Atomists and ionists
1. Chemical thermodynamics
2. Statistical thermodynamics
3. Kinetics
4. Surface science

Books:

Lecture schedule
Tutorials
Evaluation
Quantum mechanics
Statistical mechanics
Thermodynamics

Variation of heat with process
UNIVERSE

SYSTEM

SURROUNDING

OPEN  CLOSED  ISOLATED

Intensive and Extensive Variables

Pressure, Volume, Temperature, Heat, Mass
What is unique about Thermodynamics?

Independent of atomic and molecular theory.

In chemical systems, thermodynamics helps to keep a record of energy flow.

Equilibrium state of a chemical system can be understood from thermodynamics.

It is a logical science, three statements describe thermodynamics; deductions from these laws constitute the equations.

Validity of thermodynamic laws depends only on the basic laws and the logical deductions which follow from them.

Since thermodynamics is itself a science, not dependent upon the foundations of other branches, it has an existence of its own.
A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Hence the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.

Albert Einstein
System

Surroundings

Characterization of a system
Based on properties
(1) intensive properties and (2) extensive properties

Types of systems
(1) open, (2) closed, and (3) isolated systems.
(1) homogeneous or (2) heterogeneous

Chemical system
Phase, Component

Process, Path
State function, Path function
Exact and inexact differentials
Zeroth Law
A ↔ B and B ↔ C, then A ↔ C \{ ↔ = \text{thermal equilibrium}\}

First Law

Law of conservation of energy
Work, heat
Exothermic, endothermic

First Law

\[ dU = dq - dw \]
Internal energy of an isolated system is constant

Work = \(-P_{ex}dV\)
Free expansion = 0
Isothermal work = \(\int -\left(\frac{nRT}{V}\right) dV = -nRT \ln \frac{V_f}{V_i}\)
(reversible)

James Watt
q and $w$ are **positive**, when energy is transferred to the system

q and $w$ are **negative**, when energy is lost from the system

**Exact and Inexact differentials**

$$\int_a^b dU = U_b - U_a = \Delta U$$  \hspace{1cm} \text{Exact differential}

$$\int_a^b \delta w = w(\neq w_b - w_a)$$  \hspace{1cm} \text{Inexact differential}
Test for exactness-Euler's theorem

if \( z = f(x, y) \) then, 
\[
dz = \left(\frac{\partial z}{\partial x}\right)_y \, dx + \left(\frac{\partial z}{\partial y}\right)_x \, dy
\]

When
\[
\left[ \frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right)_y \right]_x = \left[ \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right]_y
\]
Then \( z \) is an exact differential

Sum of two inexact differentials can be an exact differential (first law)

Inexact differentials can be converted to exact differentials by multiplying with integrating factors
The General Expression for Work

From Physics, Work, \( w = Fd \cos \theta \)

When \( \theta = 180^0 \), Work, \( w = -Fd \)

\[ dw = -Fdz \]

But, \( F = \text{Pressure} \times \text{Area} = P.A \)

Therefore, \( dw = -P.A.dz \)

Now, \( A.dz = dV \)

\[ dw = -P.dV \]

\[ w = \int_{V_1}^{V_2} PdV \]
Concept of reversibility

SINGLE STEP COMPRESSION

\[ P_2 = \frac{mg}{A} \]

\[ w = mgh = -P_2(V_2 - V_1) \]

Two, three and infinite number of steps

Same compression can be done with less work!

\[ w = \int_{V_1}^{V_2} PdV \]
Different situations

- Free expansion
- Expansion against constant pressure

If \( P \) is constant,

\[ w = -P (V_2 - V_1) \]

- Isothermal reversible expansion

\[ w = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad \Rightarrow \quad w = -nRT \ln \frac{V_2}{V_1} \]
HEAT CAPACITY

$\frac{\partial q}{dT} = C$  \hspace{1cm} \text{Path dependant (constant V or T)}

$U$ as a function of $T$ and $V$

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

Since,

$dU = \partial q - P_{ext} dV$

$\partial q = \left( \frac{\partial U}{\partial T} \right)_V dT + \left[ P_{ext} + \left( \frac{\partial U}{\partial V} \right)_T \right] dV$

At constant volume,

$\partial q_V = \left( \frac{\partial U}{\partial T} \right)_V d$

$\frac{\partial q_V}{dT} = \left( \frac{\partial U}{\partial T} \right)_V = C_V$  \hspace{1cm} \text{Heat capacity at constant volume}
HEAT CAPACITY

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V \rightarrow \Delta U_V = \int_{T_1}^{T_2} C_V dT \]

If \( C_V \) is constant over a small range of temperature,

\[ \Delta U_V = C_V \Delta T \]

We have seen that,

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

Since Joule found that
\[ \partial q = 0; \quad \text{and} \quad \partial w = 0 \]

Since \( dV \neq 0 \),

\[ \left( \frac{\partial U}{\partial V} \right)_T = 0 \]

Internal Pressure

This is not correct for real gases.
Change of state at constant pressure

Enthalpy

\[ \Delta U = U_2 - U_1 = q_P - P \Delta V = q_p - P(V_2 - V_1) \]
\[ q_P = (U_2 + P V_2) - (U_1 + P V_1) \]
\[ q_P = H_2 - H_1 \]

\[ H = U + PV \]

\[ \partial q_P = dH \]
H as a function of \( T \) and \( P \)

\[
dH = \left( \frac{\partial H}{\partial T} \right)_P \, dT + \left( \frac{\partial H}{\partial P} \right)_T \, dP
\]

Since \( \partial q_P = dH \) and at constant \( P \),

\[
\frac{\partial q_P}{dT} = \left( \frac{\partial H}{\partial T} \right)_P = C_P
\]

Heat capacity at constant pressure

If \( C_P \) is independent of temperature,

\[
\Delta H = C_P \Delta T
\]
\( C_P - C_V = nR \)

\[
\partial q_P = \left( \frac{\partial U}{\partial T} \right)_V dT + \left[ P_{\text{ext}} + \left( \frac{\partial U}{\partial V} \right)_T \right] dV
\]

divide by \( dT \) and setting \( \frac{dq_P}{dT} = C_P \)

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

For an ideal gas, \( \left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \) and \( \left[ \left( \frac{\partial U}{\partial V} \right)_T \right] = 0 \)

\[
:\therefore \ C_P - C_V = nR
\]
Enthalpy, $H = U + PV$

Calorimetry

Isotherm and adiabat

Thermochemistry

Heat of formation, $\Delta_r^o H^o$

Hess’s Law

Born-Haber Cycle

Kirchhoff’s equation

$\Delta_r^o H^o (T_2) = \Delta_r^o H^o (T_1) + \int \Delta_r C_P^o \, dT$

Equipartition principle
Just to know
It is all about heat....

Galileo Galilei 1564-1642
Francis Bacon 1561-1626  Joseph Black, 1728 - 1799
Sadi Carnot 1796-1832
Rudolf Clausius 1822 - 1888
Lord Kelvin (William Thomson) 1824-1907
Ludwig Boltzmann 1844-1906
Jacobus Henricus van 't Hoff 1852-1911
Walther Hermann Nernst 1864 - 1941
Gilbert Newton Lewis 1875-1946