Chapter 3 of Atkins: The First Law: the machinery

Chapter 3.1 - 3.3

**State Functions**

* Exact and inexact differentials
* Changes in internal energy
* The Joule experiment
* Changes in internal energy at constant $p$

**Temperature Dependence of Enthalpy**

* Changes in enthalpy at constant volume
* Isothermal compressibility
* Joule-Thomson effect

$C_V \text{ vs. } C_p$
State vs. Path Functions

**state functions**: Properties independent of how the substance is prepared, and are functions of variables such as pressure and temperature (define the state of system)

examples: U: internal energy
            H: enthalpy

**path functions**: Properties that relate to the preparation of the state of the substance

examples: w: work done preparing a state
           q: energy transferred as heat

state functions: system possesses $U$ and $H$

path functions: states do not possess $q$ and $w$
State Functions

Initially:
state has internal energy $U_i$

Path 1:
adiabatic expansion to final state with internal energy $U_f$
work done on the system is $w$

Path 2:
non-adiabatic expansion to final state with $U_f$
$q'$ and $w'$ are both done on the system

$U$: property of state
numerically same value of $\Delta U$

$w$, $q$: property of path
Exact & Inexact Differentials

**Exact Differential:**
System is taken along a path, with $\Delta U = U_f - U_i$, and the overall change is the sum of the infinitesimal changes along the path (i.e., an integral):

$$\Delta U = \int_i^f dU$$

$U$ is independent of path - path independence is expressed by saying that $dU$ is an **exact differential** - an infinitesimal quantity, which when integrated gives a path independent result.

**Inexact Differential:**
System is heated, total energy transferred as heat is the sum of individual contributions along each point of the path:

$$q = \oint_{\text{path}} dq$$

Do not write $\Delta q$: $q$ is not a state function, energy is not $q_f - q_i$.
Numerically, $q$ depends upon the path of integration (e.g., adiabatic vs. non-adiabatic) - path dependence is expressed by saying that $dq$ is an **inexact differential** - infinitesimal quantity that depends upon the path ($dw$ is also an **inexact differential**).
Work, heat, internal energy and pathways

Consider a perfect gas in a cylinder with a piston:
Initial state \( T, V_i \)
Final state \( T, V_f \)

Change of state:

**Path 1:** free expansion against no external pressure
**Path 2:** reversible isothermal expansion
**Path 3:** irreversible isothermal expansion against \( p_{\text{ext}} \neq 0 \)

Calculate \( q \), \( w \) and \( U \) for each pathway

All pathways: internal energy arises from kinetic energy of molecules, so since processes are isothermal, \( \Delta U = 0 \), so \( q = -w \)

**Path 1:** free expansion, \( w = 0 \), so \( q = 0 \)
**Path 2:** \( w = -nRT \ln(V_f/V_i) \), so \( q = nRT \ln(V_f/V_i) \)
**Path 3:** \( w = -p_{\text{ext}} \Delta V \), so \( q = p_{\text{ext}} \Delta V \)
For a closed system of constant composition, \( U \) is function of \( V \) and \( T \) (possible to express \( p \) in terms of \( V \) and \( T \), so \( p \) is not independent here)

Say \( V \) makes a small change to \( V + dV \) at constant \( T \):

\[
U' = U + \left( \frac{\partial U}{\partial V} \right)_T dV
\]

or \( T \) changes to \( T + dT \) at constant \( V \):

\[
U' = U + \left( \frac{\partial U}{\partial T} \right)_V dT
\]

The coefficients \( (\partial U/\partial V)_T \) and \( (\partial U/\partial T)_V \) are **partial derivatives** of \( U \) with respect to \( V \) and \( T \), respectively (or, slopes of \( U \) vs \( V \) at constant \( T \) and \( U \) vs \( T \) at constant \( V \)) - if both \( V \) and \( T \) change infinitesimally (recall \( dVdT = 0 \)):

\[
U' = U + \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT
\]
Changes in Internal Energy, 2

These infinitesimal changes in conditions imply $U'$ differs from $U$ by an infinitesimal amount $dU$; thus,

$$U' = U + dU = U + \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT;$$

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

Infinitesimal changes in $V$ and $T$ result in an infinitesimal change in $U$, with constants of proportionality being the **partial derivatives**

remember: these give a *slope of property of interest against one variable*, with all other variables held constant

it is important to keep in mind that partial derivatives all have physical meaning, as well as being a useful mathematical tool

Recall that $(\partial U/\partial T)_V = C_V$ (i.e., the change in internal energy at constant volume with change temperature is the heat capacity at constant volume)
Graphic Illustration

Internal energy, \( U \)

\[ U + \left( \frac{\partial U}{\partial V} \right)_{T} \, dV \]

Volume, \( V \)

Temperature, \( T \)

Internal energy, \( U \)

\[ U + \left( \frac{\partial U}{\partial T} \right)_{V} \, dT \]

Volume, \( V \)

Temperature, \( T \)
Graphic Illustration

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

Prof. Mueller
Chemistry 451 - Fall 2003
Lecture 9 - 9
Changes in Internal Energy, 3

\[ (\partial U / \partial V)_T \], the change in internal energy as the volume a substance occupies changes, is denoted as \( \pi_T \) and is called the *internal pressure*. 
Changes in Internal Energy, 4

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

\( \pi_T \) is a measure of cohesive forces in the sample:

\[ dU = \pi_T dV + C_V dT \]

\( dU > 0 \), internal energy increases, \( dV > 0 \), volume expands isothermally and with attractive forces dominating

\( \pi_T > 0 \)

For a perfect gas, \( \pi_T = 0 \), and internal energy is independent of the volume of gas in the sample.
James Joule thought he could measure internal pressure with the apparatus at the right - high pressure gas expands into a vacuum - however, no change in temperature is measured: WHY?

# expansion into vacuum: \( w = 0 \)
# no heat transfer: \( \Delta T = 0 \), so \( q = 0 \)
# consequently: \( \Delta U = w + q = 0 \)
# therefore: \( \pi_T = 0 \)

Actually, the heat capacity of his crude apparatus was so large, that the temperature change caused by this expansion of gas was simply too small to measure - so small deviations of real gases were not detected...
Changes in Internal Energy at Constant $p$

How does internal energy vary with temperature at constant pressure?

$$dU = \pi_T dV + C_V dT$$

Divide both sides above by $dT$, and impose constant pressure:

$$\left( \frac{\partial U}{\partial T} \right)_p = \pi_T \left( \frac{\partial V}{\partial T} \right)_p + C_V$$

The differential on the RHS describes change in volume at constant pressure with changing temperature, and is related to the expansion coefficient, $\alpha$, of a pure substance:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

Large $\alpha$: big responses to changes in temperature.
Changes in Internal Energy at Constant $p$

**Table 3.1** Expansion coefficients ($\alpha$) and isothermal compressibilities ($\kappa_T$)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\alpha/10^{-4}$ K$^{-1}$</th>
<th>$\kappa_T/10^{-6}$ atm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>12.4</td>
<td>92.1</td>
</tr>
<tr>
<td>Diamond</td>
<td>0.030</td>
<td>0.187</td>
</tr>
<tr>
<td>Lead</td>
<td>0.861</td>
<td>2.21</td>
</tr>
<tr>
<td>Water</td>
<td>2.1</td>
<td>49.6</td>
</tr>
</tbody>
</table>

*More values are given in the Data section at the end of this volume.*

For an ideal gas where $pV = nRT$

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left( \frac{\partial (nRT/p)}{\partial T} \right)_p = \frac{nR}{pV} = \frac{1}{T}$$
**Changes in Internal Energy at Constant $p$**

Substitute $\alpha$ into the expression for $(\partial U/ \partial T)_p$:

$$
\left( \frac{\partial U}{\partial T} \right)_p = \alpha \pi_T V + C_V
$$

The dependence of internal energy upon temperature at constant pressure can be measured in terms of $C_V$ and $\alpha$ (two different experiments) and $\pi_T$.

For a perfect gas, since $\pi_T = 0$:

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

So we know $(\partial U/\partial T)_V = C_V$ and $(\partial U/\partial T)_p$ above - in our experiments, we can easily use the simpler first expression by **controlling volume**: i.e., at constant volume, $w = 0$, and $\Delta U = q_V$.