

## ENV-413: Thermodynamics of the Earth systems

### Exercise session for Lecture 4: Entropy and the 2nd Law

#### Reversible and irreversible processes

1. Circle the following if they are irreversible processes
  - a) Heat transfer through a finite temperature difference
  - b) Absorption of solar radiation
  - c) Expansion into a vacuum
  - d) Infinitesimally slow expansion against an opposing pressure
2. List two examples of irreversible processes in the atmosphere

#### Entropy

1. Write the first law of thermodynamics, intensive, enthalpy form, expansion work.
2. For the reversible expansion of an ideal gas, we may substitute for the specific volume from the equation of state. Make this substitution in #1. You should now have an equation that is a function only of  $q$ ,  $T$ , and  $p$ , with  $dq$  on the left hand side.
3. Divide both sides of the equation in #2 by  $T$  (you should get equation (2.23))
4. With the term involving  $dq$  on the left hand side of the equation, the two terms on the right hand side of the equation are (exact, inexact) differentials
5. The sum of two exact differentials is (always, never, sometimes) an exact differential
6. The some of two inexact differentials is (always, never, sometimes) an exact differential

From #4-5 above, it is clear that  $dq/T$  is an exact differential for reversible processes

$$\oint \left( \frac{dq}{T} \right)_{rev} = 0$$

where the subscript *rev* emphasizes that this relationship holds only for a reversible process. Dividing heat by temperature thus converts the inexact differential  $dq$  into an exact differential. We can now

define a new thermodynamic state function, the *entropy*,  $\eta$ , to be  $d\eta = \left( \frac{dq}{T} \right)_{rev}$

It is important to remember that entropy is defined so that the change in entropy from one state to another is associated with a reversible process connecting the two states.

When a change in entropy between two given states occurs via an irreversible process, the change in entropy is exactly the same as for a reversible process: this is a consequence of entropy being a state variable and  $d\eta$  an exact differential, which means that integration of  $d\eta$  does not depend on the path (reversible or irreversible). Although the change in entropy is exactly the same for reversible and irreversible processes that have the same initial and final states,  $\int dq/T$  is not the same for reversible and irreversible processes. To accomplish a given change in entropy (or state) by an irreversible process, more heat is required than when a reversible process is involved. This implies that reversible processes are more efficient than irreversible processes.

7. During a cyclic, reversible process, entropy (increases, decreases, remains the same)
8. Irreversibilities in a system cause entropy to (increase, decrease, remain the same)
9. A system undergoes a process between two fixed states first in a reversible manner and then in an irreversible manner. For which case is the entropy change of the system greater? Why?
10. Is the value of the integral  $\int_1^2 dq/T$  the same for all processes between states 1 and 2? Explain
11. Is the value of the integral  $\int_1^2 dq/T$  the same for all reversible processes between states 1 and 2?
12. To determine the entropy change for an irreversible processes between states 1 and 2, should the integral  $\int_1^2 dq/T$  be performed along the actual process path or an imaginary reversible path? Explain
13. How does the value of the integral  $\int_1^2 dq/T$  compare for a reversible and irreversible process between the same end states?
14. Is it possible to create entropy? Is it possible to destroy it?
15. Is it possible for the entropy change of a closed system to be zero during an irreversible process? Explain

- 15a. Entropy is an exact differential (true, false)  
 15b. If  $\Delta\eta > 0$ , the process is (never, sometimes, always) irreversible  
 15c.

$$4. \oint \left( \frac{dq}{T} \right)_{rev} = \eta$$

is true for (irreversible, reversible, both) processes

16. From the equation you derived in #3, write the expression for entropy change for an ideal gas in enthalpy form (you should get (2.26b))

We now would like to derive the entropy change equation for an ideal gas in internal energy form. #17 - #19

17. Write the first law of thermodynamics, intensive, internal energy form, expansion work.

18. For the reversible expansion of an ideal gas, we may substitute for the pressure from the equation of state. Make this substitution in #17. You should now have an equation that is a function only of  $q$ ,  $T$ , and  $v$ , with  $dq$  on the left-hand side.

19. From #18, write an expression for the entropy change of an ideal gas.

Use the expressions in #16 and #19 for entropy change to answer the following questions

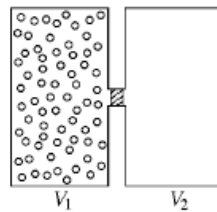
23. Entropy will (increase, decrease, remain the same) in a cyclic reversible adiabatic process  
 24. Entropy will (increase, decrease, remain the same) for isobaric cooling  
 25. Entropy will (increase, decrease, remain the same) for isothermal expansion

27. Consider the isobaric heating of air from  $T=300\text{K}$  to  $T=400\text{K}$ . What is the entropy change for this process?

28. A hot potato cools by heat transfer to the cooler air.

- a) Does entropy of the potato increase or decrease in this process?
- b) Does the entropy of the universe increase or decrease in this process?

29. Consider the system pictured below:



Gas is confined to a subvolume  $V_1$  in an insulated rigid container. The container has an adjoining subvolume  $V_2$ , initially evacuated, which can be connected to  $V_1$  by opening a valve ( $V_1 = V_2$ ). Suppose the valve is opened and the gas flows out of  $V_1$ , filling the entire volume,  $V_1 + V_2$ .

- a) The work done by the gas in this expansion is (positive, negative, zero).
- b) The internal energy of the gas after the expansion (increases, decreases, remains the same).
- c) The entropy of the gas after the expansion (increases, decreases, remains the same).
- d) Is this process adiabatic? YES NO
- e) Is this process reversible? YES NO

## 2<sup>nd</sup> Law of Thermodynamics

4. Heat can flow from a cold substance to a warmer substance

- a) never
- b) always
- c) only if work is done on the system

5. Heat flowing from a cold substance to a warmer substance would violate

- a) 1st law of thermodynamics
- b) 2nd law of thermodynamics
- c) neither the 1st or 2nd law

6. In a refrigerator, heat is transferred from a lower-temperature medium (the refrigerated space) to a higher-temperature one (the kitchen air). Is this a violation of the second law of thermodynamics? Explain

7. Consider a person who organizes his room, and thus decreases the entropy of the room. Does this process violate the second law of thermodynamics?

8. In a Carnot cycle, heat is transferred from a hot reservoir at  $T_2$ , partly converted to work, and partly discarded into a cold reservoir at  $T_1$ . The engine is returned to the initial state after one cycle. Sketch the Carnot cycle in the  $T$ - $\eta$  plane on the diagram below, labelling  $T_1$  and  $T_2$ , and the steps 1 through 4.

Step 1: isothermal expansion at  $T_2$

Step 2: adiabatic expansion to  $T_1$

Step 3: isothermal compression at  $T_1$

Step 4: adiabatic compression back to  $T_2$ .

