

## 20.3: Unlike heat, Entropy is a State Function

### Circular integrals

Because entropy is a state function, it integrates to zero over any circular path going back to initial conditions, just like  $U$  and  $H$ :

$$\oint dS = 0$$

$$\oint dH = 0$$

$$\oint dU = 0$$

As discussed previously, we can use this fact to revisit the isotherm + isochore + adiabat circular path (Figure 20.3.1 ).

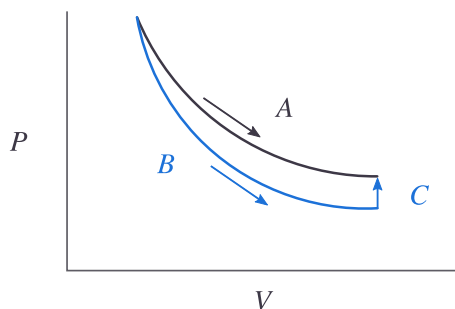


Figure 20.3.1 : A: isothermal expansion, B:adiabat, C:isochore (CC BY-NC; Ümit Kaya via LibreTexts)

#### Along adiabat B and isochore C:

- There is no heat transfer along adiabat B:

$$q_{rev,B} = 0$$

- There is no work along isochore C:

$$\delta w = 0$$

- But the temperature changes from  $T_2$  back to  $T_1$ . This requires heat:

$$q_{rev,C} = C_V \Delta T$$

#### Along the isotherm A:

- We have seen that

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

The quantities  $q_{rev,A}$ ,  $q_{rev,B}$ , and  $q_{rev,C}$  are **not** the same, which once again underlines that heat is a path function. How about entropy?

First, consider the combined paths of B and C:

$$q_{rev,B+C} = \int_{T_2}^{T_1} C_v dT$$

$$\int dS_{B+C} = \int \frac{dq_{rev,B+C}}{T} = \int_{T_2}^{T_1} \frac{C_v}{T} dT$$

We had seen this integral before from Section 19-6, albeit from  $T_1$  to  $T_2$ :

$$\Delta S_{B+C} = nR \ln \frac{V_2}{V_1} \quad (20.3.1)$$

(Notice sign in Equation 20.3.1 is positive)

Along the isotherm A:

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

$T$  is a constant so we can just divide  $q_{rev,A}$  by  $T$  to get  $\Delta S_A$ :

$$\Delta S_A = nR \ln \frac{V_2}{V_1}$$

We took two different paths to get start and end at the same points. Both paths had the same change in entropy. Clearly entropy is a *state function* while  $q_{rev}$  is not.

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