Statistical Molecular Thermodynamics

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Video 5.3

Differentials and State Functions
State Functions

A state function is a property that depends only upon the state of the system. That is, it is independent of how the system was brought to that state (independent of the path).

A key property of a state function is that its differential can be integrated in a normal, path independent way.

- **Energy** is a state function:
  \[ \int_{1}^{2} dU = U_2 - U_1 = \Delta U \]
  Energy is independent of the path from 1 to 2; it depends only on the initial (1) and final (2) states.

- **Work** and **heat** are not state functions.
  \[ w = - \int_{1}^{2} P_{\text{ext}} \, dV \]
  We’ve already seen that work depends on the path from state 1 to state 2 (different \( P_{\text{ext}} \) lead to different \( w \))
Different Differentials

Since work depends upon how a process is carried out, work is not a state function, work is a *path function*, so we write,

\[ \int_{1}^{2} \delta w = w \quad \text{(not } \Delta w \text{ or } w_2 - w_1 \text{)} \]

An *inexact differential* Cannot be integrated in the normal way

Energy is a state function, and \( dU \) is an *exact differential*.

<table>
<thead>
<tr>
<th>State functions:</th>
<th>Path functions:</th>
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<tbody>
<tr>
<td>( \int_{1}^{2} dU = U_2 - U_1 = \Delta U )</td>
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The First Law of Thermodynamics

Energy is conserved

\[ dU = \delta q + \delta w \quad \text{(differential form)} \]

\[ \Delta U = q + w \quad \text{(integral form)} \]

Even though \( \delta q \) and \( \delta w \) are path functions (inexact differentials), their sum is a state function (an exact differential).
All Reversible Roads Lead To...

\[ P_1, V_1, T_1 \rightarrow P_2, V_2, T_1 \]

**Path A:** reversible isothermal expansion

**Path B+C:** reversible *adiabatic* expansion followed by heating at constant volume.

**Path D+E:** reversible constant-pressure expansion followed by cooling at constant volume.

\( \Delta U \) must be the same for all paths, but \( q \) and \( w \)?