

ESCI 341 – Atmospheric Thermodynamics
Lesson 12 – The Energy Minimum Principle

References: *Thermodynamics and an Introduction to Thermostatistics*, Callen
Physical Chemistry, Levine

THE ENTROPY MAXIMUM PRINCIPLE

- We've seen that a reversible process achieves maximum thermodynamic efficiency.
- Imagine that I am adding heat to a system (dQ_{in}), converting some of it to work (dW), and discarding the remaining heat (dQ_{out}).
- We've already demonstrated that dQ_{out} cannot be zero (this would violate the second law).
- We also have shown that dQ_{out} will be a minimum for a reversible process, since a reversible process is the most efficient.
- This means that the net heat for the system ($dQ = dQ_{in} - dQ_{out}$) will be a maximum for a reversible process,

$$dQ_{rev} > dQ_{irrev}.$$

- The change in entropy of the system, dS , is defined in terms of reversible heat as dQ_{rev}/T . We can thus write the following inequality

$$dS = \frac{dQ_{rev}}{T} > \frac{dQ_{irrev}}{T}, \quad (1)$$

- Notice that for Eq. (1), if the system is reversible and adiabatic, we get

$$dS = 0 > \frac{dQ_{irrev}}{T},$$

or

$$dQ_{irrev} < 0$$

which illustrates the following:

- If two states can be connected by a reversible adiabatic process, then any irreversible process connecting the two states must involve the removal of heat from the system.
- Eq. (1) can be written as

$$dS \geq dQ/T \quad (2)$$

- The equality will hold if all processes in the system are reversible.

- The inequality will hold if there are irreversible processes in the system.
- For an isolated system ($dQ = 0$) the inequality becomes

$$dS \geq 0 \quad \text{isolated system,}$$

which is just a restatement of the second law of thermodynamics.

- We can divide this expression by dt and find that

$$\frac{dS}{dt} \geq 0 \quad \text{isolated system.} \quad (3)$$

- For an unconstrained, isolated system irreversible process will operate and increase the total entropy of the system until equilibrium is reached. Once equilibrium is reached,

$$\frac{dS}{dt} = 0,$$

and the irreversible processes will cease.

- This is the *entropy maximum principle*. It states that
 - For an isolated, unconstrained system, the equilibrium state will be that state which has the maximum entropy for a given internal energy.
- An example of application of the entropy maximum principle is an isolated metal bar that is initially hotter at one end than another. The temperature distribution that maximizes the entropy is one that is uniform (isothermal). Therefore, if left alone, the temperature will spontaneously adjust to an isothermal distribution.
- Some authors have mistakenly applied the entropy maximum principle in an attempt to explain why a well-mixed layer of air has an adiabatic temperature profile. However, it turns out that an isothermal layer has greater entropy than any other temperature profile for the same static energy. This was shown first by J. Willard Gibbs in 1928 (*Collected Works of J. Willard Gibbs, Vol I: Thermodynamics*, pp. 145).

THE ENERGY MINIMUM PRINCIPLE

- The first law is

$$dQ = dU + pdV. \quad (4)$$

but from Eq. (2) we can write this as

$$dU + pdV \leq TdS,$$

or

$$dU \leq TdS - pdV . \quad (5)$$

○ Eq. (5) is valid for a closed system in mechanical and thermal equilibrium, but not at material equilibrium¹.

● Dividing through by the differential of time, Eq. (5) becomes

$$\frac{dU}{dt} \leq T \frac{dS}{dt} - p \frac{dV}{dt} . \quad (6)$$

● This inequality tells us that, for a closed system at constant entropy and volume,

$$\frac{dU}{dt} \leq 0. \quad \text{Closed system, constant } S \text{ and } V \quad (7)$$

○ This means that a closed system held at constant entropy and volume will continue to change until it reaches a point where $dU/dt = 0$. At this point, the internal energy, U , will be a minimum and the system will be in material equilibrium.

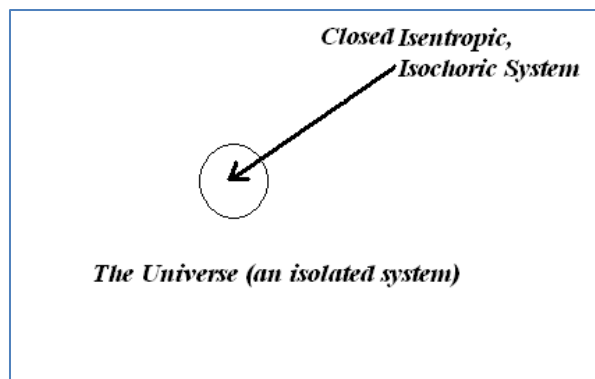
● This principle is known as the *energy minimum principle*. It states that

○ *For an unconstrained, closed system at constant volume and entropy, the equilibrium state will be that state which has the minimum internal energy.*

ENTROPY MAX AND ENERGY MIN PRINCIPLES ARE COMPLIMENTARY

● The energy minimum principle was derived from the entropy maximization principle. *The energy minimum principle and the entropy maximum principle are complimentary.*

● To see this, imagine the following closed (but not isolated) system in the diagram that is also kept at constant entropy and volume.



¹ For details, see Levine, Chapter 4.

- The system can be thought of as a subsystem embedded in the Universe. Since the system's entropy is held constant, we know that

$$Tds = 0 \geq dq.$$

So, if there is any flow of heat across the boundary of the system it must be from the system to the rest of the Universe. Since the system also cannot perform any work (due to its constant volume), the first law requires that any change in internal energy be equal to the heat, which is negative,

$$du = dq \leq 0.$$

This means that the internal energy of the system can never increase. Also, since the system is giving heat to the surroundings the entropy of the surroundings can only increase,

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{surr} \geq 0.$$

- So, the energy minimum principle applied to a closed, isentropic, isochoric system results in the internal energy of the system being minimized at equilibrium, while the entropy of the Universe (an isolated system consisting of the original system plus its surroundings) is maximized.

ENTHALPY

- Beginning with Eq. (5)

$$dU \leq TdS - pdV$$

and writing

$$pdV = d(pV) - Vdp$$

we get

$$d(U + pV) \leq TdS + Vdp.$$

- We've seen the combination $U + pV$ before...it is another state function called enthalpy (H). Therefore,

$$dH \leq TdS + Vdp \tag{8}$$

or

$$\frac{dH}{dt} \leq T \frac{dS}{dt} + V \frac{dp}{dt}$$

- For processes occurring in a closed system at constant entropy and pressure,

$$\frac{dH}{dt} \leq 0. \quad \text{Closed system, constant } S \text{ and } p \quad (9)$$

- An unconstrained system at constant entropy and pressure will spontaneously evolve into a state that minimizes enthalpy.
- This principle is known as the *enthalpy minimum principle*. It states that
 - For an unconstrained, closed system at constant pressure and entropy, the equilibrium state will be that state which has the minimum enthalpy.

HELMHOLTZ FREE ENERGY

- The energy and enthalpy minimum principles aren't often very handy for solving problems, since we don't really work with many processes that occur at constant entropy. It would be nice, therefore, to have some way of expressing a minimum principle in terms of processes where entropy is allowed to change.
- We do this by again starting with Eq. (5)

$$dU \leq TdS - pdV .$$

- From the product rule for differentiation we have

$$TdS = d(TS) - SdT .$$

- This means we can write the inequality as

$$d(U - TS) \leq -SdT - pdV .$$

- The quantity $(U - TS)$ is another state variable, and we name it the *Helmholtz free energy* ($F \equiv U - TS$). We therefore have

$$\begin{aligned} dF &\leq -SdT - pdV \\ \frac{dF}{dt} &\leq -S \frac{dT}{dt} - p \frac{dV}{dt} \end{aligned} \quad (10)$$

- For processes in a closed system under constant temperature and volume,

$$\frac{dF}{dt} \leq 0. \quad \text{Closed system, constant } T \text{ and } V \quad (11)$$

- This principle is known as the *Helmholtz free energy minimum principle*. It states that

- *For an unconstrained, closed system at constant temperature and volume, the equilibrium state will be that state which has the minimum Helmholtz free energy.*
- Notice that for a reversible process, if temperature is held constant, then $dF = -pdV$. We can therefore interpret F as the work that can be extracted from a constant temperature process.

GIBBS FREE ENERGY

- The Helmholtz free energy is handy for processes that occur at constant temperature and volume. In the atmosphere, however, we frequently are dealing with processes that occur at constant temperature and pressure. It would be nice to have another form of the energy minimum principle that we can apply to these processes.
- If we start with Eq. (8)

$$dH \leq TdS + Vdp$$

and substitute

$$TdS = d(TS) - SdT$$

we get

$$d(H - TS) \leq -SdT + Vdp.$$

- The quantity $(H - TS)$ is another state variable, and we name it the *Gibbs free energy* ($G \equiv H - TS$). We therefore have

$$dG \leq -SdT + Vdp$$

$$\frac{dG}{dt} \leq -S \frac{dT}{dt} + V \frac{dp}{dt} \quad (12)$$

- For processes that occur in a closed system under constant temperature and pressure,

$$\frac{dG}{dt} \leq 0. \quad \text{Closed system, constant } T \text{ and } p \quad (13)$$

- This principle is known as the *Gibbs free energy minimum principle*. It states that

- For an unconstrained, closed system at constant temperature and pressure, the equilibrium state will be that state which has the minimum Gibbs free energy.
- $U, H, F,$ and G are referred to as thermodynamic potentials. The inequalities associate with each potential are summarized below

$$\begin{aligned}
 U &\equiv U; & dU &\leq TdS - pdV \\
 H &\equiv U + PV; & dH &\leq TdS + Vdp \\
 F &\equiv U - TS; & dF &\leq -SdT - pdV \\
 G &\equiv H - TS; & dG &\leq -SdT + Vdp \quad .
 \end{aligned}
 \tag{14}$$

- Remember that the inequality holds if the system is not in material equilibrium, while equality in the above expressions holds when the system is in full thermodynamic equilibrium.

MAXWELL RELATIONS

- Under equilibrium conditions, the thermodynamic potentials are minimized. We therefore can write the following equations, known as the Gibbs equations, for equilibrium states

$$\begin{aligned}
 dU &= TdS - pdV \\
 dH &= TdS + Vdp \\
 dF &= -SdT - pdV \\
 dG &= -SdT + Vdp \quad .
 \end{aligned}
 \tag{15}$$

Gibbs equations

- The Gibbs equations are exact differentials (because they are differentials of state functions). One property of exact differentials is that if $df(x,y) = Mdx + Ndy$, then

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \quad . \tag{Euler reciprocity relation}$$

- This allows us to write, from the Gibbs equations,

$$\begin{aligned}
 \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\
 \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\
 \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\
 \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p .
 \end{aligned}
 \qquad \text{Maxwell relations} \quad (16)$$

- **The Maxwell relations are useful because they allow us to find information about abstract quantities (such as entropy) from directly measurable quantities such as temperature, pressure, and volume. For example, let's say I want to find out how the entropy of a particular substance changes with volume at constant temperature? This might be a tough experiment to carry out. But, I could instead use the Maxwell relation**

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

and perform an easier experiment to directly measure how pressure changes with temperature at constant volume.