

# STATISTICAL MOLECULAR THERMODYNAMICS

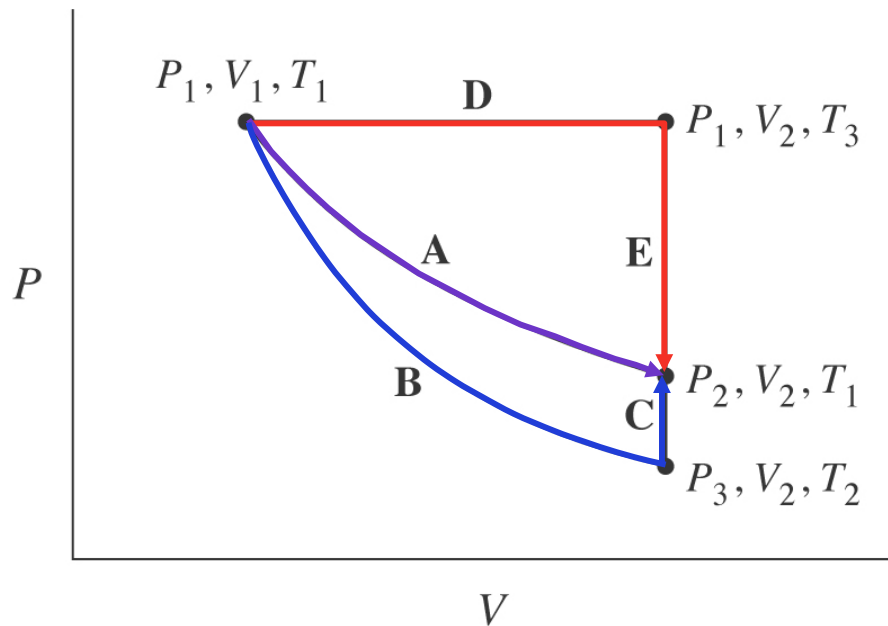
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Video 5.4

Characteristic Ideal Gas Expansion Paths

# ALL REVERSIBLE ROADS LEAD TO...

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



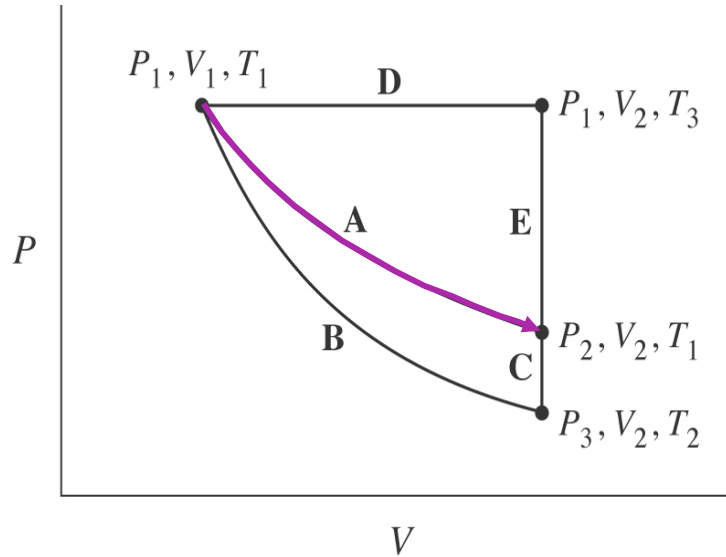
$\Delta U$  must be the same for all paths, but  $q$  and  $w$ ?

**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.

## PATH A



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

Reversible *isothermal* expansion

Since the energy of an ideal gas depends only on  $T$

$$\Delta U_A = 0 \xrightarrow{\Delta U = q + w} -q_{\text{rev},A} = w_{\text{rev},A}$$

Since the process is reversible,

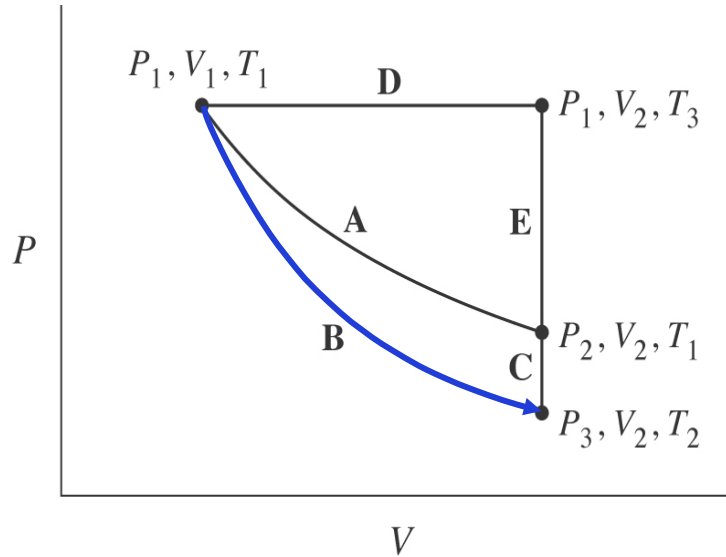
$$-\delta q_{\text{rev},A} = \delta w_{\text{rev},A} = -P_{\text{gas}} dV = -\frac{RT_1}{V} dV$$

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



$$P_1, V_1, T_1 \longrightarrow P_3, V_2, T_2$$

Reversible *adiabatic* expansion

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

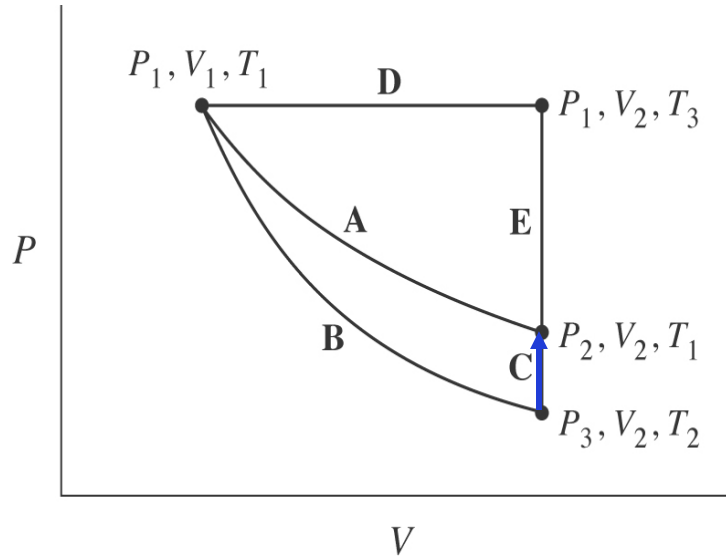
For an ideal gas,  $U$  depends only on  $T$

$$C_V(T) = \left( \frac{\partial U}{\partial T} \right)_V \xrightarrow{\text{ideal gas}} C_V(T) = \frac{dU}{dT} \longrightarrow dU = C_V(T)dT$$

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

(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

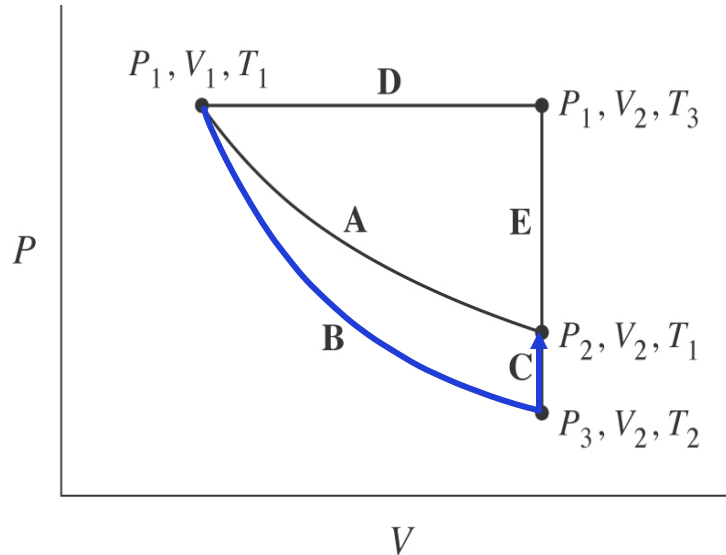
$$\Delta V = 0, \text{ so } w_{\text{rev,C}} = -PdV = 0$$

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

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

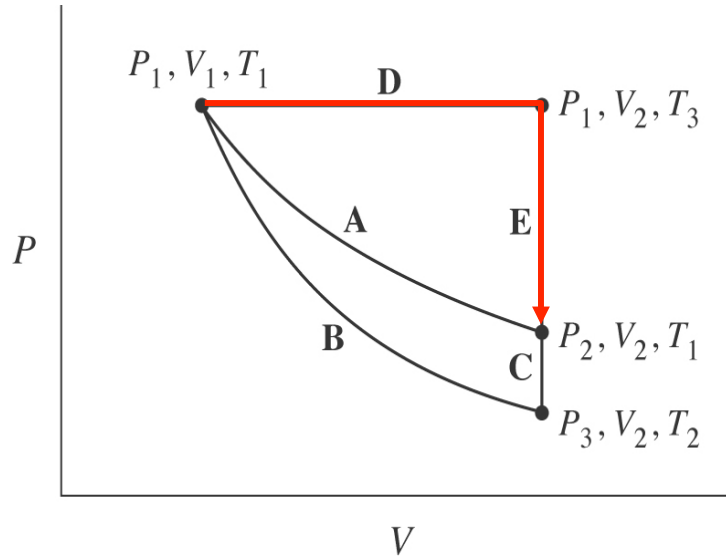
$$w_{\text{rev},B+C} = w_{\text{rev},B} + w_{\text{rev},C} = \int_{T_1}^{T_2} C_V(T) dT + 0$$

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  $w$*

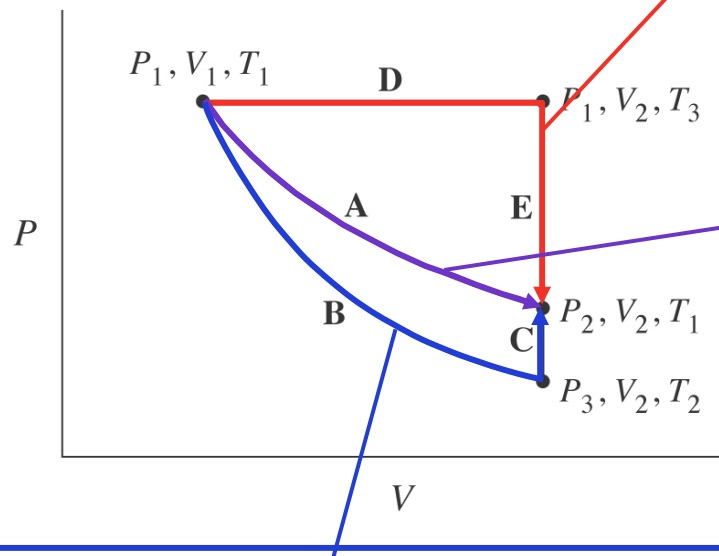
$$\text{So, } q_{\text{rev,D+E}} = P_1(V_2 - V_1)$$

# COMPARISON OF PATHS

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

$$q_{\text{rev},D+E} = P_1(V_2 - V_1)$$

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



$$w_{\text{rev},A} = -RT_1 \ln \frac{V_2}{V_1}$$

$$q_{\text{rev},A} = RT_1 \ln \frac{V_2}{V_1}$$

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

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

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