

**ESCI 341 – Atmospheric Thermodynamics**  
**Lesson 9 – Entropy**

**References:** *An Introduction to Atmospheric Thermodynamics*, Tsonis  
*Physical Chemistry (4<sup>th</sup> edition)*, Levine  
*Thermodynamics and an Introduction to Thermostatistics*, Callen  
*The Elements of Classical Thermodynamics*, Pippard

**A REVIEW OF STATE VARIABLES**

- **The thermodynamic state of a one-component, closed system in equilibrium can be completely described by any two state variables (other than mass or moles).**
- **The state variables have two important properties:**
  - **The change in any of the state variables (say  $U$ ) doesn't depend on the path of the system on a thermodynamic diagram. It only depends on the endpoints.**

$$\int_a^b dU = U(b) - U(a)$$

- **The integral of a state variable around a closed path is zero.**

$$\oint dU = 0$$

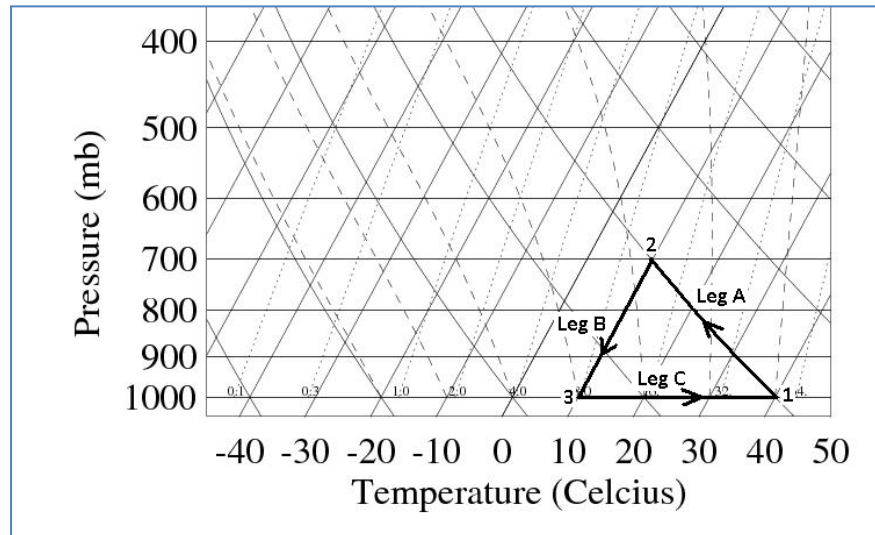
- **Mathematically, this means that differentials of state functions are *exact differentials*.**

**HEAT IS NOT A STATE VARIABLE**

- **Imagine that an air parcel starts out at Point 1 on the skew- $T$  diagram shown below. The initial pressure and temperature are  $p_1$  and  $T_1$ . The parcel moves in a reversible, closed cycle around the path shown. The three legs of the path are:**
  - **Leg A: Adiabatic expansion to pressure  $p_2$ .**
  - **Leg B: Isothermal compression back to pressure  $p_1$ .**
  - **Leg C: Isobaric heating back to temperature  $T_1$ .**
- **The integral of  $dq_{rev}$  around the closed path gives the total heat exchange between the parcel and its surroundings, and is just the sum of the heats from each leg,**

$$\oint dq_{rev} = q_{revA} + q_{revB} + q_{revC}$$

Note: We are very careful to write this as  $q_{rev}$  to indicate that all the paths are reversible.



- Leg A is reversibly adiabatic, so

$$q_{revA} = \int_{\text{Leg A}} dq_{rev} = 0 \quad (1)$$

- The temperature at Point 2 is related to the temperature at Point 1 via the Poisson relation

$$T_2 = T_1 \left( \frac{p_2}{p_1} \right)^{R_d/c_p} . \quad (2)$$

- Leg B is isothermal. The heat for this leg is therefore

$$q_{revB} = -R_d T_2 \ln \frac{p_1}{p_2} = -R_d \left[ T_1 \left( \frac{p_2}{p_1} \right)^{R_d/c_p} \right] \ln \frac{p_1}{p_2} . \quad (3)$$

- Leg C is isobaric. The heat along this path is just

$$q_{revC} = c_p (T_1 - T_2) = c_p T_1 \left[ 1 - \left( \frac{p_2}{p_1} \right)^{R_d/c_p} \right] \quad (4)$$

- For the path shown on the skew-T diagram,  $T_1 = 313\text{K}$ ,  $p_1 = 1000\text{ mb}$ , and  $p_2 = 700\text{ mb}$ . Using these numbers in Eqs. (3) and (4) gives

$$q_{revA} = 0\text{ kJ/kg}$$

$$q_{revB} = -28.95\text{ kJ/kg}$$

$$q_{revC} = 30.47\text{ kJ/kg}$$

$$q_{rev} = 1.52\text{ kJ/kg}$$

- We've demonstrated that the total heat around the closed, reversible path is not zero. Therefore, heat is not a state variable.
- The work around the path can be found from the first law of thermodynamics,

$$du = dq + dw.$$

Integrating around the closed path gives

$$\oint du = \oint dq + \oint dw \Rightarrow 0 = q + w \Rightarrow w = -q.$$

- Since heat and work are not state variables (and are therefore not exact differentials), some texts give their differentials a horizontal slash symbol,  $\overline{dw}$  and  $\overline{dq}$  to show this.

## ENTROPY

- What if, instead of evaluating  $\oint dq_{rev}$  around the closed path, we evaluate

$\oint (dq_{rev}/T)$  around the closed path?

- For Leg A,  $dq_{rev}$  was zero, so the integral is still zero

$$\int_{\text{Leg A}} \frac{dq_{rev}}{T} = 0 \quad (5)$$

- For Leg B (the isothermal leg)

$$\int_{\text{Leg B}} \frac{dq_{rev}}{T} = - \int_{\text{Leg B}} \frac{\alpha dp}{T} = -R_d \int_{\text{Leg B}} \frac{dp}{p} = -R_d \ln \frac{p_1}{p_2}. \quad (6)$$

- For Leg C (the isobaric leg)

$$\int_{\text{Leg C}} \frac{dq_{rev}}{T} = \int_{\text{Leg C}} \frac{c_p dT}{T} = c_p \int_{\text{Leg C}} \frac{dT}{T} = c_p \ln \frac{T_1}{T_2}.$$

But, from Eq. (2), we have

$$\frac{T_1}{T_2} = \left( \frac{p_1}{p_2} \right)^{R_d/c_p},$$

so

$$\int_{\text{Leg C}} \frac{dq_{rev}}{T} = c_p \ln \left( \frac{p_1}{p_2} \right)^{R_d/c_p} = R_d \ln \frac{p_1}{p_2}. \quad (7)$$

- Summing the results for the three legs [Eqs. (5), (6), and (7)] we have

$$\oint \frac{dq_{rev}}{T} = \int_{\text{Leg A}} \frac{dq_{rev}}{T} + \int_{\text{Leg B}} \frac{dq_{rev}}{T} + \int_{\text{Leg C}} \frac{dq_{rev}}{T} = R_d \ln \frac{p_1}{p_2} - R_d \ln \frac{p_1}{p_2},$$

or

$$\oint \frac{dq_{rev}}{T} = 0 \quad (8)$$

- Eq. (8) implies that  $dq_{rev}/T$  is an exact differential, and therefore, must be the differential of a state variable.

$$\oint ds = \oint \frac{dq_{rev}}{T} \quad (9)$$

- We call this state variable the specific entropy, and denote it by  $s$ . Therefore,

$$ds \equiv \frac{dq_{rev}}{T}. \quad (10)$$

- Multiplying Eq. (10) by mass, we get an extensive quantity called entropy,

$$dS \equiv \frac{dQ_{rev}}{T}. \quad (11)$$

- Entropy,  $S$ , is an extensive property, and has the units of  $\text{J K}^{-1}$ . The specific entropy ( $s = S/m$ ) is an intensive property, and has units of  $\text{J K}^{-1} \text{kg}^{-1}$ .
- Note that entropy is only defined for equilibrium states, and that it is always defined in terms of the REVERSIBLE HEAT!

## MATHEMATICAL EXCURSION

- A differential of the form

$$dw = Mdx + Ndy \quad (12)$$

is an *exact differential* if

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}. \quad (13)$$

- Sometimes an inexact differential can be made into an exact differential by multiplying it by a suitable function, called an *integrating factor*.
- Although the differential of heat,  $dq_{rev}$ , is not an exact differential, it becomes an exact differential if we multiply it by  $1/T$ .
  - Therefore,  $1/T$  is an *integrating factor* for the differential,  $dq_{rev}$ .

## ENTROPY AND THE FUNDAMENTAL EQUATION

- Recall from Lesson 2 that the fundamental equation relates internal energy to entropy, volume, and the amounts of the constituents,

$$U = f(S, V, n_i). \quad (14)$$

Taking the differential of Eqn. (14) for a system in material equilibrium ( $n_i$  constant) we get

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV. \quad (15)$$

- Comparing Eqns. Error! Reference source not found. and (15) we see that

$$T = \left( \frac{\partial U}{\partial S} \right)_V \quad (16)$$

and

$$p = - \left( \frac{\partial U}{\partial V} \right)_S \quad (17)$$

- Equation (16) is the thermodynamic definition of temperature, while Eqn. (17) is the thermodynamic definition of pressure.

## ENTROPY OF AN IDEAL GAS

- The first of Eqn. set Error! Reference source not found. can be rewritten (for an ideal gas) as

$$dS = \frac{dU}{T} + \frac{p}{T} dV = C_v \frac{dT}{T} + nR \frac{dV}{V}.$$

- If this is integrated from some initial state (with subscript 0) we get

$$S(T, V) = S_0 + C_v \ln \left( \frac{T}{T_0} \right) + nR \ln \left( \frac{V}{V_0} \right), \quad (18)$$

where  $S_0 = S(T_0, V_0)$ .

- Using the second form of the first law of thermodynamics the entropy of an ideal gas can be shown to also be

$$S(T, p) = S_0 + C_p \ln \left( \frac{T}{T_0} \right) - nR \ln \left( \frac{p}{p_0} \right), \quad (19)$$

where  $S_0 = S(T_0, p_0)$ .

- The change in entropy between two states (State 1 and State 2) for an ideal gas is

$$\Delta S = S_2(T_2, V_2) - S_1(T_1, V_1) = C_v \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \quad (20)$$

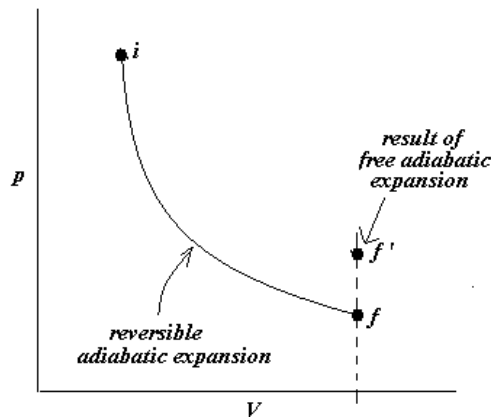
if the state variables are  $T$  and  $V$ , or

$$\Delta S = S(T_2, p_2) - S(T_1, p_1) = C_p \ln\left(\frac{T_2}{T_1}\right) - nR \ln\left(\frac{p_2}{p_1}\right) \quad (21)$$

if the state variables are  $T$  and  $p$ .

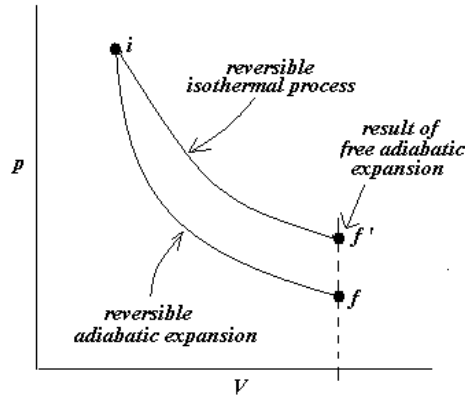
### ENTROPY CHANGE IN AN ADIABATICALLY EXPANDING IDEAL GAS

- Consider two scenarios:
  - An ideal gas reversibly and adiabatically expands from volumes  $V_i$  to  $V_f$ 
    - The change in entropy is zero, because  $dQ_{rev} = 0$ .
  - An ideal gas undergoes an adiabatic free expansion from volumes  $V_i$  to  $V_f$ 
    - No work is done in a free expansion.
    - Since no heat is added either, the internal energy does not change, so the temperature remains constant.
    - Since the expansion is isothermal, the change in entropy is equal to  $nR \ln(V_f/V_i)$
  - The two cases do not connect the same states on a thermodynamic diagram. Though they end up at the same final volume, the final pressures will differ (see diagram).



- In both cases the process is adiabatic, yet the free expansion has a non-zero entropy change. Why?

- Because the free expansion is not a reversible process, and entropy is defined in terms of reversible processes.
- You could connect points  $i$  and  $f'$  with a reversible isothermal process, but this would require  $dQ_{rev} \neq 0$ .



- There is no reversible, adiabatic process connecting points  $i$  and  $f'$ , and so the entropy change is non-zero.

### GIBBS' THEOREM

- The entropy of a mixture of ideal gasses is given by:

$$S(T, V) = \sum S_{0i} + \sum (C_{vi}) \ln \left( \frac{T}{T_0} \right) + R \left( \sum n_i \right) \ln \left( \frac{V}{V_0} \right) \quad (22)$$

where the subscript  $i$  refers to the  $i^{\text{th}}$  gas in the mixture.

- Equation (22) is known as Gibbs' Theorem, which in words states:

*The entropy of a mixture of ideal gases is the sum of the entropies that each gas would have if it alone were to occupy the volume  $V$  at temperature  $T$ .*

### ENTROPY OF MIXING

- Imagine several gasses separated by rigid, impermeable partitions. Each gas is at the same temperature and pressure.

1	2	3	4	...	i - 1	i
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Before mixing. Each gas at same  $T$  and  $P$ .

- If the partitions are removed, each gas expands and mixes throughout the entire volume.
  - The mixing is adiabatic, so the temperature remains constant during mixing.
  - The volume of each gas expands, and so therefore each gas increases its entropy by an amount

$$\Delta S_i = n_i R \ln \left( \frac{V}{V_i} \right). \quad (23)$$

- The total entropy change is the sum of the changes for each gas,

$$\Delta S = \sum \Delta S_i = \sum n_i R \ln \left( \frac{V}{V_i} \right). \quad (24)$$

- Since we are dealing with ideal gases we have the relation

$$\frac{n_i}{n} = \frac{V_i}{V} = \chi_i \quad (25)$$

where  $\chi_i$  is the mole fraction for gas  $i$ . So, (24) becomes

$$\Delta S = \sum \Delta S_i = \sum n_i R \ln \left( \frac{1}{\chi_i} \right) = - \sum n_i R \ln \chi_i = -nR \sum \frac{n_i}{n} \ln \chi_i = -nR \sum \chi_i \ln \chi_i.$$

- This entropy change is called the *entropy of mixing*.

$$\Delta S_{\text{mixing}} = -nR \sum \chi_i \ln \chi_i. \quad \text{Entropy of mixing} \quad (26)$$

- The entropy of mixing is always a positive value, so mixing of gasses always increased the entropy.

## EXERCISES

1. Starting with the first law of thermodynamics, show that the specific entropy for an ideal gas is

$$s(T, p) = s_0 + c_p \ln \left( \frac{T}{T_0} \right) - R' \ln \left( \frac{p}{p_0} \right).$$

2. What are the units for entropy? For specific entropy?
3. a. 6240 J of heat are supplied to 2 moles of helium (He, molecular weight 4 g/mol) at constant volume. The initial temperature and pressure are 15°C and 1000 mb. What are the final temperature and pressure?



- b. The helium is now allowed to expand isothermally to twice its initial volume. What is the new pressure?
- c. What is the total change in entropy and specific entropy for the helium?
4. a. 100 grams of helium (He) is mixed with 100 grams of nitrogen (N<sub>2</sub>, molecular weight 28 g/mol) at a pressure of 1000 mb and temperature of 20°C. What is the entropy of mixing?
- b. The mixing process is adiabatic, yet your answer from part a. is not zero. Why?

5. The First Law of Thermodynamics for an ideal gas can be written as

$$dq_{rev} = c_p dT - \alpha dp \quad (27)$$

a. Show that Eq. (27) can also be written as

$$dq_{rev} = c_p dT - \frac{R'T}{p} dp \quad (28)$$

b. Eq. (28) has the form of Eq. (12) where  $x \rightarrow T$ ;  $y \rightarrow p$ ;  $M = c_p$ ;  $N = R'T/p$ .

Show that Eq. (28) is not an exact differential by showing that the condition of Eq. (13) is not met.

c. Show that  $dq_{rev}/T$  is an exact differential, by multiplying Eq. (28) by  $T^{-1}$  and then showing that the condition of Eq. (13) is met.