

## Spontaneity, Equilibrium, and Entropy

- The First Law of thermodynamics states that energy is conserved.
  - We have examined a number of processes, both reversible and irreversible that obey this.
- There are processes which obey the First Law, but which we know from experience are impossible.
  - Consider the example of all the molecules of air in the room being in one corner at the same time.
  - This would obey the First Law.
  - Another example would be that of putting an ice cube in hot water.
  - If the ice cube became colder and the water warmer, the First Law would still be obeyed.
  - We know that this is not possible.
  - Therefore we need more than the First Law.

## The Second Law of Thermodynamics

- Must distinguish between natural and unnatural processes.
- Must permit prediction of final equilibrium state of a system as the result of a natural process.
- Characterize a state function, entropy, to quantify this.
- Entropy will be considered from three perspectives:
  - Statistical
  - Thermodynamically
  - Mathematically

## A Statistical View of Entropy

- Consider a cubic box of  $N$  molecules in a microscopic configuration or microstate characterized by:
  - 1/3 moving only in  $x$  direction
  - 1/3 moving only in  $y$  direction
  - 1/3 moving only in  $z$  direction
  - All molecules moving with equal speed
  - For this (or any other microstate) the probability of a molecule being in within the volume  $V$  of the box is unity.

$$W_1(V) = 1$$

- The probability of molecule being within a subvolume  $V'$  of the box is:

$$W_1(V') = \frac{V'}{V}$$

- The probability of all  $N$  particles being within subvolume  $V'$  is:

$$W_N(V') = \left(\frac{V'}{V}\right)^N$$

- Therefore the larger  $N$  is the less likely that all  $N$  particles are within subvolume  $V'$ .
- Consider properties of  $W$ :
  - no units since it is a probability.
  - double the number of particles, square  $W$ .
- Wish to relate  $W$  to  $S$ .
  - $S$  has units.
  - $S$  should be additive.
- This suggests:

$$S = k \ln \left( \frac{W_f}{W_i} \right)$$

### A Thermodynamic View of Entropy

- Carnot (1824) proposed a cycle, now known as the Carnot cycle, and reached conclusions about the efficiency of heat engines.
  - This work predated the First Law of Thermodynamics by half a century.
- Carnot cycle:
  - Step 1: reversible isothermal expansion at  $T_1$ .
  - Step 2: reversible adiabatic expansion during which temperature drops from  $T_1$  to  $T_2$ .
  - Step 3: reversible isothermal compression at  $T_2$ .
  - Step 4: reversible adiabatic compression accompanied by temperature rise from  $T_2$  to  $T_1$ .
- For any fluid (ideal gas or other) undergoing a Carnot cycle, we observe:
  - $U = 0$  and  $q_{cy} = -w_{cy}$
  - $q_{cy} = q_1 + q_3$  (Steps 2 and 4 are adiabatic)
  - $q_1 > 0$  (Step 1 is an expansion)
  - $q_3 < 0$  (Step 3 is a compression)
  - $w_{cy} = w_1 + w_2 + w_3 + w_4$
  - $w_1, w_2 < 0$  (Steps 1 and 2 are expansions)
  - $w_3, w_4 > 0$  (Steps 3 and 4 are compressions)
- The net sign of the  $w_{cy}$  is negative and work is done on the surroundings while heat is taken from the surroundings at  $T_1$  and discharged to the surrounding at the lower temperature  $T_2$ .

### Efficiency

- Efficiency is defined as:

$$\varepsilon = \frac{\text{work done by system}}{\text{heat from surroundings}}$$

- For the Carnot cycle, this is:

$$\varepsilon = \frac{-w_{cy}}{q_1} = \frac{q_1 + q_3}{q_1} = 1 + \frac{q_3}{q_1}$$

- Since  $q_1$  and  $q_3$  have opposite signs,  $\epsilon < 1$ .
- If the working fluid is an ideal gas, then:

$$\epsilon = 1 - \frac{T_2}{T_1}$$

### Thermodynamic Temperature Scale

- From the equation for efficiency, we can show:

$$\frac{q_3}{q_1} = -\frac{T_2}{T_1}$$

or:

$$\frac{q_3}{T_2} + \frac{q_1}{T_1} = 0$$

- This has a property associated with a state function, i.e. sums to zero over a cycle.
  - $q/T$  is related to entropy and is entropy if the cycle is reversible.
- The thermodynamic definition of entropy is:

$$dS = \frac{dq_{rev}}{T}$$

(in formal differential form).

### What is the entropy change associated with the Joule expansion?

- irreversible process
- isothermal
- ideal gas
- Need to find an imaginary reversible path between the initial and final state such as a reversible isothermal expansion.
- Since the gas is ideal and the expansion is isothermal,  $\Delta U = 0$ , and

$$dq_{rev} = -dw_{rev} = PdV = \frac{nRT}{V}dV$$

- Therefore:

$$\begin{aligned}\Delta S &= \int_{S_i}^{S_f} dS = \int_{path} \frac{dq_{rev}}{T} \\ &= nR \int_{V_i}^{V_f} \frac{dV}{V} = nR \ln \frac{V_f}{V_i}\end{aligned}$$

- If we compare this with the equation that we determined from the statistical approach:

$$\Delta S = Nk \ln (V_f/V_i)$$

then the two are the same if  $Nk = nR$ .

- Therefore

$$k = R/N_A$$

### A Mathematical View of Entropy

- Recall the properties of an exact differential:

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$$

and that state functions have exact differentials.

- Carathéodory exploited this in his formulation of entropy.

$$dq = dU - dw$$

$$dq = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT - dw$$

- Specifying a reversible path, along which

$$dw_{rev} = -PdV$$

this becomes:

$$dq_{rev} = \left( \frac{\partial U}{\partial T} \right)_V dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] dV$$

which is not an exact differential.

- Does there exist some function by which both sides of the equation may be multiplied that would allow the equation to have the properties of an exact differential?
  - This function does exist (since the equation has only two variables) and it is  $1/T$ .
  - Therefore:

$$\frac{dq_{rev}}{T} = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] dV$$

$$dS = \frac{dq_{rev}}{T}$$

### The Zeroth Law of Thermodynamics

- If system A is in thermal equilibrium with system B, and if B is in thermal equilibrium with system C, then A and C must also be in thermal equilibrium.

**B is a thermometer!**

### Properties of temperature scales

- Consider an ideal gas.
  - The change in PV is empirically proportional to any arbitrary change in temperature.

- Mathematically this is:

$$PV = \alpha(T' + \theta)$$

where  $T'$  is any arbitrary temperature scale.

### The Second Law of Thermodynamics

- Summarizes possible, natural processes.
- Some statements of the second law are:
  - "No process is possible in which the only transfer of heat is as heat transferred from a colder to a hotter system." (Clausius 1850)
  - "No cyclic process can transfer a quantity of energy as heat from a reservoir of energy at one temperature and produce work without some fraction of this energy appearing as heat transferred to a colder reservoir." (Thomson, Planck)
  - "From any arbitrary state of any system there are a finite number of states arbitrarily close to the initial state that cannot be reached by an adiabatic process, reversible or irreversible." (Carathéodory)
- Consider an ideal gas in the state  $(P_i, V_i, T_i)$ .
  - If the gas expanded reversibly and adiabatically to some  $V_f$  then  $T_f < T_i$ . This is the minimum value of  $T_f$ .
  - If the gas expanded adiabatically and freely (i.e against zero external pressure, then  $T_f = T_i$ . This is the maximum value of  $T_f$ .
  - Therefore an irreversible adiabatic process will give a final temperature between these values.
  - Another, nonadiabatic process is required to access other values of  $T_f$ .
  - How does this relate to the two other statements of the Second Law?
- Consider a reversible adiabatic process in  $(T, V)$  space (Figure 3.4) that takes the system from state 1 to state 2.
  - Now consider an isotherm that takes the system from state 2 to state 3.
  - Postulate that there is an adiabatic path from state 3 back to state 1.
  - Since this is a cycle

$$\Delta U = q_{cy} + w_{cy} = 0$$

- Since only the isotherm was nonadiabatic,

$$q_{cy} = q_{23} = -w_{cy}$$

- Therefore this equation indicates that all the heat transferred at one temperature.
- Therefore an adiabatic path from 3 to 1 does not exist.

### General Properties of Entropy Changes

- Consider some natural irreversible processes:
  - Joule expansion
  - Equilibration of metal cubes of different temperatures
- The systems are characterized in macroscopic terms, not microscopic terms.

- Macroscopic variables include:  $P$ ,  $V$ ,  $T$ ,  $n$ ,  $U$ ,  $H$ , and  $S$ .
- Entropy change of Joule expansion:

$$\Delta S = nR \ln \left( \frac{V_f}{V_i} \right)$$

- Entropy change for the equilibration of metal cubes of different temperatures:
  - Two identical cubes, one at  $T_a$ , the other at  $T_b$ .
  - $T_a > T_b$ .
  - When brought into thermal contact, spontaneously reach the equal temperature,  $T$ .
  - Cube  $a$  transfers heat energy to cube  $b$  since  $T_a > T_b$ :
  - The heat transfer for cube  $a$  is:

$$q_a = \int_{path} dq_P = \int_{T_a}^T C_P dT = C_P(T - T_a) < 0$$

- The energy change for cube  $b$  is:

$$q_b = \int_{path} dq_P = \int_{T_b}^T C_P dT = C_P(T - T_b) > 0$$

- But, because of the first law, heat lost by one cube is gained by the other and  $q_a + q_b = 0$ . Thus:

$$-C_P(T - T_a) = C_P(T - T_b)$$

or:

$$T = \frac{1}{2}(T_a + T_b)$$

- Now consider the entropy change for one cube:

$$\Delta S = \int_{S_i}^{S_f} dS = \int_{path} \frac{dq_{rev}}{T}$$

- We must now think about the path.
  - It is a constant pressure path. Therefore  $dP = 0$  and  $dq = dq_P = C_P dT = dH$ .
  - Therefore for cube  $a$ :

$$\Delta S_a = \int \frac{dq_P}{T} = \int \frac{dH}{T} = \int_{T_a}^T \frac{C_P}{T} dT$$

- Since  $C_P$  is constant,

$$\Delta S_a = C_P \ln \left( \frac{T}{T_a} \right)$$

- Similarly for cube  $b$ :

$$\Delta S_b = C_P \ln \left( \frac{T}{T_b} \right)$$

- and for the entire system:

$$\Delta S_{tot} = \Delta S_a + \Delta S_b = C_P \ln \left( \frac{T^2}{T_a T_b} \right)$$

**Proof that entropy increases in this case.**

- Recall that  $T = (T_a + T_b)/2$ .
- Then,  $T^2/(T_a T_b) = (T_a + T_b)^2/(4T_a T_b)$  which is always greater than 1.

$$\frac{(T_a + T_b)^2}{4T_a T_b} > 1$$

$$\frac{(T_a^2 + 2T_a T_b + T_b^2)}{4T_a T_b} > 1$$

$$(T_a^2 + 2T_a T_b + T_b^2) > 4T_a T_b$$

$$(T_a^2 + T_b^2) > 2T_a T_b$$

$$(T_a^2 - 2T_a T_b + T_b^2) > 0$$

$$(T_a - T_b)(T_a + T_b) > 0$$

- Therefore  $S_{tot} > 0$ .

**Is this the maximum entropy possible under the circumstances?**

- There is a constraint that energy be conserved.
- Consider final temperatures for each of cube  $a$  and  $b$ ,  $T'_a$  and  $T'_b$ .
- From the first law:

$$C_P(T'_a - T_a) = -C_P(T'_b - T_b)$$

- Therefore:

$$T'_a = T_b + T_a - T'_b$$

- The total entropy change is:

$$\Delta S_{tot} = S_a + S_b = C_P \ln \left( \frac{T'_a T'_b}{T_a T_b} \right)$$

$$= C_P \ln \left[ \frac{(T_a + T_b - T'_b) T'_b}{T_a T_b} \right]$$

- For what values of  $T_a$  and  $T_b$  is the change in entropy a maximum?
  - We need to find the maximum of:

$$y(x) = \ln \left( \frac{(A - x)x}{B} \right)$$

where  $y(x) = S_{tot}/C_P$ ,  $x = T'_b$ ,  $A = T_a + T_b$ , and  $B = T_a T_b$ .

$$\frac{dy}{dx} = \frac{2x - A}{x^2 - Ax}$$

- At a maximum:

$$0 = \frac{2x - A}{x^2 - Ax}$$

$$x = \frac{A}{2} = \frac{T_a + T_b}{2}$$

- Thus the only process observed (i.e. equal final temperature) is the one in which the energy is maximized.

- The Second Law of Thermodynamics may be stated as:

“The entropy change in any spontaneous process occurring in an **isolated** system is positive. Moreover the process will continue until the entropy has increased to the maximum allowed by the constraints imposed on the system.”

- Consider a system in contact with surroundings and consider the system with its surroundings as an isolated super- system. Then:

“The sum of entropy changes in the system and the surroundings can never be negative for any natural process.”

### Entropy and Surroundings

- Consider a cube at temperature,  $T_i$ .
- Bring the cube into a room at a warmer temperature,  $T_f$ .
- **Assume** that the room is so large that the cube can be warmed up to  $T_f$  without the room changing temperature.
- The entropy change of the cube is:

$$\Delta S_{cube} = C_P \ln \left( \frac{T_f}{T_i} \right)$$

- From the first law,  $q_{cube} = -q_{surr} = C_P(T_f - T_i)$ .
- Therefore:

$$\Delta S_{surr} = \frac{q_{surr}}{T_f} = C_P \left( \frac{T_i}{T_f} - 1 \right)$$

- Therefore the total entropy change is:

$$\Delta S_{tot} = C_P \left[ \ln \left( \frac{T_f}{T_i} \right) + \frac{T_i}{T_f} - 1 \right]$$

- It can be shown that  $\Delta S_{tot} \geq 0$ :

- Case 1:  $T_i = T_f$ ;

$$\Delta S_{cube} = 0, \Delta S_{surr} = 0, \Delta S_{tot} = 0$$

- Case 2:  $T_i < T_f$ ;

$$\Delta S_{cube} > 0, \Delta S_{surr} < 0, \Delta S_{tot} > 0$$

- Case 3:  $T_i > T_f$ ;

$$\Delta S_{cube} < 0, \Delta S_{surr} > 0, \Delta S_{tot} > 0$$

### Thermal Reservoirs

- In thermodynamics, an ideal thermal reservoir transfers heat without changing its state.
  - In practice this is achieved by making the reservoir large compared to the system.



- Consider the case of two cubes.
  - This time the cubes have different heat capacities.

$$C_P^a(T - T_a) = -C_P^b(T - T_b)$$

- Solving for  $T$  gives:

$$T = \frac{C_P^a T_a + C_P^b T_b}{C_P^a + C_P^b}$$

### Consequences of Entropy as a State Function

- Entropy has been defined as:

$$dS = \frac{dq_{rev}}{T}$$

- But from the First Law,

$$dq_{rev} = dU - dw_{rev}$$

- From the definition of pressure-volume work:

$$dw_{rev} = -PdV$$

- Thus

$$dS = \frac{dU}{T} + \frac{P}{T}dV$$

or:

$$TdS = dU + PdV$$

$$dU = TdS - PdV$$

### Master Equation of Thermodynamics

- The Master Equation of Thermodynamics combines the First and Second Law:

$$dU = TdS - PdV$$

- Compare this with First Law:

$$dU = dq + dw$$

- From the derivation above:

$$S = S(U, V)$$

- Therefore:

$$dS = \left( \frac{\partial S}{\partial U} \right)_V dU + \left( \frac{\partial S}{\partial V} \right)_U dV$$

- Similarly for  $U$ :

$$U = U(S, V)$$

- Therefore:

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

- Therefore, from examination of the differential for  $dS$ :

$$\left( \frac{\partial S}{\partial U} \right)_V = \frac{1}{T}; \quad \left( \frac{\partial S}{\partial V} \right)_U = \frac{P}{T}$$

- From the differential for  $dU$ :

$$\left( \frac{\partial U}{\partial S} \right)_V = T; \quad \left( \frac{\partial U}{\partial V} \right)_S = -P$$

- For an exact differential of  $U$ :

$$\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right) = \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)$$

and

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$$

- This is a Maxwell relation. (We will see more of these later!)

### More “Fun” with the Master Equation

- It can be used to find  $(\partial U / \partial V)_T$  from an equation of state. Recall that:

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

and

$$dS = \frac{dU}{T} + \frac{P}{T} dV$$

- Therefore:

$$dS = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left( \frac{\partial U}{\partial V} \right)_T dV + \frac{P}{T} dV$$

or:

$$dS = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] dV$$

- But  $S$  is a state function and has an exact differential.

$$\frac{\partial}{\partial V} \left[ \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V \right] = \frac{\partial}{\partial T} \left( \frac{1}{T} \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \right)$$

or:

$$\begin{aligned} \frac{1}{T} \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right)_T &= -\frac{1}{T^2} \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \\ &+ \frac{1}{T} \left[ \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T + \left( \frac{\partial P}{\partial T} \right)_V \right] \end{aligned}$$

- This reduces to:

$$0 = -\frac{1}{T^2} \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] + \frac{1}{T} \left( \frac{\partial P}{\partial T} \right)_V$$

- multiplying through by  $T^2$ :

$$0 = - \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] + T \left( \frac{\partial P}{\partial T} \right)_V$$

or:

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

- This is turn can be used to derive an expression for  $C_P - C_V$  starting with:

$$dS = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] dV$$

- Multiplying through by  $T$  gives:

$$TdS = \left( \frac{\partial U}{\partial T} \right)_V dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] dV$$

- But  $TdS = dq_{rev}$  and  $C_V = (\partial U / \partial T)_V$

- Therefore:

$$dq_{rev} = C_V dT + \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] dV$$

differentiating with respect to  $T$  at constant  $P$ :

$$\left( \frac{\partial q_{rev}}{\partial T} \right)_P = C_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P$$

or:

$$C_P - C_V = \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P$$

but:

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

therefore:

$$C_P - C_V = \left( T \left( \frac{\partial P}{\partial T} \right)_V - P \right) \left( \frac{\partial V}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P$$

or:

$$C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$$

- Recall the definition of isobaric bulk thermal expansivity,  $\alpha$ :

$$\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

- Therefore:

$$C_P - C_V = TV\alpha \left( \frac{\partial P}{\partial T} \right)_V$$

- From the cyclic rule:

$$\left( \frac{\partial P}{\partial T} \right)_V = - \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial V} \right)_T$$

- Recall the definition of isothermal bulk compressibility,  $\kappa$  :

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

- Therefore:

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\kappa}$$

and

$$C_P - C_V = \frac{TV\alpha^2}{\kappa}$$

- since  $\kappa$  is positive,  $C_P > C_V$ .
- Consider the Joule-Thomson coefficient:

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H$$

- From the chain rule:

$$\left( \frac{\partial T}{\partial P} \right)_H = -\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P} = -\frac{(\partial H/\partial P)_T}{C_P}$$

- Now need to find an expression for  $(\partial H/\partial P)_T$ .
- Starting with the definition of  $H = U + PV$ :

$$dH = dU + PdV + VdP$$

$$dU = dH - PdV - VdP$$

- Substituting in the Master Equation:

$$TdS - PdV = dH - PdV - VdP$$

or:

$$dS = \frac{dH}{T} - \frac{V}{T}dP$$

- Using the total differential of  $dH$ :

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

we get:

$$dS = \frac{1}{T} \left( \frac{\partial H}{\partial T} \right)_P dT + \frac{1}{T} \left[ \left( \frac{\partial H}{\partial P} \right)_T - V \right] dP$$

- Taking the cross derivatives (which are equal since a state function has an exact differential:

$$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P$$

which gives:

$$\mu_{JT} = \frac{1}{C_P} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right]$$