Statistical Molecular Thermodynamics

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Video 5.4

Characteristic Ideal Gas Expansion Paths
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 \( w \)?
Since the process is reversible,
\[-\delta q_{\text{rev},A} = \delta w_{\text{rev},A} = -P_{\text{gas}}\, dV = -\frac{RT_1}{V}\, dV\]

And we have,
\[-q_{\text{rev},A} = w_{\text{rev},A} = -RT_1 \int_{V_1}^{V_2} \frac{dV}{V} = -RT_1 \ln \frac{V_2}{V_1}\]

Note that heat transfer in is required to maintain temperature
Path B

\[ P_1, V_1, T_1 \quad \rightarrow \quad P_3, V_2, T_2 \]

Reversible adiabatic expansion

Adiabatic means no energy is transferred as heat, i.e., \( q = 0 \), and therefore \( \Delta U = w \) and \( dU = \delta w \)

For an ideal gas, \( U \) depends only on \( T \)

\[
C_V(T) = \left( \frac{\partial U}{\partial T} \right)_V \quad \xrightarrow{\text{ideal gas}} \quad C_V(T) = \frac{dU}{dT} \quad \rightarrow \quad dU = C_V(T)dT
\]

\[ w_{\text{rev}, B} = \Delta U_B = \int_{T_1}^{T_2} dU = \int_{T_1}^{T_2} C_V(T)dT \]

(from \( T_1 \) to \( T_2 \))
**Path C**

\[ P_3, V_2, T_2 \xrightarrow{C} P_2, V_2, T_1 \]

Reversibly heat at constant volume

\[ \Delta V = 0, \text{ so } w_{\text{rev,C}} = -PdV = 0 \]

That leaves only heat, i.e., \( \Delta U_C = q_{\text{rev,C}} + w_{\text{rev,C}} = q_{\text{rev,C}} + 0 \)

\[ q_{\text{rev,C}} = \Delta U_C = \int_{T_2}^{T_1} C_V(T) dT \]

(from \( T_2 \) to \( T_1 \))
**Paths B + C**

For the sum of B + C

\[ q_{\text{rev,B+C}} = q_{\text{rev,B}} + q_{\text{rev,C}} = 0 + \int_{T_2}^{T_1} C_V(T) dT \]

\[ w_{\text{rev,B+C}} = w_{\text{rev,B}} + w_{\text{rev,C}} = \int_{T_1}^{T_2} C_V(T) dT + 0 \]

For the energy,

\[ \Delta U_{B+C} = \Delta U_B + \Delta U_C = \int_{T_1}^{T_2} C_V(T) dT + \int_{T_2}^{T_1} C_V(T) dT = 0 \]

\( \Delta U = 0 \), the same as for path A (as must be true for a state function), but \( w_{\text{rev,A}} \neq w_{\text{rev,B+C}} \), \( q_{\text{rev,A}} \neq q_{\text{rev,B+C}} \)
Paths D + E

For the sum of D + E

\[ w_{\text{rev,D+E}} = w_{\text{rev,D}} + w_{\text{rev,E}} = -P_1(V_2 - V_1) + 0 \]

\[ \Delta U_{\text{D+E}} = \int_{T_1}^{T_3} C_V(T)dT + \int_{T_3}^{T_1} C_V(T)dT = 0 \]

Another illustration that it’s usually easiest to get \( q \) by difference from more easily computed \( \Delta U \) and \( w \)

So, \( q_{\text{rev,D+E}} = P_1(V_2 - V_1) \)
Comparison of Paths

\[ w_{\text{rev},D+E} = -P_1(V_2 - V_1) \quad q_{\text{rev},D+E} = P_1(V_2 - V_1) \]

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

\[ w_{\text{rev},A} = -RT_1 \ln \frac{V_2}{V_1} \quad q_{\text{rev},A} = RT_1 \ln \frac{V_2}{V_1} \]

\[ w_{\text{rev},B+C} = \int_{T_1}^{T_2} C_V(T) dT \quad q_{\text{rev},B+C} = \int_{T_1}^{T_2} C_V(T) dT \]

\[ \Delta U = 0 \text{ for all paths (state function), but } q_{\text{rev}} \text{ and } w_{\text{rev}} \text{ differ} \]