The Second Law of Thermodynamics

* Returning to the "original" (internal energy) form of the first law:

$$\delta q = c_v dT + p d\alpha \qquad (1)$$

It is the only inexact differential we have in the eqn

Recall: $\int \delta q = \int (c_v dT + p d\alpha)$

$\int \delta q$: cannot integrate with limits

$c_v dT$: can integrate from T_1 to T_2

$p d\alpha$: cannot integrate explicitly (with limits) unless you know how p evolves

How can we ameliorate this problem?

We can divide Eq. (1) by T

$$\frac{\delta q}{T} = \frac{c_v dT}{T} + \frac{p d\alpha}{T}$$

and use the ideal gas law

$p\alpha = R_d T$

(ignore virtual T correction)

$p = \frac{R_d T}{\alpha}$

Using ideal gas:

$$\frac{\delta q}{T} = c_v \frac{dT}{T} + R_d \frac{d\alpha}{\alpha} \qquad (2)$$

$$= c_v \, d\ln T + R_d \, d\ln\alpha$$

We will now do an integral along a closed path on Eq. (2) ("that returns to the original position)

$$\oint \frac{\delta q}{T} = c_v \oint d\ln T + R_d \oint d\ln\alpha$$

T and α are state variables by definition

$$\oint dT = \oint d\alpha = 0$$

state vars. only care about initial and final positions

$$\text{If}: \quad c_v \oint d\ln T + R_d \oint d\ln\alpha = 0$$

$$\oint \frac{\delta q}{T} = 0$$

Even though δq is a process variable

$\frac{\delta q}{T}$ is a state variable

This new state variable is known as the entropy!

$$ds = \frac{\delta q}{T} \quad \text{where } s = \text{entropy}$$

Entropy form of the first law

ds means that entropy changes follow exact diff. entropy cares only about initial and final state

We can rewrite Eq. (1) as:

$$ds = c_v \, d\ln T + R_d \, d\ln \alpha \qquad (3)$$
$$ds = c_p \, d\ln T - R_d \, \ln p \qquad (4)$$

Note: the right-hand side terms in Eq. (4) are the terms that define θ, so that

$$ds = c_p \, d\ln\theta$$ (see θ derivation from last lecture)

entropy - potential temperature relation

yet another form of the first law.

Recall: $\theta = T\left(\frac{p_0}{p}\right)^{\frac{R_d}{c_p}}$