

# 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,

$$\int_1^2 \delta w = w \quad (\text{not } \Delta w \text{ or } w_2 - w_1)$$

An *inexact differential*

Cannot be integrated in the normal way

Energy is a state function, and  $dU$  is an *exact differential*.

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*State functions:*

$$\int_1^2 dU = U_2 - U_1 = \Delta U$$

*Path functions:*

$$\int_1^2 \delta q = q \quad (\text{not } \Delta q \text{ or } q_2 - q_1)$$

$$\int_1^2 \delta w = w \quad (\text{not } \Delta w \text{ or } w_2 - w_1)$$

# THE FIRST LAW OF THERMODYNAMICS

Energy is conserved

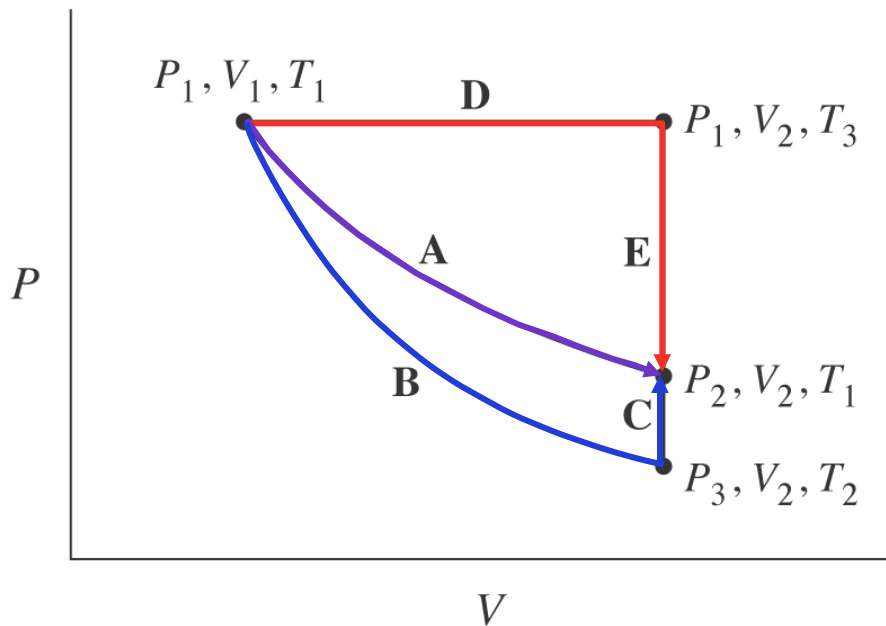
$$dU = \delta q + \delta w \quad (\text{differential form})$$

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

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...

$$P_1, V_1, T_1 \rightarrow P_2, V_2, T_1$$



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

**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.