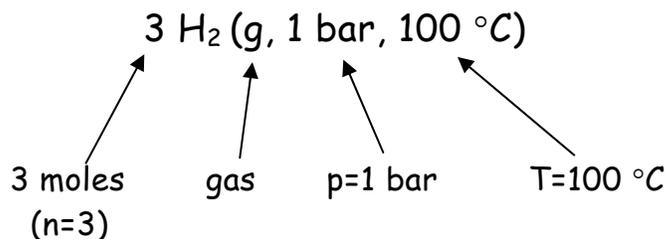
- *Extensive:* Depend on the size of the system
(n, m, V, \dots)
- *Intensive:* Independent of the size of the system
($T, p, \bar{V} = \frac{V}{n}, \dots$)

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, \dots)
[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.

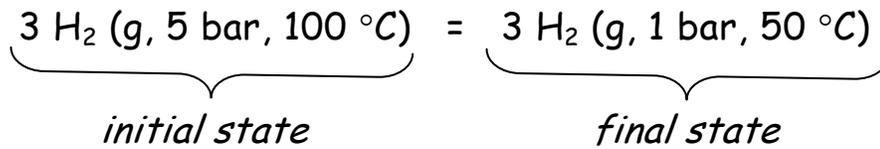
$$V = f(n, p, T) \quad \text{or} \quad p = g(n, V, T)$$

- Notation:

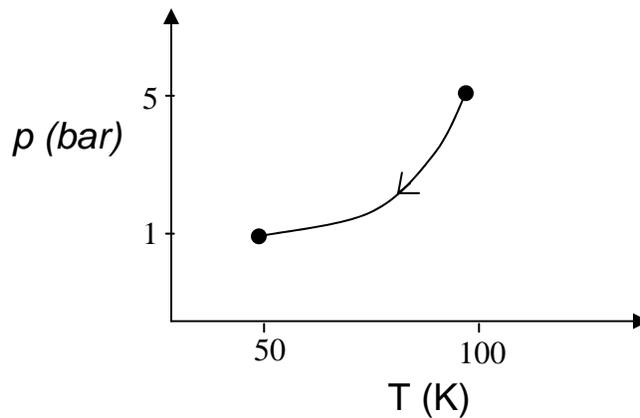


Change of State: (Transformations)

- *Notation:*



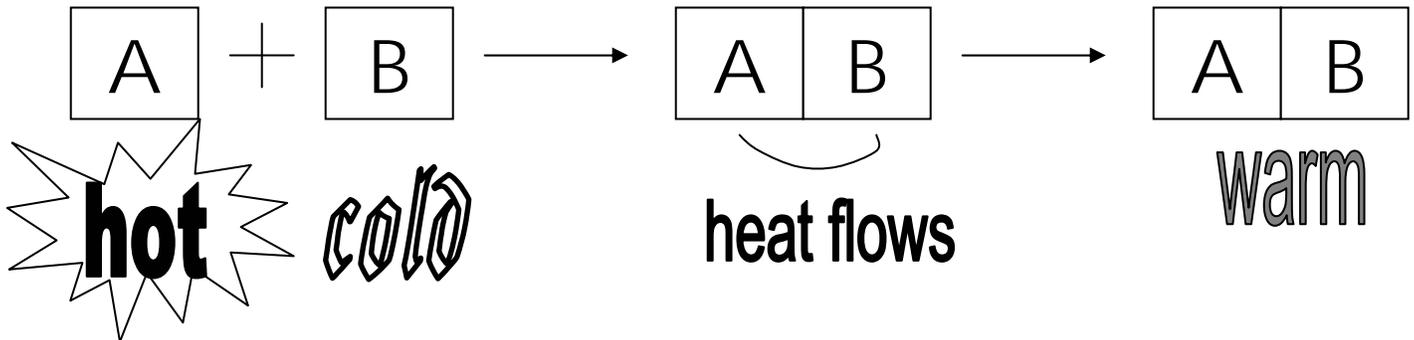
- *Path:* Sequence of intermediate states



- *Process:* Describes the Path

- Reversible (always in Equilibrium)
- Irreversible (defines direction of time)
- Adiabatic (no heat transfer between system and surroundings)
- 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 **0th Law of thermodynamics** and is made practical through the development of thermometers and temperature scales.

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

If A and B are in thermal equilibrium and
B and C are in thermal equilibrium,
 then A and C are in thermal equilibrium.

Consequence of the zero'th law:

B acts like a thermometer, and A , B , and 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.

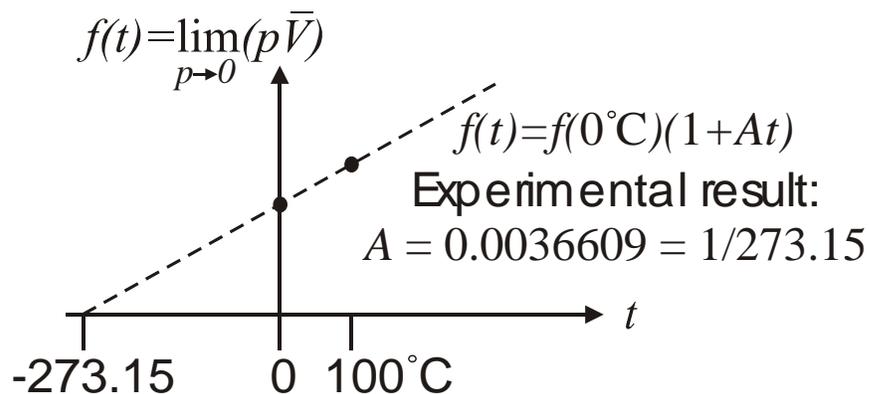
Example: Ideal Gas Thermometer with the Celsius scale.

Based on Boyle's Law

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

for fixed t depends on t

- the substance is a gas
- $f(t)$ is the property
- the *boiling point* ($t_b = 100^\circ\text{C}$) and *freezing point* ($t_f = 0^\circ\text{C}$) of water are the reference points
- the interpolation is *linear*



Note: ($t = -273.15^\circ\text{C}$) is special
 $t = -273.15^\circ\text{C}$ is called the absolute zero,

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This suggests defining a new temperature scale (Kelvin)

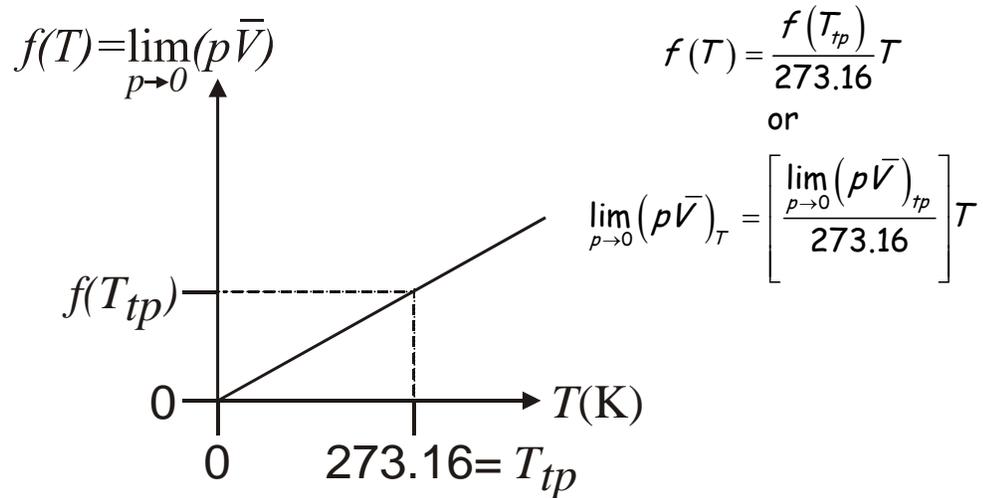
$$T(K) = t(^{\circ}C) + 273.15$$

$T = 0K$ corresponds to absolute zero ($t = -273.15^{\circ}C$)

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Better reference points used for the Kelvin scale today are

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



Ideal Gases

Boyle's Law and the Kelvin scale

$$\lim_{p \rightarrow 0} (p\bar{V})_T = \left[\frac{\lim_{p \rightarrow 0} (p\bar{V})_{tp}}{273.16} \right] T \equiv RT \quad \text{valid for all gases for } p \rightarrow 0$$

define \nearrow \nwarrow
 the "gas constant"

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

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

The Ideal gas law

$$\boxed{p\bar{V} = RT} \quad \text{or} \quad \boxed{pV = nRT}$$

This is an example of an equation of state

$$V = f(n, p, T)$$

Equations of state

IDEAL GAS LAW: $pV = nRT$ \rightarrow $p\bar{V} = RT$

Mixture of ideal gases comprising n_i moles of each

$$p_i = \frac{n_i RT}{V} \quad \leftarrow \text{Partial pressure of } i^{\text{th}} \text{ gas}$$

$$p = p_{\text{Total}} = \sum_i p_i ; \quad X_i = \frac{n_i}{n} \quad \text{mole fraction of } i^{\text{th}} \text{ gas}$$

$$p_i = \frac{n_i}{n} p = X_i p \quad \text{Dalton's Law}$$

Real Gases -- do not necessarily obey ideal gas law

(a) Compressibility factor

$$p\bar{V} = ZRT \quad Z = \frac{\bar{V}_{\text{real}}}{\bar{V}_{\text{ideal}}}$$

High T \Rightarrow Repulsions dominate $Z > 1$ $\bar{V}_{\text{real}} > \bar{V}_{\text{ideal}}$

Low T \Rightarrow Attractions dominate $Z < 1$ $\bar{V}_{\text{real}} < \bar{V}_{\text{ideal}}$

(b) Virial Expansion

$$\frac{p\bar{V}}{RT} = Z(T) = 1 + \overbrace{\frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \dots}^{\text{generally neglect}}$$

As $p \rightarrow 0, \bar{V} \rightarrow \infty, \Rightarrow$ ideal gas $B = 0 \Rightarrow$ ideal gas
(neglect C and higher order terms)

(c) van der Waals Equation of state

only two parameters, derived from molecular concepts

- First assume "hard sphere" molecules

$$p\bar{V} = RT \quad \text{becomes} \quad p(\bar{V} - b) = RT$$

- Now put in attraction

$$\text{So } p = \left(\frac{RT}{\bar{V} - b} \right) \quad \text{becomes} \quad p = \left(\frac{RT}{\bar{V} - b} \right) - \frac{a}{\bar{V}^2}$$

$$\text{Rearranging} \quad \Rightarrow \quad \boxed{\left(p + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT}$$