

10/30 and 11/1 Lecture outline

- More examples of ΔS . Consider two different ideal gasses, one with n_1 , and T_1 , and V_1 , and the other with n_2 , T_2 , and V_2 . Suppose that $T_1 = T_2$, so they would be in thermal equilibrium if brought together in thermal contact, but separated by a partition. If $T_1 = T_2$, bringing the systems in thermal contact is reversible, so $\Delta S = 0$. Now we remove the partition between them, and let them mix. We get an increase in S (disorder) from their intermixing:

$$\Delta S_{mixing} = n_1 R \ln \left(\frac{V_1 + V_2}{V_1} \right) + n_2 R \ln \left(\frac{V_1 + V_2}{V_2} \right) > 0.$$

This answer makes sense if the two types of gas are distinguishable, e.g. Nitrogen and Oxygen. Gibbs asked the following question: how does this answer change when the two gasses are the same? In this case, removing the partition really has no effect, so we should get $\Delta S_{mixing} = 0$, instead of the above answer. This is called the ‘‘Gibbs paradox.’’ We will discuss the resolution of the puzzle in a few weeks.

- Example 2: object 1, with initial temperature T_1 is placed in thermal contact with object 2, with initial temperature $T_2 > T_1$. Find the final temperature T_f and all the entropy changes. Suppose that the objects have unchanging volume.

Take object 1 to have $C_V = C_1(T)$, and object 2 to have $C_V = C_2(T)$. Take $T_2 > T_1$. Find T_f by equating the heat transfer

$$\Delta Q = \int_{T_1}^{T_f} C_1(T) dT = \int_{T_f}^{T_2} C_2(T) dT.$$

The entropy changes are

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{C_1(T)}{T} dT > 0, \quad \Delta S_2 = - \int_{T_f}^{T_2} \frac{C_2(T)}{T} dT < 0.$$

If $T_1 \neq T_2$, this process is irreversible, so we must find

$$\Delta S_{total} = \Delta S_1 + \Delta S_2 > 0.$$

Let’s check that. To make things easier, suppose $C_1 = C_2 = C$. Then we get from the above $T_f = (T_1 + T_2)/2$, and

$$\Delta S_{total} = C \ln \left(\frac{T_f^2}{T_1 T_2} \right) = 2C \ln \left(\frac{\frac{1}{2}(T_1 + T_2)}{\sqrt{T_1 T_2}} \right) > 0,$$

where the last inequality follows from noting that $\left(\frac{\frac{1}{2}(T_1+T_2)}{\sqrt{T_1T_2}}\right) = 1 + \left(\frac{(\sqrt{T_1}-\sqrt{T_2})^2}{2\sqrt{T_1T_2}}\right) > 1$.

- Example 2: System with temperature T_i is in contact with a reservoir at temperature $T_0 < T_i$. The two systems reach isobaric equilibrium. Compute ΔS 's.

The final temperature of the system is T_0 , that of the reservoir. The heat transfer is $\Delta Q = C_P(T_i - T_0)$. We get

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{res} = C_P \ln\left(\frac{T_0}{T_i}\right) + C_P \frac{(T_i - T_0)}{T_0}$$

(Assuming C_P is T independent here, otherwise use $\int C_P dT$ and $\int C_P dT/T$. Get

$$\Delta S_{total} = C_P ((r - 1) - \ln r)$$

where $r = T_i/T_0 > 1$. Let's show that this $\Delta S_{total} \geq 0$. Consider $f(r) = r - 1 - \ln r$, and note $f'(r) = 1 - 1/r$ vanishes only at $r = 1$. Since $f''(r) = 1/r^2 > 0$, the function $f(r)$ has a minimum at $r = 1$. Since $f(r = 1) = 0$, we see $f(r) > 0$ for all $r > 1$. So $\Delta S_{total} \geq 0$.

- Let's go back to entropy and available energy. Consider a Carnot engine, where the heat bath is T_2 and the cold bath is T_0 . In this case, for a given heat Q extracted from the heat reservoir, the maximum work is $W_{max} = Q(1 - T_0/T_2)$. But suppose that the Carnot engine gets heated only up to $T_1 < T_2$. Then W_{max} is reduced to $W'_{max} = Q(1 - T_0/T_1)$. Energy $Q(\frac{T_0}{T_1} - \frac{T_0}{T_2}) = T_0 \Delta S_{total}$ has become unavailable, degraded in form FOREVER! Illustrates how ΔS_{total} is a measure of the degradation of energy. Quality vs quantity: energy is the quantity, conserved regardless, irrespective of whether or not it is useful. But ΔS accounts for the inevitable, and irreversible, degradation of energy, towards a useless quality form.

After the midterm, we'll discuss stat-mech, where we'll relate S to molecular disorder: $S = k \ln \Omega$, where Ω is the number of available states. Increasing T or V increases Ω , so it increases S , as we have seen. The "3rd law" is $S = 0$ when $\Omega = 1$, which is perfect order, and this is possible only if $T = 0$.

Entropy and the arrow of time: if the time is $t_f > t_i$, then $(S_f)_{total} > (S_i)_{total}$. So the progress of time from initial to final states, i.e. from past to future, is accompanied by an increase in entropy. This is the only known explanation for our observed arrow of time (aside from tiny, and irrelevant, quantum effects).

- More on T, S diagrams. Plot an isentropic curve, $\Delta Q = 0$: since $\Delta S = 0$, this is a vertical line in an T, S diagram. In isochoric curve, $V = const.$, has slope $(dT/dS)_V =$

T/C_V , which follows from the definition of C_V and $dQ = TdS$. Similarly, an isobaric curve has slope $(dT/dS)_P = T/C_P$.

- Back to $dU = TdS - PdV$. Note that U , S , and V are extensive (we can divide them by the mass to form the specific versions, u and s and v , which are intensive). On the other hand, T and P are intensive. Now the relation $dU = TdS - PdV$ naturally gives $U = U(S, V)$. Recall that, because we assume equilibrium, we only need 2 state variables to completely specify the state, and here we take them to be S and V . This is natural because

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

where the important thing to note is that there are the same differentials, dS and dV , in the two expressions. Comparing the two expressions for dU , we see that

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

We will later take $U(S, V)$ and invert it to write $S = S(U, V)$. We will write this later as $S = k \ln \Omega(U, V)$. The above relations will then be rewritten as

$$T^{-1} = \left(\frac{\partial S}{\partial U}\right)_V, \quad \text{and} \quad P = -\left(\frac{\partial U}{\partial V}\right)_S.$$

- Other thermodynamic potentials. Start from $dU = TdS - PdV$. Because T and S appear together, they are called conjugate variables. Likewise, P and V are conjugate variables.

$$T \leftrightarrow S, \quad P \leftrightarrow V.$$

The thermodynamic state is specified by two variables, where we can pick one from either pair of conjugate variables. If we're talking about U , we picked S and V . Then the conjugate variables are fixed in terms of U derivatives, as expressed above.

It is possible to do Legendre transforms to exchange S and/or V with the corresponding conjugate variable, i.e.

$$T \leftrightarrow S, \quad P \leftrightarrow V.$$

Then, again, the conjugates are fixed via derivatives of thermodynamic potentials.

Explicitly, to Legendre transform from $P \rightarrow V$, we define the *enthalpy*

$$H \equiv U + PV = H(S, P).$$

Note that $U = U(S, V)$, but $H = H(S, P)$. To see that, note

$$dH = dU + PdV + VdP = TdS + VdP.$$

Since the last line has dS and dP , we get $H = H(S, P)$. Writing out dH , we then get

$$T = \left(\frac{\partial H}{\partial S} \right)_P, \quad \text{and} \quad V = \left(\frac{\partial H}{\partial P} \right)_S.$$

Likewise, we define the *Helmholtz free energy* $F(T, V) = U - ST$, and get

$$S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad \text{and} \quad P = - \left(\frac{\partial F}{\partial V} \right)_T.$$

Likewise we define the *Gibbs function* $G(T, P) = U + PV - TS$ and get

$$S = - \left(\frac{\partial G}{\partial T} \right)_P, \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P} \right)_T.$$

• Suppose that a system has initial energy U_0 , and goes via some process to having energy $U(S, V)$. The system has P , T , and V , and the exterior surroundings to the system has pressure P_0 and temperature T_0 . What is the work done? It depends on the process. We get

$$dU_{sys} = -\not{d}W_{mech} - P_0dV_{sys} + \not{d}Q_{sys},$$

where we wrote the work done by the system as mechanical work (pushing a piston) plus the work done in expanding against the external pressure P_0 . Moreover,

$$\not{d}Q_{sys} = -\not{d}Q_{surr} = -T_0dS_{surr}.$$

Using $dS_{universe} = dS_{sys} + dS_{surr} \geq 0$, we get $-dS_{surr} \leq dS_{sys}$, and thus

$$\not{d}W_{mech} = -dU_{sys} - P_0dV_{sys} + T_0dS_{surr} \leq d(U - T_0S + P_0V)_{sys}.$$

Let's write this again, in terms of the *availability* $A \equiv U - T_0S + P_0V$,

$$|\not{d}W|_{max} = -d(U - T_0S + P_0V) \equiv -dA.$$

If in equilibrium, we can use $dU = TdS - PdV$ to write

$$\not{d}W_{mech} \leq -((T - T_0)dS - (P - P_0)dV).$$

Let's interpret the two terms. The first term is the maximum work a Carnot engine would do, operating between $T_H = T$ and $T_C = T_0$: if everything were reversible, the heat leaving our system would be $Q_H = -TdS$, and that heat drives the Carnot engine, producing work $\phi W_{carnot} = -(T - T_0)dS$. The second term is the mechanical work, subtracting out the work done against the environment.

- If T is held fixed, e.g. the system is in contact with a reservoir, we have $\phi W \leq -dF_{system}$. Also, if T and V are constant in the process, we can write the above as $\phi W_{mech} \leq -dF_{sys}$. Here W_{mech} includes configuration work, e.g. $\phi W_{elec} = \vec{E} \cdot dP$, and F_{sys} can still change, for that reason. If T and P are constant, we get $\phi W_{mech} \leq -dG_{sys}$. If S and P are constant, we have $\phi W_{mech} \leq -dH_{sys}$.