Work and heat

Chapter 2 of Atkins: The First Law: Concepts
Sections 2.3- 2.4 of Atkins

Expansion Work
General Expression for Work:
Free Expansion
Expansion Against Constant Pressure
Reversible Expansion
Isothermal Reversible Expansion

Heat Transactions
Calorimetry
Heat Capacity

Prof. Mueller Chemistry 451 - Fall 2003 Lecture 6 - 1

Expansion Work

1. Work required to move an object over distance \( dz \) against a force of opposing magnitude \( F \):

\[
dw = -Fdz
\]

Negative sign: since the system moves against the opposing force \( F \), there will be a decrease in the internal energy of the system

2. System: massless, frictionless, rigid, perfectly fitting piston of area \( A \)
3. Force on outer face of the piston: \( F = p_{\text{ext}}A \)
4. Work done against external pressure:

\[
dw = -p_{\text{ext}}Adz
\]
5. Change in volume

\[
dV = Adz
\]

Prof. Mueller Chemistry 451 - Fall 2003 Lecture 6 - 3

Work and heat

Must focus upon infinitesimal changes in state and energy, and be able to connect the contributions of small changes in heat and work to the total energy.

Work done on a system: \( dw \)
Energy supplied as heat: \( dq \)

\[
dU = dq + dw
\]

Expansion work: Work that leads to a change in volume - gas expanding, driving force against atmospheric pressure

Examples: thermal decomposition of CaCO3
combustion of octane

Prof. Mueller Chemistry 451 - Fall 2003 Lecture 6 - 2

Expansion Work

If we need to know the total work done expanding the volume of a system, we can integrate the above expression over the initial and final volumes

\[
w = -\int_{V_i}^{V_f} p_{\text{ext}}dV
\]

• Force acting on the piston, \( p_{\text{ext}}A \), is the same as raising a weight as the system expands (e.g., \( F = mg \))
• Compressing the system is analogous, excepting that \( V_f > V_i \)

If we have free expansion, there is no opposing force, despite increase in volume. (e.g., expand into vacuum)

\[
w = 0
\]

Prof. Mueller Chemistry 451 - Fall 2003 Lecture 6 - 4
Types of Work

There are various types of work from different sources which work much in the same way, resulting from the product of:

- an intensive factor (e.g., \( P \)) x an extensive factor (e.g., \( V \))

<table>
<thead>
<tr>
<th>Type of work</th>
<th>( \text{dw} )</th>
<th>Comments</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lifting</td>
<td>(-mg , dh)</td>
<td>( dh ) is change in height</td>
<td>( N )</td>
</tr>
<tr>
<td>Expansion</td>
<td>(-pV , dV)</td>
<td>( p ) is external pressure</td>
<td>( Pa )</td>
</tr>
<tr>
<td>Surface expansion</td>
<td>( \gamma , d\sigma )</td>
<td>( \gamma ) is surface tension</td>
<td>( N , m^{-1} )</td>
</tr>
<tr>
<td>Extension</td>
<td>( f , dl )</td>
<td>( f ) is the tension</td>
<td>( N )</td>
</tr>
<tr>
<td>Electrical</td>
<td>( \phi , dq )</td>
<td>( \phi ) is electric potential</td>
<td>( V )</td>
</tr>
<tr>
<td>Generalized work</td>
<td>( dw = -F , dz )</td>
<td>( F ) is &quot;generalized force&quot; and ( dz ) is &quot;generalized displacement&quot;</td>
<td></td>
</tr>
</tbody>
</table>

Expansion Against Constant Pressure

During expansion, external pressure \( p_{ex} \) is constant (e.g., atmosphere)

\[
w = -p_{ex} \int_{V_i}^{V_f} dV
\]

If \( .dV = V_f - V_i \), then the work can be written

\[
w = -p_{ex}(V_f - V_i)
\]

The integral above is interpreted as area, as we watch work done by a gas expanding against a constant pressure.

The magnitude of work, \( |w| \), is equal to the area beneath the line with \( p = p_{ex} \) between final and initial volumes - \( pV \) graphs to calculate expansion work are called indicator diagrams.

Reversible Processes

Reversible process: a process during which the system is never more than infinitesimally far from equilibrium and an infinitesimal change in external conditions can reverse the process at any point - a change can be reversed by infinitesimal modification of a variable.

Irreversible process: a process which cannot be reversed by an infinitesimal change in external conditions; during the process, the system makes finite departures from equilibrium.

Consider a sample of gas in thermal and mechanical equilibrium with the surroundings, i.e., with \( T_{gas} = T_{surroundings} \) and \( p_{gas} = p_{external} \). If the external pressure is decreased infinitesimally at constant \( T \), the gas will expand infinitesimally; if the external pressure is increased infinitesimally at constant \( T \), the gas will be compressed by an infinitesimal amount.

Strictly speaking, a reversible process cannot be achieved, since to carry out a finite transformation in a series of infinitesimal steps would require infinite time. All real processes are therefore irreversible. A reversible process is an idealization (but still a very useful one).

Reversible Expansion

In order for the gas to expand, \( p_{in} \) must be smaller than \( p \) (the pressure of the gas). At the same time, the system must be infinitesimally close to equilibrium throughout the expansion. This means that \( p_{in} \) must equal \( p - dp \) at all times during the expansion. Therefore,

\[
w = -\int_{V_i}^{V_f} p_{in} \, dV = -\left[ (p - dp) \, dV \right]_{V_i}^{V_f} = -pdV
\]

The \( dpdV \) part of the integral disappears, since the integral of two infinitesimal quantities gives another infinitesimal quantity. Thus,

\[
dw = -p_{in} \, dV = -pdV
\]

This is work of reversible expansion. The integral on the right can be evaluated with knowledge of how pressure of the defined gas depends on the volume (i.e., if we know the equation of state of the gas, \( p \) can be expressed in terms of \( V \)).
Isothermal Reversible Expansion

Expansion is **isothermal** if system is in contact with constant thermal surroundings (i.e., a constant temperature bath or heating element).

1. Each stage of expansion, \( p = \frac{nRT}{V} \)
2. Temperature \( T \) is constant, so treated outside of the integral
   \[ w = -nRT \left( \frac{dV}{V} \right) = -nRT \ln \left( \frac{V_f}{V_i} \right) \]
   - When \( V_f > V_i \), gas expands, and work done to expand the gas causes the system to lose internal energy, \( w < 0 \)
   - Constant supply of energy at constant \( T \) replenishes internal energy
   - More work is done for a given change in volume at higher temperature
     - Pressure of confined gas needs higher opposing pressure for reversibility.

Here, \( w \) is equal to the area under the \( p = \frac{nRT}{V} \) isotherm, and this represents work of a reversible expansion at constant temperature, where external pressure is continually matched against the internal pressure.

Maximum work obtained from system operating between specific initial and final states is obtained when change is reversible.

Heat Transactions

Internal energy can be written as:
\[ dU = dq + dw_{\text{exp}} + dw_{\text{ext}} \]
- \( dq \): heat energy transferred across boundary due to difference in \( T \)
- \( dw_{\text{exp}} \): work due to expansion
- \( dw_{\text{ext}} \): extra sources of work (e.g., electrical current)
  - At constant \( V \), \( dw_{\text{exp}} = 0 \) (system cannot expand)
  - If no additional work (no battery, etc.), \( dw_{\text{ext}} = 0 \) and then:
    \[ dU = dq \]

Write \( dU = dq_v \), which implies infinitesimal change at constant volume. Thus for a measurable finite change:
\[ \Delta U = q_v \]

- \( q > 0 \) (heat supplied to system)
- \( q < 0 \) (heat lost from system)

Calorimetry

How do we study changes in energy due to addition or subtraction of heat in a system? We can use an **adiabatic bomb calorimeter**

- **Adiabatic:** Implies that the device is isolated from the outside world, such that no thermal transfer of energy can take place between system and surroundings
- **Bomb:** The sturdy vessel with constant volume inside which very vigorous reactions, combustions and explosions can take place at high pressure
- **Calorimeter:** From the cgs unit of energy, the calorie, implying the measurement of energy
How does the calorimeter work?

1. Reaction is conducted in the constant volume bomb.
2. Bomb is immersed in a stirred water bath, forming the calorimeter.
3. Calorimeter is immersed in a second water bath, the temperature of which is continuously adjusted to the temperature of the bomb bath, thereby ensuring an adiabatic system.

A chemical reaction either releases or absorbs heat, causing a proportional change in temperature $\Delta T$ of the calorimeter.

Measuring $\Delta T$ allows us to determine $q$, and therefore $\Delta U$. BUT... we must calibrate the calorimeter using known energy to get the calorimeter constant, $C$.

1. Use electrical current $I$ at fixed potential $V$ through a heater for time $t$.
2. Burn an exact mass of substance with known heat output.

Heat Capacity

Increasing temperature increases the internal energy of a system.

The exact increase depends upon the heating conditions.

Heat cannot be detected or measured directly. (There is no heat meter.)

One way to determine the magnitude of a heat transfer is to measure the work needed to bring about the same change in the thermodynamic state of the system as was produced by the heat transfer.

Another approach is to deduce the magnitude of a heat transfer from its effects, namely, a temperature change. The temperature change resulting from a particular transfer of heat is determined by the heat capacity of the system, which is defined as follows:

- **Heat capacity** (of a system): the heat required to raise the temperature of the system by one Kelvin (or one °C).

Heat capacity is an extensive property.

Heat Capacity & Internal Energy

Here is a plot of the internal energy of a system versus temperature.

The slope of the curve at a given temperature is defined as the heat capacity of the system at that $T$.

The heat capacity at constant volume is formally defined as:

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

The RHS is a partial derivative, which is a derivative where all variables are held constant except for one - it gives the slope of the plot of $U$ vs. $T$.

The heat capacity at temperature $A$ is lower than that at temperature $B$.

Partial Derivatives: A Closer Look

The internal energy depends upon more variables than just the $T$ of the system:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$
Molar Heat Capacity

Heat capacity is an extensive property; for instance, we know that 100 g of water has 100x the heat capacity of 1 g of water.

So, we can also have an intensive property, the molar heat capacity at constant volume, which is a measure of heat capacity at constant volume per mole of material: \( C_V \).

There is also the specific heat capacity, which gives us a useful measure of heat capacity per unit mass of sample.

Generally:

Heat capacities are temperature dependent, decreasing at lower \( T \).

Over small ranges near room temperature, \( C_V \) are almost invariant to changes in temperature.

Molecular Interpretation of Heat Capacity

We previously showed that the internal energy of an atomic ideal system is given by

\[
U_m = U_m(0) + \frac{3}{2} RT
\]

so that \( C_V = \frac{\partial U_m}{\partial T} |_{V} \approx \frac{3}{2} R \).

For non-linear polyatomic molecules in an ideal gas system:

\[
C_V = \left( \frac{\partial U_m}{\partial T} \right) |_{V} = 3R
\]

Then \( C_V \) is independent of temperature, and ca. 24.94 J K\(^{-1}\) mol\(^{-1}\).

When vibration is considered as well, for frequency \( \nu \):

\[
C_V = \frac{\partial U_m}{\partial T} |_{V} = 3R
\]

\[
f = \frac{\hbar}{h^2} \nu \left( \frac{T}{k} \right) \left( 1 - e^{-\hbar \nu/kT} \right)
\]

At \( T = 0 \), \( f = 0 \), and \( f \) is approx. 1 when \( kT > h \). Vibrational contributions to heat capacity are 0 at \( T = 0 \), and climb steadily to the “classical value” of \( k \) with increasing \( T \), more and more energy levels become accessible and \( k \) appears that the vibrations are no longer quantized.

Relating \( U \) and \( T \) at Constant \( V \)

Heat capacity is used (say in a calorimeter) to relate internal energy changes and changes in temperature.

As usual, an infinitesimal change in temperature changes energy slightly:

\[
dU = C_V dT \text{ at constant volume}
\]

Over a measurable range of temperatures, if \( C_V \) is a constant,

\[
\Delta U = C_V \Delta T \text{ at constant volume}
\]

Change in energy can be noticed with heat supplied at a constant \( V \):

\[
q_V = C_V \Delta T \text{ at constant volume}
\]

1. Supply a controlled known amount of heat to the sample (say with an electric current in a heater)
2. Monitor the resulting increase in temperature
3. The ratio heat supplied/ temperature increase is the heat capacity

Large heat capacity: large supply of heat, small change in measured \( T \)
Small heat capacity: large supply of heat, large change in measured \( T \)
Infinite heat capacity: at a phase transition, energy changes phases!