Chapter 19 → First Law

We will study the 3 laws of thermodynamics now.

0th Law: Statement about equilibrium

Ch. 19 1st Law: Statement about conservation of energy

Ch. 20 2nd Law: Statement about irreversibility (arrow of time)

Ch. 21 3rd Law: Statement about absolute zero (temperature)

**0th Law:** if systems A, B are in equilibrium and systems B, C are in equilibrium, then systems A, C are in equilibrium.

There are different kinds of equilibrium:

- **Mechanical equilibrium:** $P$ is the variable
  
  ![Mechanical equilibrium diagram](image)

  Wall will move until $P_A = P_B$.

- **Thermal equilibrium:** $T$ is the variable
  
  ![Thermal equilibrium diagram](image)

  Heat will flow until $T_A = T_B$.

  thermally conducting wall → diathermic wall
  thermally insulating wall → adiabatic wall
1st Law:

define heat, \( q \), to be the energy transfer that results from a temperature difference between the system and its surroundings.

system \( \rightarrow \) what we are focusing on

surroundings \( \rightarrow \) everything else.

Define work, \( W \), to be the transfer of energy between the system and its surroundings as a result of unbalanced forces between them.

Work can always be related to the raising or lowering of a mass in the surroundings.

\[
F = ma \quad ; \quad W = F \cdot l
\]

\( l \) = vector length of path,

\[ Fext \]

force on outer face of plate is \( F_{ext} \cdot A \).

This force is equivalent to a weight pressing down on the system.

\[
m = \frac{F_{ext} \cdot A}{g}
\]

mass \( m \), acceleration \( g \), so \( \frac{F_{ext} \cdot A}{g} \) would be the mass.
Plate moves up a distance $dz$.

Work done is $Sw = -P_{ext}A \, dz = -P_{ext} \, dV$

negative because work done by system

other way around: $Sw = P_{ext} \, dV$ for compression

$= -P_{ext} \, dV$ positive because work done

on system.

If $P_{ext}$ not constant,

generalizes to $w = - \int_{V_i}^{V_f} P_{ext} \, dV$

Work and heat depend on the path so we need to know the precise path followed to compute them.

What does this mean?

The state of a system is defined by specifying enough properties that the equation of state fills in the rest.

E.g., for ideal gas $PV = nRT$ so given $n, P, V, T$ is determined

$q, w$ are not state functions: if you are given the initial and final states of the system,
this is not enough info. to compute $q, w$. 

E.g. \( w = - \int_{V_i}^{V_f} P_{ext} \; dV \): \( P_{ext} \) can have any value provided it is large enough to compress the gas (assuming \( V_f < V_i \)).

**Important Concept: reversible process.**

The minimum work required to compress the gas is when \( P_{ext} \) is barely greater than the pressure of the gas throughout the compression.

For this case we can replace \( P_{ext} \) with \( P \), the gas pressure. Called reversible because an infinitesimal change in \( P_{ext} \) at any stage would reverse the compression to an expansion.

**Ex:** isothermal not reversible compression of an ideal gas:

\[
w_{rev} = -\int_{V_i}^{V_f} P \; dV = -\int_{V_i}^{V_f} \frac{nRT}{V} \; dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \left( \frac{V_f}{V_i} \right)
\]

Work and heat are defined only for processes in which energy is transferred between a system and its surroundings.

\[
\delta U = \delta q + \delta w
\]

**First Law:** \( U \) (energy) is a state function.

For a state function we don't need to know the path.

\[
\int_{V_i}^{V_f} \delta U = U_2 - U_1 = \Delta U
\]

We can write \( \Delta U = q + w \).
Even for reversible processes, heat and work depend on the path. We will prove this using an ideal gas, but first we need one fact:

**Equipartition Theorem:**

Molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion, and that energy is:

$$\frac{1}{2} k_B T \text{ per molecule} \quad k_B = \text{Boltzmann's constant}$$

$$\frac{1}{2} RT \text{ per mole} \quad R = \text{gas constant}$$

Therefore \( U = \frac{3}{2} k_B T \) per molecule or \( \frac{3}{2} RT \) per mole for an ideal monoatomic gas (3 translational degrees of freedom).

**Fig 19.5:**

Path A: reversible isothermal expansion

\( U \) depends on \( T \) only so \( dU = 0 \) \( \Rightarrow \) \( -q = w \)
\[ \delta W = -PdV = -\frac{RT_i}{V} dV \]

So \[ W = -q = -RT_i \int \frac{V_j}{V_i} dV = -RT_i \ln \left( \frac{V_j}{V_i} \right) \]

Note: work is done by the gas. \[ q > 0 \] because heat enters the system to maintain the temperature constant because the system used energy to do work.

Path B+C: adiabatic expansion (\( q = 0 \)) then heat at constant volume.

For the adiabatic expansion we will use a state function to compute \( W \) because this often makes things easier.

\[ W = \Delta U = U_2 - U_1 = \int_{V_1}^{V_2} \frac{dU}{dT} = \int_{T_1}^{T_2} \frac{dU}{dT} dT \]

Where we changed limits from \( U_1 \) and \( U_2 \) to \( T_1 \) and \( T_2 \) since \( U = U(T) \) only.

Also, \( \frac{dU}{dT} = \left( \frac{\partial U}{\partial T} \right)_V \equiv C_V(T) \) definition of constant volume heat capacity.

So \[ W = \int_{T_1}^{T_2} C_V(T) dT \] and \[ q = \int_{T_1}^{T_2} C_V(T) dT \]

\[ \rightarrow \text{heating step C.} \]

For \( U = \frac{3}{2}RT \), \( \frac{dU}{dT} = \frac{3}{2}R \) and \[ W = \frac{3}{2}R(T_2 - T_1) \]

For the constant volume path \( W = 0 \) since \( dV = 0 \). Therefore \( W \) is different for path A vs path B+C.
At constant \( V \), \( Sw = 0 \) so \( \delta q_v = dW \)

Define a new state function \( H = U + PV \) = enthalpy

Chemistry is commonly done at constant \( P \), not constant \( V \), so the work \(-PVdV\) is not zero.

\[
\delta h = \delta u + PdV \quad (+ \nu dP \text{ but constant } P)
\]

\[
= \delta q_v - \nu P_{\text{ext}} dV + PdV = \delta q_p
\]

\( \Rightarrow Sw = -\nu P_{\text{ext}} dV \) and \( P_{\text{ext}} = P = \text{constant} \)

This is useful because heat transfer can be measured accurately in experiments.

**Constant Volume**

\[
\Delta u = q_v
\]

\[
C_v \approx \frac{q_v}{\Delta T} \equiv \frac{\partial u}{\partial T}_v
\]

**Constant Pressure**

\[
\Delta h = q_p
\]

Heat Capacity

\[
C_p \approx \frac{q_p}{\Delta T} \equiv \frac{\partial H}{\partial T}_p
\]

For an ideal gas, \( H = U + PV = U + nRT \)

and \( U = U(T) \) only, so same for \( H \)

\[
\Rightarrow \frac{\partial h}{\partial T} = \frac{\partial u}{\partial T} + nR \Rightarrow \frac{\partial h}{\partial T}_p = \frac{\partial u}{\partial T}_v + nR
\]

\[
\Rightarrow C_p - C_v = nR
\]

\( C_p \) larger because we do work against atmospheric pressure as the gas expands as it is heated.
At constant $P$, 
\[ \text{d}H = q_p = C_p(T) \text{d}T \]
\[ \Rightarrow \Delta H = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p(T) \text{d}T \]

\[ \Rightarrow H(T) = H(0) + \int_0^T C_p(T) \text{d}T \]

but this ignores phase transitions where a substance absorbs heat without changing temperature. We have to include the heat of fusion (melting) and the heat of vaporization etc.

\[ \Rightarrow H(T) = H(0) + \int_0^{T_{\text{fus}}} C_p^S \text{d}T + \Delta H_{\text{fus}} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} C_p^L \text{d}T \]

\[ + \Delta H_{\text{vap}} + \int_{T_{\text{vap}}}^T C_p^g \text{d}T \ldots \]

where $S =$ solid, $L =$ liquid, $g =$ gas; $\Delta H_{\text{fus}} = H^S(T_{\text{fus}}) - H^S(T_{\text{fus}})$

See Figs. 19.6, 19.7

Exothermic / Endothermic Reactions

\[ \Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}} \quad \text{negative = exothermic} \]

Then, since $H$ is a state function, $\Delta H_{\text{rxn}}$ is additive which is very useful: called Hess' Law
\[ \text{eg: } C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g) \quad \Delta H = -110.5 \text{ kJ} \]
\[ \text{CO}(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g) \quad \Delta H = -283.6 \text{ kJ} \]

Add: \( C(s) + O_2(g) \rightarrow CO_2(g) \)
\[ \Delta H = -393.5 \text{ kJ} \]

So we don't need to determine \( \Delta H \) values experimentally for every reaction; we can use a library of measured reactions to build the reaction of interest.

\[ \Delta H \text{ (reverse)} = - \Delta H \text{ (forward)} \] for a reaction since the sum of the forward and backwards reactions would be zero.

§ 19.11 \( \rightarrow \) \( \Delta H \text{rxn} \) can be computed from heats of formation. This is a systematic way of doing \( \Delta H \text{rxn} \) calculations.

How does this work?

\( \text{Standard reaction enthalpy} \, \Delta H \text{rxn} \) is \( \Delta H \) for one mole of the specified reagent when all reactants and products are in their standard states.

What does standard state mean?

- \text{gas} \rightarrow 1 \text{ bar} \text{ pressure} , \text{ any } \text{T}
- \text{solid} \rightarrow 1 \text{ bar} \text{ pressure} , \text{ any } \text{T} , \text{ pure crystalline form}
- \text{liquid} \rightarrow 1 \text{ bar} \text{ pressure} , \text{ any } \text{T}
Standard molar enthalpy of formation $\Delta H^\circ_f$

$\Delta H^\circ_f$: formation of one mole from constituent elements

ex: $\Delta H^\circ_f$ of $\text{H}_2\text{O}(l) = -285.8 \text{ kJ/mol}$ at $T = 298 \text{ K}$

This is: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(l)$

So the liquid lies "downhill" in enthalpy relative to its constituent elements.

Convention: put $\Delta H^\circ_f = 0$ for all the elements in their most stable physical state at 1 bar pressure.

So $\text{C}(\text{diamond}) \neq 0$ because graphite is more stable.
Also $\text{I}_2(\text{g}) \neq 0$ since solid I is more stable at 1 bar pressure, room temperature.

How do we use $\Delta H^\circ_f$ to calculate $\Delta H_{rxn}$?

(first limit ourselves to 298 K, then remove this limitation)
Consider $\text{aA} + \text{bB} \rightarrow \text{yY} + \text{zZ}$

(pg. 796)

- $\alpha \delta H_f(A)$
- $\beta \delta H_f(B)$

Elements in standard state

$\Delta H_{\text{rxn}}$

Now add the final piece: use heat capacities and heats of fusion etc. for phase changes to handle other temps.

$T \xrightarrow{\Delta H_{\text{rxn}}} T$

$T \xrightarrow{\Delta H_{\text{rxn}} \text{ at } 298K} 298K$

Need to know heat capacities of the reactants and products and info. about $\delta H$ for any phase transitions.

With this $\Delta H_{\text{rxn}}$ can be calculated for many reactions.
Joule-Thompson Expansion "throttling" basis for gas liquefaction, industrially important. Adiabatic expansion of a gas from $P_1$ to $P_2$ through a nozzle.

Initial: $V_2 = 0$, all gas on left side.
Final: $V_1 = 0$, all gas on right side.

Gas: $V_1, P_1 \rightarrow V_2, P_2$ (temperature ?) might change.

Work done on left: $P_1 V_1$.
Work done on right: $-P_2 V_2$.
Total: $\Delta U = W = P_1 V_1 - P_2 V_2 = U_2 - U_1$.

$\Rightarrow U_2 + P_2 V_2 = U_1 + P_1 V_1$.

$\Rightarrow H_2 = H_1 \Rightarrow \Delta H = 0$ isentropic process.

Writing $H = H(P, T) \Rightarrow \Delta H = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$.

At constant $H$ ($\Delta H = 0$) divide through by $dT$:

$0 = \left(\frac{\partial H}{\partial P}\right)_T \frac{dP}{dT} + \left(\frac{\partial H}{\partial T}\right)_P \frac{dT}{dT}$.

$\frac{dP}{dT} = -\frac{1}{C_p} \frac{\partial H}{\partial T}$.

$\frac{dP}{dT} < 0$ for real gases as $P$ decreases, $T$ should decrease.

$C_T = \frac{\partial T}{\partial P}$.

$\frac{dP}{dT} = 0$ for ideal gases because $H = U + PV = \frac{3}{2}RT + RT$.

$\approx 5/2$ RT due to intermolecular attraction.