Topic 5 – The 1st Law of Thermodynamics

Content & Objectives: Chapter 5 involves the “1st Law” of thermodynamics – i.e. the principle of conservation of energy applied to thermal systems. The summary begins with a brief review of some of the elementary calculus required for understanding the interconnections among thermodynamic quantities, which we now begin to explore. (MathChapter 5 and especially the Blinder article provide more detailed background.) The main content of this section involves the concepts of work and heat interactions in various processes, exemplified using ideal gas expansions. These examples make use of the microscopic relations derived for $C_v$ in Chapter 4, but 1st law considerations are inherently macroscopic in nature. We also discuss heats of formation and reaction as our first look into thermochemistry.


Other Sources:
- Gases and $PV$ Work: Rock Ch. 3, Carrington Ch. 3
- Thermochemistry: Rock Ch. 3 & Ch. 7

Basic Calculus of Thermodynamics

1) Partial Derivatives:
- The partial derivatives of a function of two variables $z = z(x, y)$ are defined by:
  \[
  \left( \frac{\partial z}{\partial x} \right)_y = \lim_{\Delta x \to 0} \frac{z(x + \Delta x, y) - z(x, y)}{\Delta x}, \quad \left( \frac{\partial z}{\partial y} \right)_x = \lim_{\Delta y \to 0} \frac{z(x, y + \Delta y) - z(x, y)}{\Delta y}
  \]
- If the relation $z = z(x, y)$ is viewed as a surface in 3d space, these partial derivatives are simply the slopes of tangents to this surface along the $x$ and $y$ directions.
- Partial derivatives are calculated using the usual rules of differentiation by treating all but one variable as constants.
- Some useful relations among partial derivatives are:
  \[
  \left( \frac{\partial z}{\partial t} \right)_y \left( \frac{\partial t}{\partial x} \right)_y + \left( \frac{\partial z}{\partial x} \right)_y = \frac{1}{(\partial z / \partial x)_y}, \quad \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial z}{\partial y} \right)_y = -1
  \]
  \[
  \frac{\partial^2 z}{\partial x \partial y} = \left[ \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x \right]_y = \left[ \frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right)_y \right]_x = \frac{\partial^2 z}{\partial y \partial x}
  \]
2) Differential Expressions:

- The **total differential of a function** \( z = z(x, y) \) specifies the change in the function brought about by simultaneous infinitesimal changes in all variables

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

This type of differential is termed an **exact differential**.

- More generally, one can write (Pfaff) **differential expressions** of the form

\[
dQ = X(x, y)dx + Y(x, y)dy
\]

where \( X \) and \( Y \) are arbitrary functions of \( x \) and \( y \). \( dQ \) is an exact differential if there is some function \( F(x, y) \) for which \( dQ \) is the total differential. If not, \( dQ \) is termed an **inexact differential**. A necessary and sufficient condition for exactness, and for the existence of a function \( F(x, y) \), is **Euler’s reciprocity relation**:

\[
\left( \frac{\partial X}{\partial y} \right)_x = \left( \frac{\partial Y}{\partial x} \right)_y
\]

3) Integration:

- The **ordinary or Riemann integral** of a continuous function \( f(x) \) is defined by:

\[
\int_a^b f(x)dx \equiv \lim_{n \to \infty} \lim_{\Delta x_i \to 0} \sum_{i=1}^n f(x_i)\Delta x_i
\]

Such integrals can be thought of in geometric terms as the area bounded by the values \( y=0 \) and \( y=f(x) \) between \( x=a \) and \( b \).

- If \( f(x) \) is the derivative of some function \( F(x) \), i.e.

\[
f(x) = \frac{dF}{dx}
\]

then

\[
\int_a^b f(x)dx = \int_a^b dF(x) = F(b) - F(a)
\]

- A **line integral** is a generalization of a Riemann integral, defined as the limit of a summation of a differential expression \( dQ(x, y) \) along a particular path \( C \).

\[
Q \equiv \int_C dQ \equiv \int_{x^*, y^*}^{x'', y''} \{X(x, y)dx + Y(x, y)dy\}
\]

\[
= \lim_{n \to \infty} \lim_{\Delta x_i \to 0} \lim_{\Delta y_i \to 0} \sum_{i=1}^n \{X(x_i, y_i)\Delta x_i + Y(x_i, y_i)\Delta y_i\}
\]
• If the curve C represents some functional relationship between \( x \) and \( y \), for example, \( y = g(x) \)
then
\[
Q = \int_{x', y'}^{x, y} \left\{ X(x, g(x))dx + Y(x, g(x)) \frac{dg}{dx} \right\} dx
\]

(Line integrals usually cannot generally be interpreted in terms of the areas under curves.)

• If \( dQ \) is an inexact differential, the value of the integral will depend upon the path taken; if it is an exact differential of some function \( F(x, y) \), then the value of the line integral is simply \( F(x', y') - F(x', y') \), and is independent of path.

<table>
<thead>
<tr>
<th>Work, Heat, and the First Law of Thermodynamics</th>
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</table>

• Work is defined as the energy associated with some generalized movement \( d\vec{X} \) against an opposing force \( \vec{F} \):

\[
\delta w = \vec{F} \cdot d\vec{X} \quad \text{or} \quad w = \int_{\text{path}} \vec{F} \cdot d\vec{X}
\]

• Many sorts of work terms are associated with the variety of forces in nature. Examples are:

<table>
<thead>
<tr>
<th>Type of Work</th>
<th>( \delta w )</th>
<th>Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>volume expansion (&quot;PV&quot;)</td>
<td>- PdV</td>
<td>( V = \text{volume, } P = \text{pressure} )</td>
</tr>
<tr>
<td>electrochemical</td>
<td>- EdQ</td>
<td>( E = \text{cell voltage, } Q = \text{charge} )</td>
</tr>
<tr>
<td>surface expansion</td>
<td>( \sigma dA )</td>
<td>( \sigma = \text{surface tension, } A = \text{surface area} )</td>
</tr>
<tr>
<td>gravitational</td>
<td>( mgdh )</td>
<td>( m = \text{mass, } h = \text{height, } g = \text{grav. acceleration constant} )</td>
</tr>
<tr>
<td>elastic extension</td>
<td>( TdL )</td>
<td>( T = \text{tension, } L = \text{length} )</td>
</tr>
<tr>
<td>electrical</td>
<td>( EdD )</td>
<td>( E = \text{electric field, } D = \text{electric displacement} )</td>
</tr>
<tr>
<td>magnetic</td>
<td>( HdM )</td>
<td>( H = \text{magnetic field, } M = \text{magnetic polarization} )</td>
</tr>
</tbody>
</table>

(adapted from Rock, Table 3-2)

Different types of work are equivalent in the sense that they may be inter-converted by suitable machines. (For example, Joule referred all types of work to the work required to lift a certain weight in the Earth’s gravitational field.)

• The First Law of Thermodynamics is simply a statement of the principle of energy conservation in the presence of thermal interactions:

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

- \( U \) is the internal energy of the system. It is a state function measurable only in terms of differences \( \Delta U \) brought about through work (\( w \)) and heat (\( q \)) interactions

- Defining \( U \) to be a state function means that \( dU \) is an exact differential (i.e. \( \Delta U = U_2 - U_1 \) depends only on the initial and final states of the system). However, the net work and heat exchanged depend on the process considered and are not determined by merely specifying the initial and final states of the system. The notation \( \delta w \) and \( \delta q \) is used as a reminder that they are inexact differentials.
• **Heat** is the energy transferred to a system as a result of a temperature differential. Heat cannot be measured directly but can always be quantified in terms of an equivalent amount of work using the 1st law.

<table>
<thead>
<tr>
<th>PV Work &amp; Process Descriptors</th>
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- For many thermodynamic problems, the only work terms of importance involve volume expansion:

\[
\delta w = -P_{ext} dV \\
\end{equation}

\[
w = -\int_1^2 P_{ext} dV \neq w_2 - w_1
\end{equation}

\[
P_{ext} \text{ denotes the external pressure acting on the system, which is not generally equal to the internal pressure of the system. (The internal pressure of a system undergoing compression or expansion may not even be well-defined quantity.)}
\]

- A quasi-static process represents an idealized limit in which changes to the system are made sufficiently slowly that the system maintains internal equilibrium throughout the process.

- During a reversible expansion the external pressure \( P_{ext} \) acting on the system is only infinitesimally different from the internal pressure of the system \( P \), so that the net PV work may be calculated from a knowledge of the (equilibrium) equation of state, \( P = P(V, T, N) \):

\[
w_{qs} = -\int_1^2 P(V, T, N) dV
\]

<table>
<thead>
<tr>
<th>General Process</th>
<th>Quasi-Static Process</th>
</tr>
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</table>

- In general the following inequalities hold:

<table>
<thead>
<tr>
<th>compression</th>
<th>( \Delta V &lt; 0 )</th>
<th>( P_{ext} \geq P )</th>
<th>( w \geq 0 )</th>
<th>( w \geq w_{qs} )</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>expansion</th>
<th>( \Delta V &gt; 0 )</th>
<th>( P_{ext} \leq P )</th>
<th>( w \leq 0 )</th>
<th>( -w \leq -w_{qs} )</th>
</tr>
</thead>
</table>

- Other process descriptors to remember are:

  - **isothermal** - processes in which the initial and final temperatures are identical
  - **adiabatic** - processes occurring without heat flow
Energy and Enthalpy Changes in Equilibrium Systems

- **Enthalpy** $H$ is a state function which is analogous to the internal energy but often more convenient for analyzing constant pressure processes:
  \[ H \equiv U + PV \]

- Except at high pressures (>100 bar), the difference between $\Delta U$ and $\Delta H$ is often negligible for condensed-phase processes (where $\Delta PV$ is usually small). For gases, where volume changes are large, the distinction may be significant.

- The molar internal energy and enthalpy of single-component, single-phase systems in equilibrium can be conveniently summarized by the equations of state $U = U(T, V)$ and $H = H(T, P)$. Changes in these energies can therefore be written:
  \[
  dU = \left( \frac{\partial U}{\partial T} \right)_P dT + \left( \frac{\partial U}{\partial V} \right)_T dV \\
  dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP
  \]

- The temperature derivatives in these expressions define the heat capacities:

  **constant volume heat capacity**
  \[
  C_v \equiv \left( \frac{\partial U}{\partial T} \right)_P = \frac{1}{n} C_v
  \]

  **constant pressure heat capacity**
  \[
  C_p \equiv \left( \frac{\partial H}{\partial T} \right)_P = \frac{1}{n} C_p
  \]

  When either volume (for $U$) or pressure (for $H$) are held constant, these heat capacities describe the flow of heat to the system via:

  \[
  \Delta U_v = U(T_2, V) - U(T_1, V) = \int_{T_1}^{T_2} C_v(T, V) dT = q_v \quad (w=0)
  \]

  and

  \[
  \Delta H_p = H(T_2, P) - H(T_1, P) = \int_{T_1}^{T_2} C_p(T, P) dT = q_p \quad (w = -P\Delta V)
  \]

  (Note that when $V$ or $P$ is fixed the net heat exchanged with the system $q$ is path independent.)

- Extensive tabulations of thermodynamic data exist listing molar enthalpies over wide temperature ranges. Enthalpies are referred to some fixed reference temperature $T_{ref}$, usually taken to be 0 K or 298.15 K. Such data are obtained from integrations of $C_p$ of the form:

  \[
  \overline{H}^\circ (T) - \overline{H}^\circ (T_{ref}) = \int_{T_{ref}}^{T_1} C_p(T) dT + \Delta_{T_1} \overline{H}^\circ + \int_{T_1}^{T_2} C_p(T) dT + \Delta_{T_2} \overline{H}^\circ \ldots
  \]
This expression accounts for the fact that phase transitions occurring between \( T_{ref} \) and \( T \) produce finite jumps in \( H \) at the transition temperatures.

Note that \( P \) is not explicitly shown as a variable in this expression. The "°" superscripts denote a standard state, which specifies a fixed standard pressure of 1 bar.

Sample heat capacity and enthalpy data for benzene, taken from M&S, are illustrated at the right.

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### Ideal Gas Expansions

- In the general case \( \overline{C}_v \) depends on both \( T \) and \( V \) and \( \overline{C}_p \) depends on both \( T \) and \( P \). However, for ideal gases we have calculated \( \overline{U} \) and \( \overline{C}_v \) from a knowledge of the molecular energy levels and have found them to be independent of volume. Thus, for an ideal gas it is easy to show:

\[
\overline{U}^{IG} = \overline{U}^{IG}(T) \quad \overline{C}_v^{IG} = \overline{C}_v^{IG}(T) \\
\overline{H}^{IG} = \overline{H}^{IG}(T) = \overline{U}^{IG}(T) + RT \quad \overline{C}_p^{IG} = \overline{C}_p^{IG}(T) = \overline{C}_v^{IG}(T) + R
\]

- For an **isothermal process in an ideal gas**:

\[
T_2 = T_1 \quad \Delta \overline{U}^{IG} = 0 \quad w = -q \quad w_{rev} = -\int P(\overline{V},T)d\overline{V} = -RT \int \frac{P}{\overline{V}}d\overline{V} = -RT \ln \frac{\overline{V}_2}{\overline{V}_1}
\]

- For an **adiabatic process in an ideal gas**:

\[
q = 0 \quad \Delta \overline{U}^{IG} = w \quad w_{rev} = -\int P(\overline{V},T)d\overline{V} = -R \int \frac{T}{\overline{V}}d\overline{V}
\]

but now \( T \) is not constant during the process. To find the relationship between \( T \) and \( V \) note that for \( \delta q = 0 \),

\[
d\overline{U}^{IG} = -Pd\overline{V} = \overline{C}_v^{IG}(T)dT \quad \text{so that} \quad d\overline{V}/\overline{V} = -(\overline{C}_v^{IG}(T)/RT)dT.
\]

If \( \overline{C}_v^{IG} \) is independent of temperature, one can show that:

\[
VT\overline{C}_v^{IG}/R = \text{a constant} \quad \text{reversible, adiabatic expansion} \\
PV\overline{C}_v^{IG}/\overline{C}_v = \text{a constant} \quad \text{of an ideal gas with temperature-} \\
PT\overline{C}_v^{IG}/R = \text{a constant} \quad \text{independent} \overline{C}_v
\]

- Except for monatomic gases, \( \overline{C}_v^{IG}(T) \) does depend significantly on temperature. It is often convenient to express this \( T \)-dependence in a power series:
The constants $a$, $b$, … in this representation can be derived from fits to either experimental data or, more commonly, from statistical calculations like those discussed in Chapter 4.

### Enthalpies of Reaction and Formation

- **Under constant pressure conditions**, the heat given off or taken up by a chemical reaction can be easily measured and used to define the *enthalpy of reaction* $\Delta H$.

- **Hess’s Law** states that the enthalpy of a reaction that can be decomposed into a sequence of component reactions is the sum of the enthalpies of the component reactions. This law is a direct result of the fact that enthalpy is a state function.

- The *standard enthalpy of reaction*, $\Delta_r H^\circ(T)$, is the enthalpy associated with complete conversion of reactants to products of a molar quantity of the reaction (as written). All species are in pure form at the standard pressure of 1 bar and at some specified temperature $T$.

- Combustion reactions are particularly useful for collecting thermodynamic data on substances. The *standard enthalpy of combustion* $\Delta_c H^\circ(T)$ is the standard enthalpy change for complete combustion (i.e. complete oxidation) of one mole a compound into $H_2O$, $CO_2$, etc.

- Data on reaction enthalpies and the relative enthalpies of various compounds can be conveniently summarized in terms of *standard molar enthalpies of formation* $\Delta_f H^\circ(T)$: the enthalpy associated with formation of 1 mole of a given substance ($P=1$ bar, and some particular $T$) from its elements in their standard states.

  **Note**: Enthalpies of formation and reaction depend on the particular states of the reactants and products considered. (i.e. $\Delta_f H^\circ[H_2O(liquid)] \neq \Delta_f H^\circ[H_2O(vapor)]$).

- **Standard states of elements** are defined to be the simplest stable state of an element under conditions of $P = 1$ bar and the temperature of interest. (If an element is gaseous, the standard state refers to the hypothetical ideal gas rather than the real gas.) The energy zero used to compare different chemicals is set by defining $\Delta_f H^\circ(T)$ of an element in its standard state to be zero for all $T$.

- The stoichiometry of a general chemical reaction, $\alpha A + \beta B + \ldots \rightarrow \rho R + \sigma S + \ldots$, can be succinctly described by the relation:

$$\sum_i v_i A_i = 0$$

with $v_i$ being the stoichiometric coefficient, defined to be positive for products and negative for reactants and $A_i$ being a generic species label. Using this notation, reaction enthalpies can be computed from enthalpies of formation via:

$$\Delta_r H^\circ(T) = \sum_i v_i \Delta_f H^\circ_i(T)$$
A similar relation can also be written in terms of enthalpies of combustion, which are also extensively tabulated: \( \Delta_r H^\circ(T) = -\sum_i n_i \Delta_c H_i^\circ(T) \). (Note sign difference from \( \Delta_f H^\circ \) eq.)

Relating reaction enthalpies at different temperatures requires knowledge of the heat capacity of the various species involved:

\[
\Delta_r H^\circ(T) = \Delta_r H^\circ(T_{\text{ref}}) + \sum_i n_i \int_{T_{\text{ref}}}^{T} C_p^0(T')dT',
\]

BOND ENTHALPIES

(Average) bond enthalpies \( H_b(X-Y) \) are useful for understanding chemical energy storage and for making approximate calculations of reaction enthalpies. Bond enthalpies are approximate values of the enthalpy required to break bonds of type \( X—Y \) in the gas phase. Bond enthalpies are obtained by averaging observed values of enthalpies of reactions in which \( X—Y \) bonds are broken in specific molecules.

Bond enthalpies can be used to interpret and/or estimate enthalpies of reaction using the relation:

\[
\Delta_r H^\circ \approx \sum_{\text{bonds } i} n_i H_b(i) - \sum_{\text{bonds } j} n_j H_b(j)
\]

Reaction enthalpies of gas-phase species calculated in this manner are expected to be accurate to the level of about 10%.

The following table of bond enthalpies is adapted from Rock’s text

**Average Bond Enthalpies at 298 K (kJ mol\(^{-1}\))**

<table>
<thead>
<tr>
<th>Bond</th>
<th>( H_b )</th>
<th>Bond</th>
<th>( H_b )</th>
<th>Bond</th>
<th>( H_b )</th>
<th>Bond</th>
<th>( H_b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>464</td>
<td>Si-Cl</td>
<td>381</td>
<td>C-I</td>
<td>234</td>
<td>H-Br</td>
<td>368</td>
</tr>
<tr>
<td>O-O</td>
<td>138</td>
<td>Si-Br</td>
<td>310</td>
<td>C-Si</td>
<td>285</td>
<td>H-I</td>
<td>297</td>
</tr>
<tr>
<td>O=O</td>
<td>494</td>
<td>Si-I</td>
<td>234</td>
<td>C-N</td>
<td>259</td>
<td>N=N</td>
<td>159</td>
</tr>
<tr>
<td>O-F</td>
<td>188</td>
<td>C-H</td>
<td>414</td>
<td>C≡N</td>
<td>879</td>
<td>N≡N</td>
<td>418</td>
</tr>
<tr>
<td>O-Cl</td>
<td>188</td>
<td>C-C</td>
<td>335</td>
<td>C-S</td>
<td>259</td>
<td>N≡N</td>
<td>946</td>
</tr>
<tr>
<td>O-Br</td>
<td>188</td>
<td>C-O</td>
<td>339</td>
<td>C=S</td>
<td>477</td>
<td>N-H</td>
<td>389</td>
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<tr>
<td>S-F</td>
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<td>732</td>
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<td>N-F</td>
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<tr>
<td>S-Cl</td>
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<td>C≡C</td>
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<td>F-F</td>
<td>155</td>
<td>N-Cl</td>
<td>192</td>
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<tr>
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<td>Cl-Cl</td>
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<td>490</td>
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<tr>
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<td>644</td>
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<td>427</td>
<td>Br-Br</td>
<td>192</td>
<td>P-Cl</td>
<td>326</td>
</tr>
<tr>
<td>B-Cl</td>
<td>456</td>
<td>C-Cl</td>
<td>322</td>
<td>H-F</td>
<td>565</td>
<td>P-Br</td>
<td>264</td>
</tr>
<tr>
<td>Si-F</td>
<td>565</td>
<td>C-Br</td>
<td>268</td>
<td>H-Cl</td>
<td>431</td>
<td></td>
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</tbody>
</table>
The chart below summarizes the use of enthalpies of formation, enthalpies of combustion, and bond energies for calculating reaction enthalpies.

**Reaction Enthalpy Calculations**

**Enthalpies of Formation: \( \Delta_f H^\circ \)**

\[
\Delta_f H^\circ (T) = \sum_i v_i \Delta_f H_i^\circ (T)
\]

Reactants: \(\alpha A + \beta B + \ldots\)

*Elements*: \(n_1E_1 + n_2E_2 + \ldots\)

Products: \(\rho R + \sigma S + \ldots\)

**Combustion Enthalpies: \( \Delta_c H^\circ \)**

\[
\Delta_c H^\circ (T) = -\sum_i v_i \Delta_c H_i^\circ (T)
\]

Reactants: \(\alpha A + \beta B + \ldots\)

*Oxidized Species*: \(nCO_2 + mH_2O + oN_2 + \ldots\)

Products: \(\rho R + \sigma S + \ldots\)

**Bond Enthalpies: \( H_b(X - Y) \)**

\[
\Delta_f H^\circ \approx \sum_{\text{reactant bonds } i} n_i H_b(i) - \sum_{\text{product bonds } j} n_j H_b(j)
\]

Reactants: \(\alpha A + \beta B + \ldots\)

*Atoms*: \(n_1A_1 + n_2A_2 + \ldots\)

Products: \(\rho R + \sigma S + \ldots\)