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:

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

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:

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

$$= nR \int_{V_i}^{V_f} \frac{dV}{V} = nR \ln \frac{V_f}{V_i}$$

- 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 is 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, on 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.

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

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

$$(T_a^2 + 2T_aT_b + T_b^2) > 4T_aT_b$$
$$(T_a^2 + T_b^2) > 2T_aT_b$$
$$(T_a^2 - 2T_aT_b + T_b^2) > 0$$
$$(T_a - T_b)(T_a - T_b) > 0$$

- 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:

$$\Delta S_{tot} = S_a + S_b = C_P \ln\left(\frac{T_a'T_b'}{T_aT_b}\right)$$
$$= C_P \ln\left[\frac{(T_a + T_b - T_b')T_b'}{T_aT_b}\right]$$

- 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 $B = T_aT_b$.

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

- 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:

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

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

- 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, α:

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

  - 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, κ :

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

- Therefore:

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

  and

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

  - since κ 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:

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