Physics 467/667: Thermal Physics **Spring 2019**

Lecture 10: Entropy and Pressure

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10.1 Mechanical Equilibrium and Pressure

In the last lecture, we just learned the relation between S and T, is there any analogy between S and P?

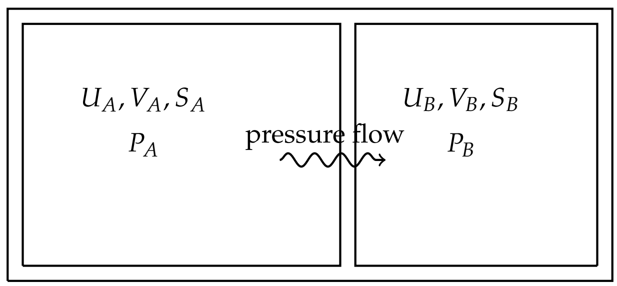

Figure 10.1: A schematic pressure flow between two gases.

Again, we start from the condition when the system reaches its equilibrium,

$$\frac{\partial S_{\text{total}}}{\partial U_A} = 0 \qquad \rightarrow \qquad \frac{\partial S_{\text{total}}}{\partial V_A} = 0 \tag{10.1}$$

as S is a function of U and V.

We already applied the 1st condition in the previous lecture. How about the 2nd condition?

$$\frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = 0 \qquad \rightarrow \qquad \frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \tag{10.2}$$

What's the physical meaning of $\partial S_A/\partial V_A$?
If we dig a bit on the units, we will find $\partial S_A/\partial V_A$ has a unit of N·m/K, about P/T hence we guess

$$\frac{P}{T} = (\frac{\partial S}{\partial V})_{U,N} \qquad \rightarrow \qquad P = T(\frac{\partial S}{\partial V})_{U,N} \tag{10.3}$$

Recall that we know how to calculate S,

$$S = Nk\ln V + 3/2Nk\ln U - Nk\ln(f(N)) \tag{10.4}$$

$$P = T(\frac{\partial S}{\partial V}) = \frac{NkT}{V} \tag{10.5}$$

$$PV = NkT \tag{10.6}$$

Again, we proved the ideal gas law.

10.2 Thermodynamic Identity

From the above sections, it seems that ΔS can be divided into two parts,

1. ΔU, to account for the heat flow
2. ΔV, to account for the pressure flow

Let's say,

$$\Delta S = (\frac{\Delta S}{\Delta U})\Delta U + (\frac{\Delta S}{\Delta V})\Delta V \tag{10.7}$$

Suppose each step is very small, we use

$$dS = (\frac{\partial S}{\partial U})dU + (\frac{\partial S}{\partial V})dV \tag{10.8}$$

$$dS = \frac{dU}{T} + \frac{PdV}{T} \tag{10.9}$$

$$TdS = dU + PdV \tag{10.10}$$

$$dU = TdS - PdV \tag{10.11}$$

This is the **Thermodynamic Identity**. If you compare it with the 1st law, it just substitutes TdS with Q, which is actually the old definition of entropy.

1. $\Delta U = 0, TdS = PdV$
2. $\Delta V = 0, dU = TdS$

Exercise Under constant entropy

$$(\frac{\partial S}{\partial U})dU + (\frac{\partial S}{\partial V})dV = 0 \tag{10.12}$$

$$dU = -PdV \tag{10.13}$$

isentropic = quasistatic + adiabatic

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_P}{T} dT \tag{10.14}$$

$S(300K)$ = $S(0K) + C_P \int_0^{300} \frac{1}{T} dT$ = 5.8 + 3.5*8.31*ln(300) = 173.89 J/K.
This value looks much smaller than the reference value in the appendix (197.67 J/K), because a constant volume assumption is not realistic. A more realistic solution is

$$\Delta S = C_V \ln \frac{P_B}{P_A} + C_P \ln \frac{V_B}{V_A} \tag{10.15}$$

when you consider $Q = \Delta U - W$.

$$\Delta S = \frac{Q}{T} \qquad \text{quasistatic} \tag{10.16}$$

$$\Delta S > \frac{Q}{T} \qquad \text{in practice} \tag{10.17}$$

1. Very faste compression
2. free expansion

10.3 Homework

Problem 3.5, 3.8, 3.11, 3.14, 3.16, 3.27, 3.30, 3.31, 3.32, 3.33