Chapter 2. First Law of thermodynamics

**Important Topics**
- First law of thermodynamics
- Work, heat and internal energy
- Expansion work
- Heat capacity
- Reversible and irreversible process
- Enthalpy
- Isothermal & adiabatic changes
- Joule-Thomson expansion
- Thermochemistry

**You should review**
- Law of Conservation of Energy
- Heat Capacity $C_v, C_p$
- Standard State
- Newton, Joule units

**Math**
- Vectors
- Scalar products
- Properties of $\ln$
**System and environment**

- **System** The part of world we want to describe thermodynamically e.g. matter, reaction vessel, engine; completely enclosed within a well-defined boundary.
- Anything outside of the system are the **surroundings**.

**Type of system**

- **Open system** Open for both matter and energy
- **Closed system** Closed for matter but open for energy
- **Isolated system** Closed for both matter and energy

**Universe**

- **System** The part of world we want to describe thermodynamically e.g. matter, reaction vessel, engine; completely enclosed within a well-defined boundary.
- **Surroundings** Anything outside of the system.

Wall can be either diathermic (heat can flow) or adiabatic (insulating).
**Processes**

- **Process**: What is done to or by the system to cause a change of state (gas expansion, heating, mixing, reaction)

- **Isothermal** process: the temperature does not change

- **Adiabatic** process: no heat enters or leaves system; $q = 0$

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**Figure 2A.2** (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, then energy leaves as heat, and the process is isothermal.
Work is associated with a thermodynamic process. Transfer of Energy

Some kinds of work:
1. mechanical work
2. electrical work
3. magnetic work
4. gravitational work

Will concentrate on special case of mechanical work called **PV work**.

Mechanical work is defined as

\[ w = \int_{x_1}^{x_2} F(x)dx \]

**Sign convention**

- work done on system, heat supplied to system: +
- work done by system, heat removed from system: -

Example:
1. compression of spring, turn of shaft
2. charging of battery
3. magnetizing a system
4. raising of a weight
- **State**: Described when we specify values for enough intensive variables such that all additional properties are fixed.
- **State Function**: Physical property that has a specific value once the state is defined; e.g., Volume $V(T, P)$; *independent of path* (i.e., how we got to that state).
- **Path function**: A property of a system that depends on the previous history of the current state of the system. (heat, work)
- **Internal Energy**: State variable, $U$. Don't confuse with potential $E$ or intermolecular potential. Total energy of system.

  - Only **changes** in energy, $\Delta U$, are calculable $\Delta \equiv \text{final} - \text{initial}$
The total amount of energy is the universe is constant.

Energy may be neither created nor destroyed, but it may be converted from one form to another.

\[
\Delta U \equiv U_2 - U_1 = q + w
\]

\[
dU = dw + dq
\]

Change in \(U\) is the sum of the heat and work supplied to a system in going from state 1 to state 2.

Energy is conserved only for system + surroundings; system & surroundings can exchange energy.

In terms of the operation of machines, it is impossible to construct a device which will work continuously without the input of energy to the device.

The best that you can do is break even; you can't win.
Gas expanding against a piston

\[ w = - \int_{x_1}^{x_2} F \, dx \]  

(- sign b/c work done by gas)

Rewrite as

\[ w = - \int_{x_1}^{x_2} \frac{F}{A} \, Adx \]

Opposing pressure is

\[ P_{ex} = \frac{F}{A} \]

Pressure of gas = \( P \); and volume change is \( dV = Adx \)

Therefore, work:

\[ w = - \int_{V_1}^{V_2} P_{ex} \, dV \]

\[ \begin{align*}
P > P_{ex} & \quad \text{gas will expand;} \\
P < P_{ex} & \quad \text{gas will be compressed} \\
P = P_{ex} & \quad \text{equilibrium. No change in volume of gas.} \end{align*} \]
Figure 2A.6  The work done by a gas when it expands against a constant external pressure, $p_{\text{ex}}$, is equal to the shaded area in this example of an indicator diagram.
Gas expansions are technologically important for steam engine, internal combustion engine, refrigerator, air conditioner.

**Isothermal Expansion**  
the gas is in thermal contact with its surroundings; temperature is constant; $\Delta T = 0$

**Adiabatic Expansion**  
No heat enters gas during expansion; $q = 0$

Work done by gas expanding  
$$-w = \int_{V_1}^{V_2} P_{\text{ex}} \, dV$$
Larger the opposing pressure, the more work done. (But $P_{\text{ex}} < P$, or 0 work done)

How to maximize work? Consider ideal gas with $P_1 = 10$ atm and $V_1 = 1$ L. $P_{\text{ex}} = 10$ atm (1 atm from air and 9 atm from weights)

If remove all weights at once, gas will expand until $P_1 = P_{\text{ex}}$; final volume of 10

$$-w = (1 \text{ atm})(10 - 1 \text{ L}) = 9 \text{ L} - \text{ atm} = 912 \text{ J}$$

If move weights in 2 steps

**step 1:** $P_{\text{ex}} = 5$, gas expands to 2 L

$$-w = 5(2 - 1) = 5 \text{ L} - \text{ atm}$$

**step 2:** $P_{\text{ex}} = 1$, gas expands to 10 L

$$-w = (1)(10 - 2) = 8 \text{ L} - \text{ atm}$$

More work!

$$-w = 13 \text{ L} - \text{ atm} = 1318 \text{ J}$$
Can maximize work if $P = P_{ex} + dP$ at each stage of expansion.

In the limit of $dP \to 0$ with $P_{ex} = P = \frac{nRT}{V}$ for reversible expansion or compression of ideal gas:

$$w = -\int_{V_1}^{V_2} P_{ex} \, dV = -\int_{V_1}^{V_2} \frac{nRT}{V} \, dV = -nRT \ln(V_2 / V_1)$$

This limiting case is an example of a reversible process.

**Reversible change**: a change that occurs through a series of equilibrium states; has to occur slowly enough to establish an equilibrium.

- Occurs in the limit of an infinite number of infinitesimal steps.
- Tells us the maximum work that can be obtained from a process.
- Important because it simplifies thermodynamic calculations.
  -- Can use $P$ in place of $P_{ex}$
  -- State Variables depend only on final and initial state and not on path. Can calculate changes along reversible path; will be the same for an irreversible path between the same points.

**Irreversible expansion**: external pressure and the pressure of the gas are *not* in equilibrium during the expansion e.g. expansion into a vacuum.
### Table 2A.1 Varieties of work*

<table>
<thead>
<tr>
<th>Type of work</th>
<th>$dw$</th>
<th>Comments</th>
<th>Units$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expansion</td>
<td>$-p_{ex}dV$</td>
<td>$p_{ex}$ is the external pressure, $dV$ is the change in volume</td>
<td>Pa m$^3$</td>
</tr>
<tr>
<td>Surface expansion</td>
<td>$\gamma d\sigma$</td>
<td>$\gamma$ is the surface tension, $d\sigma$ is the change in area</td>
<td>N m$^{-1}$ m$^2$</td>
</tr>
<tr>
<td>Extension</td>
<td>$f dl$</td>
<td>$f$ is the tension, $dl$ is the change in length</td>
<td>N m</td>
</tr>
<tr>
<td>Electrical</td>
<td>$\phi dQ$</td>
<td>$\phi$ is the electric potential, $dQ$ is the change in charge</td>
<td>V C</td>
</tr>
<tr>
<td></td>
<td>$Q d\phi$</td>
<td>$d\phi$ is the potential difference, $Q$ is the charge transferred</td>
<td>V C</td>
</tr>
</tbody>
</table>

$\Delta U = q + w_{\text{exp}} + w_e$

* In general, the work done on a system can be expressed in the form $dw = -|F|dz$, where $|F|$ is the magnitude of a ‘generalized force’ and $dz$ is a ‘generalized displacement’.

$^+$ For work in joules (J). Note that 1 N m = 1 J and 1 V C = 1 J.
### Temperature vs. Heat

<table>
<thead>
<tr>
<th>Temperature (T, K)</th>
<th>Heat (q, J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensive</td>
<td>Extensive</td>
</tr>
<tr>
<td>Based on ideal gas in limit of low P (true for real gases)</td>
<td>All forms of energy transfer not due to work.</td>
</tr>
<tr>
<td>Ind. of material used</td>
<td>Associated w/ a thermodynamic process.</td>
</tr>
<tr>
<td>Scale chosen so entropy at 0 K is 0; $T = k \lim_{P \to 0} (PV)$</td>
<td>The transfer of energy by heat to a pure substance will change its T, depending on its heat capacity.</td>
</tr>
</tbody>
</table>
Heat Capacity

Proportionality between the $q$ and the $T$-change it produces

$C(T) = \frac{dq}{dT}$

$C$ not constant, depends on $T$

Depends on whether material is allowed to expand

Extensive property

**Heat capacity at constant volume**

$C_v = \left(\frac{dq}{dT}\right)_v$

**Molar Heat Capacity**

$C_{vm} = \frac{1}{n}\left(\frac{dq}{dT}\right)_v$

**Specific Heat**

$c_v = \frac{1}{w}\left(\frac{dq}{dT}\right)_v$

_(w = mass)_

Figure 2A.9 The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A.
Consider \( U(T,V) \); Use slope formula

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

Change state infinitesimally: \( dU = dq + dw \)

1. only PV work: \( dU = dq - P_{ex} dV \)
2. If constant volume \( dV = 0 \)

\[
C_{Vm} = \left( \frac{dq}{dT} \right)_V \quad \Box \quad C_{Vm} = \left( \frac{\partial U}{\partial T} \right)_V
\]

What about second slope? \( \left( \frac{\partial U}{\partial V} \right)_T \)

Called Internal Pressure, \( \pi \). (will derive later)

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P
\]

Find internal Pressure of Ideal Gas \( P = \frac{nRT}{V} \)

Internal energy of an ideal gas depends only on temperature!
Putting the slopes together, we get

$$dU = C_v dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV$$

1. Ideal gases: second term is 0.
2. Real gases at low to moderate $P$: second term is small. "near ideal"
3. Constant Volume ($dV=0$): Second term is 0.
4. Condensed Phases: Internal Pressure is large, but $dV$ is small. Often neglect second term.

So, in many cases, consider $U(T)$:

$$\Delta U = \int_{T_1}^{T_2} C_v dT$$

Shows that internal energy is useful for constant volume processes.
Figure 2E.1 To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas. In the second step, the temperature of the system is reduced at constant volume. The overall change in internal energy is the sum of the changes for the two steps.
Enthalpy (H)

**Definition of enthalpy**

\[ H = U + PV \]

Changes in *enthalpy* of the system is equivalent to the *heat* exchanged between the system and surroundings under *constant pressure*.

\[ dH = dU + d(PV) = dq - PdV + PdV + VdP \]

Thus,

\[ dH = dq + VdP \]

\[ dH = dq \text{ (at constant } P) \]

Enthalpy is convenient to describe heat transfer in and out of the system during the physical and chemical changes under constant pressure conditions. e.g. under atmospheric pressure.
Equation of State for $H(T,P)$

Slope equation

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

- Take this at constant $P$ ($dP = 0$)
  $$dH = \left( \frac{\partial H}{\partial T} \right)_P dT = (dq)_P$$
- First term is heat capacity at constant $P$
  $$C_P = \left( \frac{\partial H}{\partial T} \right)_P$$
- Second term is (will derive later)
  $$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P$$
- Overall equation of state
  $$dH = C_P dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

1. Ideal gases: second term is 0. For ideal gases, enthalpy depends only on $T$.
2. Constant pressure ($dP=0$): Second term is 0. First term tends to be more important

Change in enthalpy when $T$ is changed from $T_1$ to $T_2$ at constant $P$

$$\Delta H = \int_{T_1}^{T_2} C_P dT$$

$C_{Pm}$ depends on $T$ for polyatomic gases, liquids and solids
Comparison of internal energy and enthalpy

- $\Delta U$ - used in constant V processes
- $\Delta H$ - used in constant P processes
- $C_v$ - constant volume heat capacity, related to $\Delta U$
- $C_p$ - constant pressure heat capacity, related to $\Delta H$
- If $\Delta V = 0$, $w = 0$, so $\Delta U = q$
- If $\Delta P = 0$, $\Delta H = q$
- For an ideal gas, if $\Delta T = 0$, $\Delta H = \Delta U = 0$!!!
Why does C change w/T?

- Average translation energy is (per molecule; $k_b$ (JK$^{-1}$) or permole $R$ (JK$^{-1}$mole$^{-1}$))
  \[ \varepsilon_{tr} = \frac{3}{2} k_b T \quad \varepsilon_{tr} = \frac{3}{2} RT \]

- Energy increase upon addition of heat is reflected in an increase in temperature
  \[ q = \frac{3}{2} R(T_2 - T_1) \quad q/\Delta T=C \]

- Therefore, molar heat capacity is
  \[ C_{vm} = \frac{3}{2} R \]
  - Only correct for closed shell atoms at low densities. (He, Ne, Ar, Xe...)

Molecules have types of energy that atoms do not.
- Energy forms of molecules: translation; rotation; vibration
- Each translational term ($x,y,z$) contributes $\frac{1}{2} k_b T$

**Equipartition of Energy** - Each term contributes the same amount

**Equipartition Theorem to Calculate Energy in Diatomic Molecule:**
- translation: 3
- rotation: 2 (2 angles)
- vibration: 2 (1 for kinetic, 1 for potential)

\[ \varepsilon_{molecular} = \frac{7}{2} k_b T \]

- Predicted heat capacity: \[ C_{vm} = \frac{7}{2} R \]

- In general vibrational modes 3N-5 linear; 3N-6 non-linear
  Fails in 2 ways: Does not predict variation of C with T & Incorrect values at low T
Energy is quantized.

The translation and rotational energy levels are close together. Even at room temperature, molecules have enough energy to occupy excited states. Vibrational energy levels are farther apart. At room temperature, the excited vibrational energy levels do not contribute to energy of molecule. Only at high T does the vibrational energy contribute, \( C_{vm} = \frac{7}{2} R \)

\[ C_p(T) \text{ given in Table 2.B1 and Resource Section} \]

\[ C_{p,m} = a + bT + \frac{c}{T^2} \]

Note that \( C_p \) depends on \( P \) too!

\[ \left( \frac{\partial C_p}{\partial P} \right)_T = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P \]

<table>
<thead>
<tr>
<th>[ C(s, \text{ graphite}) ]</th>
<th>[ a ]</th>
<th>[ b/(10^{-3} \text{ K}^{-1}) ]</th>
<th>[ c/(10^5 \text{ K}^2) ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{CO}_2(\text{g}) ]</td>
<td>44.22</td>
<td>8.79</td>
<td>-8.62</td>
</tr>
<tr>
<td>[ \text{H}_2\text{O}(\text{l}) ]</td>
<td>75.29</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[ \text{N}_2(\text{g}) ]</td>
<td>28.58</td>
<td>3.77</td>
<td>-0.50</td>
</tr>
</tbody>
</table>

* More values are given in the Resource section.
Volume Changes: Thermal Expansion and Compressibility

- Volume is a function of only two variables, e.g. P and T
  \[ dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial P}\right)_T dP \] (slope equation)

- Slopes themselves are a function of T and P, but for small changes in condensed phases, they can be considered to be constant.
- Better to consider fractional volume change
  \[ \frac{dV}{V} = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p dT + \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T dP \]

- Coefficient of thermal expansion
  \[ \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \]

- Isothermal compressibility (not the same as compressibility factor!)
  \[ \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \]

- Coefficient of thermal expansion and isothermal compressibility are related
  \[ \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa_T} \]

Table 2D.1* Expansion coefficients ($\alpha$) and isothermal compressibilities ($\kappa_T$) at 298 K

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\alpha/(10^{-4} \text{ K}^{-1})$</th>
<th>$\kappa_T/(10^{-6} \text{ bar}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>12.4</td>
<td>90.9</td>
</tr>
<tr>
<td>Diamond</td>
<td>0.030</td>
<td>0.185</td>
</tr>
<tr>
<td>Lead</td>
<td>0.861</td>
<td>2.18</td>
</tr>
<tr>
<td>Water</td>
<td>2.1</td>
<td>49.0</td>
</tr>
</tbody>
</table>

* More values are given in the Resource section.
The Relationship between $C_v$ and $C_P$

- Given $C_P = \left( \frac{\partial H}{\partial T} \right)_P$ and $H=U+PV$, $C_P = \left( \frac{\partial (U+PV)}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P$

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

- Substituting in for $C_v$ and factoring out: $C_P = C_V + \left( \frac{\partial V}{\partial T} \right)_P \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right]$

For an ideal gas $\left( \frac{\partial U}{\partial V} \right)_T = 0$ and $\left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}$ So, $C_P = C_V + nR$

$C_{pm} = C_{Vm} + R$

For a real gas, using the formula for internal pressure

$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{T}{\partial T} \right)_V - P$

$C_P = C_V + T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_V$

- Can rewrite in terms of $\alpha$ and $\kappa_T$

$C_P = C_V + \frac{TV\alpha^2}{\kappa_T}$
Figure 2B.3  The constant-pressure heat capacity at a particular temperature is the slope of the tangent to a curve of the enthalpy of a system plotted against temperature (at constant pressure). For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and $C_{p,m}$ is larger than $C_{V,m}$. 
Adiabatic Reversible Expansion

- q = 0 so dU = dw or dU = -P_ex dV
- With the assumptions
  1) Expansion is reversible P = P_ex
  2) Gas is ideal so P = \( \frac{nRT}{V} \), and dU = C_V dT

Rearranging \( C_V m \frac{dT}{T} = -R \frac{dV}{V} \)

For a change of (T_1, V_1) to (T_2, V_2) integrate each side

\[
\int_{T_1}^{T_2} C_V m \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}
\]

- If it is reasonable to assume \( C_v m \) does not vary with T (monatomic gases)
- Otherwise need to get T dependence of \( C_v m \)
- What if know P of the final state, not V?

If Ideal gas, dH = \( C_P dT \) and V = \( \frac{nRT}{P} \)

Rearranging: \( C_{P_m} \frac{dT}{T} = R \frac{dP}{P} \)

\[
C_{P_m} \ln \frac{T_2}{T_1} = R \ln \frac{P_2}{P_1}
\]

- If \( C_P \) doesn't vary with T,
Adiabat and isotherm of ideal gas

For isotherm

\[ p_1 V_1 = p_2 V_2 \]

For adiabat

\[ p_1 V_1^\gamma = p_2 V_2^\gamma \]

\[ \gamma = \frac{C_p}{C_v} \]

\[ \frac{C_v}{R} \ln \left( \frac{T_2}{T_1} \right) = -R \ln \left( \frac{V_2}{V_1} \right) \]

\[ \Delta U = \int_{T_1}^{T_2} C_v dT \]

\[ w = -nRT \ln(V_2/V_1) \]
Figure 2D.1  As the volume and temperature of a system are changed, the internal energy changes. An adiabatic and a non-adiabatic path are shown as Path 1 and Path 2, respectively: they correspond to different values of $q$ and $w$ but to the same value of $\Delta U$. 
Isenthalpic (\(\Delta H=0\)) expansion of gas through throttle.

- Used in refrigeration and gas liquefaction
- A gas at pressure \(P_1\) is expanded through a throttle valve into a region of lower pressure \(P_2\).

\[
q=0, \quad \Delta U = U_2 - U_1 = w = p_1 V_1 - p_2 V_2
\]

\[
U_1 + p_1 V_1 = U_2 + p_2 V_2
\]

\((H_f=H_i)\) isenthalpic process

\[
\mu = \left( \frac{\partial T}{\partial p} \right)_H
\]

Joule-Thomson coefficient

Use Cyclic Rule

\[
\left( \frac{\partial T}{\partial P} \right)_H = -\left( \frac{\partial T}{\partial H} \right)_P \left( \frac{\partial H}{\partial P} \right)_T = -\frac{1}{C_p} \left( \frac{\partial H}{\partial P} \right)_T
\]

Remember,

\[
\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P
\]

Then,

\[
\mu = \frac{T \left( \frac{\partial V}{\partial T} \right)_P - V}{C_p}
\]

For ideal gas, \(\mu=0\).

For real gas, \(\mu\) can be either positive (cooling on expansion) or negative (heating on expansion).

**Joule-Thomson inversion temperature:** temperature above which \(\mu\) is negative and below which \(\mu\) is positive.
**Joule-Thomson Coefficients**

Figure 2D.11 The inversion temperatures for three real gases, nitrogen, hydrogen, and helium.

Figure 2D.12 The principle of the Linde refrigerator is shown in this diagram. The gas is recirculated, and so long as it is beneath its inversion temperature it cools on expansion through the throttle. The cooled gas cools the high-pressure gas, which cools still further as it expands. Eventually liquefied gas drips from the throttle.
Formation Reactions

$\Delta = \text{Final State} - \text{Initial State}$

$\Delta_{\text{rxn}}(\text{property}) = (\text{property of prods}) - (\text{property of reacts})$

$$aA + bB \rightarrow cC + dD$$

Enthalpy change:

$$\Delta_{\text{rxn}}H = cH_{m,c} + dH_{m,d} - aH_{m,a} - bH_{m,b}$$

To simplify, define $v_i$, to be stoichiometric coefficient of reactant $i$ (+ for prods, - for reactants)

Entropy change becomes:

$$\Delta_{\text{rxn}}H = \sum_i v_i H_{m,i}$$

- **Formation reaction** of a compound is the reaction by which a compound is formed from the elements in their standard states.
  
  e.g. Formation reaction for liquid water:

  $$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

- Elements must be in their most stable form and phase at the specified T and standard P.
- At 25 °C, most elements are solids. Must specify form:
  
  e.g. C graphite vs diamond
  
  S rhombic vs monoclinic

- Only two elements are liquids: Br$_2$ and Hg
- Gases: Rare gases and H$_2$, N$_2$, O$_2$, F$_2$, and Cl$_2$

$\Delta_iH$ commonly tabulated for 25 °C (Table 2C.4)

- $\Delta_iH = 0$ for elements in their most stable states

<table>
<thead>
<tr>
<th></th>
<th>$\Delta_iH^\ominus$ (kJ mol$^{-1}$)</th>
<th>$\Delta_iH^\ominus$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene, C$_6$H$_6$(l)</td>
<td>49.0</td>
<td>-3268</td>
</tr>
<tr>
<td>Ethane, C$_2$H$_6$(g)</td>
<td>-84.7</td>
<td>-1560</td>
</tr>
<tr>
<td>Glucose, C$_6$H$_12$O$_6$(s)</td>
<td>-1274</td>
<td>-2808</td>
</tr>
<tr>
<td>Methane, CH$_4$(g)</td>
<td>-74.8</td>
<td>-890</td>
</tr>
<tr>
<td>Methanol, CH$_3$OH(l)</td>
<td>-238.7</td>
<td>-721</td>
</tr>
</tbody>
</table>

* More values are given in the Resource section.
Hess’s Law: The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

Example: What is the heat of combustion of C\(_3\)H\(_8\)?

Write the rxn:

C\(_3\)H\(_8\)(g) + 5O\(_2\)(g) → 3CO\(_2\)(g) + 4H\(_2\)O(liq)

Write equation with \(\Delta_fH\): (\(\Delta_fH\) for els in std state = 0)

1. C\(_3\)H\(_8\)(g) + 5O\(_2\)(g) → 3CO\(_2\)(g) + 4H\(_2\)O(liq)
2. 3C(s, graphite) + 3O\(_2\)(g) → 3CO\(_2\)(g) \(\Delta_fH_{CO_2}\)(g)
3. 4H\(_2\)(g) + 2O\(_2\)(g) → 4H\(_2\)O(ℓ) \(\Delta_fH_{H_2O}\)(ℓ)
4. 3C(s, graphite) + 4H\(_2\)(g) → C\(_3\)H\(_8\)(g) \(\Delta_fH_{C_3H_8}\)(g)

\[ \Delta_{rxn}H = \Delta_fH(CO_2) + 4\Delta_fH(H_2O) - \Delta_fH(C_3H_8) - 5\Delta_fH(O_2) \]

Substitute in data from tables:

\[ \Delta_{rxn}H = 3(-393.509) + 4(-285.830) - (-103.8) - 5(0) \]

\[ \Delta_{rxn}H = -2220.0\text{kJ} \]
Temperature Dependence of Reaction Enthalpies

If want $\Delta_{\text{rxn}}H$ at a different temp:

$$\Delta_{\text{rxn}}H^\theta = \Delta_{\text{rxn}}H_{\text{ref}}^\theta + \int_{T_{\text{ref}}}^{T} \Delta_{\text{rxn}}C_p \, dT$$

Kirchoff’s Law (Follows from $dH=C_p\,dT$)

$$\Delta_rC_p^\theta = \sum v_i C_{p,m}^\theta$$

- Assume $\Delta C_p$ constant
- Formula for $C_p(T)$
### Table 2C.1*  Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{\text{tr,}}H^{\ominus}$/ (kJ mol$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>$T_f$/K</th>
<th>Fusion</th>
<th>$T_v$/K</th>
<th>Vaporization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>83.81</td>
<td>1.188</td>
<td>87.29</td>
<td>6.506</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>278.61</td>
<td>10.59</td>
<td>353.2</td>
<td>30.8</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>273.15</td>
<td>6.008</td>
<td>373.15</td>
<td>40.656 (44.016 at 298 K)</td>
</tr>
<tr>
<td>He</td>
<td>3.5</td>
<td>0.021</td>
<td>4.22</td>
<td>0.084</td>
</tr>
</tbody>
</table>

* More values are given in the Resource section.

### Table 2C.2  Enthalpies of transition

<table>
<thead>
<tr>
<th>Transition</th>
<th>Process</th>
<th>Symbol$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition</td>
<td>Phase $\alpha \rightarrow$ phase $\beta$</td>
<td>$\Delta_{\text{tr,}}H$</td>
</tr>
<tr>
<td>Fusion</td>
<td>$s \rightarrow l$</td>
<td>$\Delta_{\text{fus,}}H$</td>
</tr>
<tr>
<td>Vaporization</td>
<td>$l \rightarrow g$</td>
<td>$\Delta_{\text{vap,}}H$</td>
</tr>
<tr>
<td>Sublimation</td>
<td>$s \rightarrow g$</td>
<td>$\Delta_{\text{sub,}}H$</td>
</tr>
<tr>
<td>Mixing</td>
<td>Pure $\rightarrow$ mixture</td>
<td>$\Delta_{\text{mix,}}H$</td>
</tr>
<tr>
<td>Solution</td>
<td>Solute $\rightarrow$ solution</td>
<td>$\Delta_{\text{sol,}}H$</td>
</tr>
<tr>
<td>Hydration</td>
<td>$X^+(g) \rightarrow X^+(aq)$</td>
<td>$\Delta_{\text{hyd,}}H$</td>
</tr>
<tr>
<td>Atomization</td>
<td>Species($s$, $l$, $g$) $\rightarrow$ atoms($g$)</td>
<td>$\Delta_{\text{at,}}H$</td>
</tr>
<tr>
<td>Ionization</td>
<td>$X(g) \rightarrow X^+(g) + e^-(g)$</td>
<td>$\Delta_{\text{ion,}}H$</td>
</tr>
<tr>
<td>Electron gain</td>
<td>$X(g) + e^-(g) \rightarrow X^-(g)$</td>
<td>$\Delta_{\text{eg,}}H$</td>
</tr>
<tr>
<td>Reaction</td>
<td>Reactants $\rightarrow$ products</td>
<td>$\Delta_rH$</td>
</tr>
<tr>
<td>Combustion</td>
<td>Compound($s$, $l$, $g$) $+$ O$_2$(g) $\rightarrow$ CO$_2$(g), H$_2$O(l, g)</td>
<td>$\Delta_H$</td>
</tr>
<tr>
<td>Formation</td>
<td>Elements $\rightarrow$ compound</td>
<td>$\Delta_fH$</td>
</tr>
<tr>
<td>Activation</td>
<td>Reactants $\rightarrow$ activated complex</td>
<td>$\Delta^aH$</td>
</tr>
</tbody>
</table>

* IUPAC recommendations. In common usage, the transition subscript is often attached to $\Delta H$, as in $\Delta H_{\text{tr,}}$. 

![Diagram showing enthalpy changes](image)
Heats of reaction are measured with **Calorimetry** (Ch. 2B)

A rxn is carried out in contact with a water bath. The heat released by the rxn raises the T of the bath. The T rise can be related to $\Delta H$ (constant P) or $\Delta U$ (constant V). $H=U+PV$

For reactions with solids and liquids, small changes in volume, so $\Delta H \approx \Delta U$.

$$\Delta H = \Delta U + \Delta n_g RT$$

**Exothermic**: A reaction in which heat is released

**Endothermic**: A reaction that requires heat to be supplied

The heat *added* to the system is *positive*, so an exothermic reaction has a negative $\Delta H$ or $\Delta U$.

**Differential Scanning Calorimetry** is used in modern research (phase transitions e.g. glass phase transitions in polymers; protein denaturation)

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**Figure 2A.8** A constant-volume bomb calorimeter. The ‘bomb’ is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

**Figure 2C.3** A differential scanning calorimeter. The sample and a reference material are heated in separate but identical metal heat sinks. The output is the difference in power needed to maintain the heat sinks at equal temperatures as the temperature rises.
Major Concept Review

- First Law of Thermodynamics, \( \Delta U = q + w \)
- Heat (q) -- All forms of energy transfer not due to work.
- Work (w) is the transfer of energy; many types defined.
- PV work defined as force \( \cdot \) displacement:
  \[
  w = - \int_{V_1}^{V_2} P_{ex} \, dV
  \]
- Sign convention for work and heat:
  - w done on system, q supplied to system: +
  - w done by system, q removed from system: -
- State variables depend on final & initial state; not path.
- Reversible change occurs in series of equilibrium states.
- Adiabatic q = 0; Isothermal \( \Delta T = 0 \)
- Equations of state for enthalpy, H and internal energy, U
  \[
  \begin{align*}
  \text{d}U &= C_v \, dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V \right]_V \, dV \\
  \text{d}H &= C_p \, dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right]_P \, dP
  \end{align*}
  \]
- \( \Delta U \) - used w/ constant V
- \( \Delta H \) - used w/ constant P
- \( C_v \) - related to \( \Delta U \)
- \( C_p \) - related to \( \Delta H \)
  - If \( \Delta V = 0 \), \( \Delta U = q \)
  - If \( \Delta P = 0 \), \( \Delta H = q \)
- For an ideal gas, if \( \Delta T = 0 \), \( \Delta H = \Delta U = 0 \)!!!

- Reversible work (ideal gas):
  \[
  w_{\text{max}} = -nRT \ln \left( \frac{V_2}{V_1} \right)
  \]
- Adiabatic, reversible expansions:
  \[
  C_{V_m} \ln \left( \frac{T_2}{T_1} \right) = -R \ln \left( \frac{V_2}{V_1} \right)
  \]
- \( C_{P_m} \) ln \( \frac{T_2}{T_1} \) = R ln \( \frac{P_2}{P_1} \)
  \[
  \ln \frac{P_2}{P_1} = -\frac{C_{P_m}}{C_{V_m}} \ln \frac{V_2}{V_1}
  \]
- Adiabats vs. isotherms
- Joule-Thomson expansion (\( \Delta H = 0 \));
  Joule-Thomson coefficient, inversion temperature
- Formation reaction; enthalpies of reaction, other changes
- Calorimetry