

Notes for today

- Reminder, web address: rossgroup.tamu.edu/408page.html
Has syllabus and slides posted there.
- Reading: Ch. 1 this week, plus added section 2.1 of chapter 2, followed by ch. 15.
- Homework not quite ready, I will post on web-page this afternoon, due Wednesday.
- Lecture recordings etc.: I will record lecture for those needing to quarantine or be absent. Update: we are now also allowed to have concurrent zoom during lecture, but only for those with documented Covid quarantine (or other University excuse). You need to let me know in case; also zoom setup in this room is not working completely yet, we will get something working shortly.

From last time:

recall, $dS = \frac{\delta Q}{T}$ defines entropy change for a controlled process.

Also recall, $dU = \delta Q + \delta W$ with mechanical work $= -PdV$, also for controlled process. (And specifically, work with no heat flow has $dS = 0$)

$$\Rightarrow dU = TdS - PdV$$

First law in terms of system variables

$$dU = TdS - PdV + \mu dN$$

↗
Defines T

↗
Defines chemical potential μ

More general defined in a 3-dimensional parameter space

Also from last time:

Thus: $dU = TdS \overset{\text{heat}}{- PdV} \overset{\text{generalized work}}{+ \mu dN}$

Form for $S = S(U, V, N)$
parameter choice: $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$

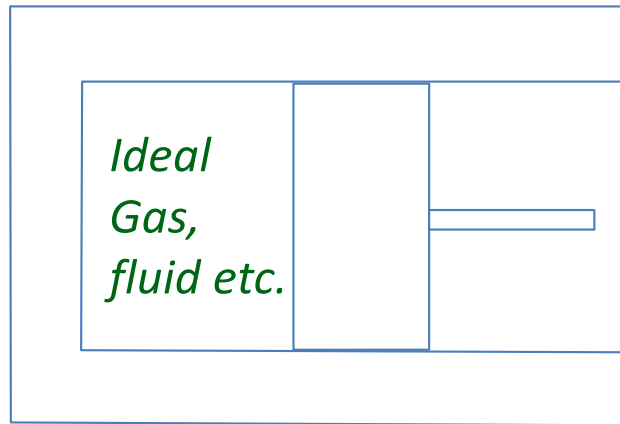
Specific example: Ideal gas (monatomic, e.g. helium)

$$U = \frac{3}{2} N k_B T. \quad \text{Energy, can show (independent of volume)}$$

$$PV = N k_B T. \quad \text{Equation of state showed last time.}$$

- Heating with no work (& const. N): can show from first law, $\Delta S = \frac{3}{2} N k_B \ln \left(\frac{U_2}{U_1} \right) = \frac{3}{2} N k_B \ln \left(\frac{T_2}{T_1} \right)$
- Adiabatic case from first law & $U = \frac{3}{2} PV$: $P_2 = P_1 \left(\frac{V_2}{V_1} \right)^{-5/3}$

($N = \text{const inside}$)



Expand suddenly to 2x volume.
sign of Q , W ? ΔU ? ΔT ?

Further process: slowly return piston to original position.

>>> *Now can calculate this.*

- Find, work done: $W = \frac{3}{2} P_1 V_1 (2^{2/3} - 1)$
- Entropy change? For this process & entire process?

We find:

- For ideal gas, entropy change in general must have the form,

$$\Delta S = \frac{3}{2} Nk_B \ln \left(\frac{U_2}{U_1} \right) + Nk_B \ln \left(\frac{V_2}{V_1} \right) + (\textit{other terms})$$

Actual full result see equation 16.73 in text:

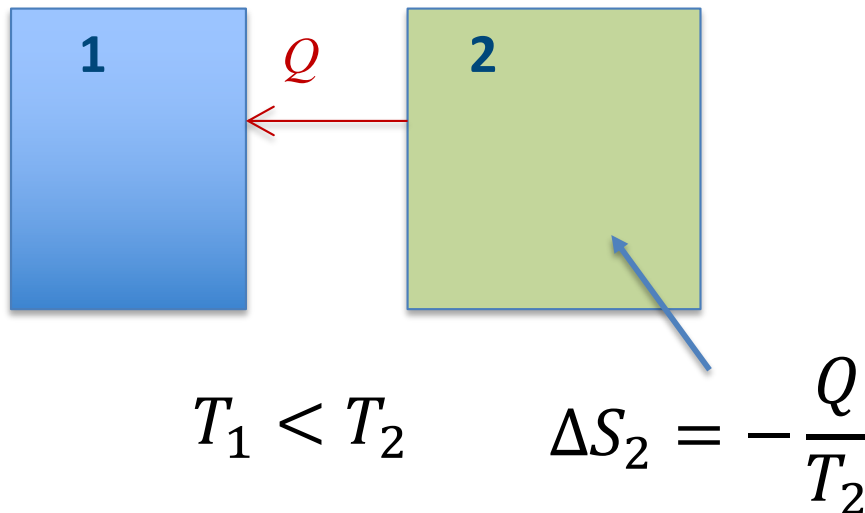
$$S = Nk_B \ln \left[\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} Nk_B$$

Note this is Sackur-Tetrode equation; h = Planck's constant. Classical-limit result, but relies on counting states that may be occupied in position-momentum space; h^3 is state "volume".

Regarding $\Delta S = Nk_B \ln \left(\frac{V_2}{V_1} \right)$ result: Result will reappear next chapter, $S = Nk_B \times (\log \textit{ of number of available states})$

Entropy increase:

- Associated with heating or spontaneous process. $\Delta S > 0$ either case. Connected to entropy maximum postulate.
- & note, reversing the spontaneous process will not reverse ΔS .
- Can reduce S to original situation by reverse heat flow, but not in a global sense! S can only increase, not decrease.

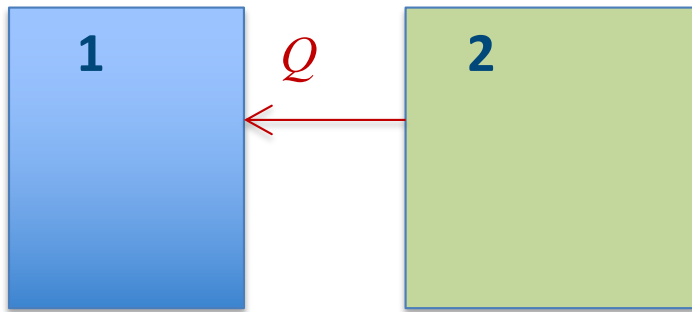


$$dS = \frac{1}{T} dU + \frac{P}{T} dV \dots$$

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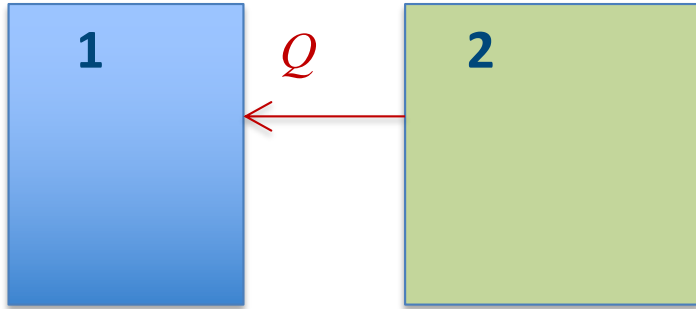
$$T_1 < T_2$$



$$\text{Overall } \Delta S = +\frac{Q}{T_1} - \frac{Q}{T_2} > 0$$

Entropy increase:

$$T_1 < T_2$$



$$\text{Overall } \Delta S = +\frac{Q}{T_1} - \frac{Q}{T_2} > 0$$

- *Entropy maximum principle* assures heat flow from high to low temperature.

2nd law corollary

- Individual S can decrease; overall always increases toward equilibrium = maximum.
- Universe entropy thus always increasing.
- At equilibrium, $T_1 = T_2$; $\Delta S_1 = -\Delta S_2$ for fluctuations at *extremum*, where $dS = 0$.

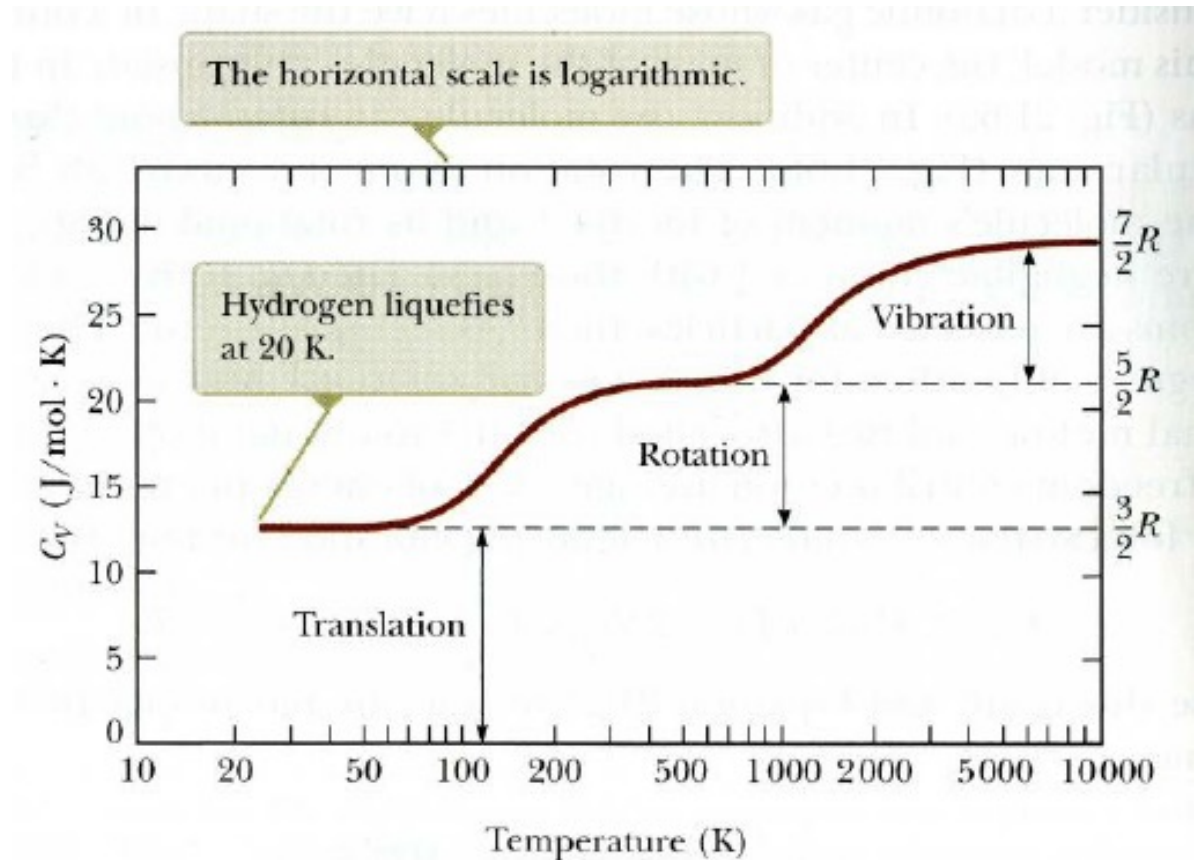
Note ideal gases can be more general:

Ideal gas *can* have internal degrees of freedom: $PV = NkT$ in all cases due to spatial motion of molecules. However internal energy larger if internal modes contribute.

Note C_V = specific heat, C measures dQ/dT , V means constant volume:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

(General results we found for monatomic case will be the same.)



Hydrogen = H_2 , nitrogen = N_2 , etc. "ideal gases" to very good approx. at RT

Summary:

$$\Delta U = Q + W \quad \Rightarrow \quad dU = TdS - PdV + \mu dN$$

- Have identified $W = -PdV$.
- Then consideration of general differential forms gave the more general form.
- μdN and other possible additive terms we will discuss in more detail later.
- Identification of TdS with heat term follows form of entropy found to agree with experimental observations (some of which we have seen).
- $dS = \frac{dQ}{T}$: Sadi Carnot early 1800s. Eventually wide application.
- Boltzmann 1870s successful statistical model which we discuss next.

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$S = S(U, V, N)$ or $U = U(S, V, N)$ fundamental equation

$$\text{With } T = \left(\frac{\partial U}{\partial S}\right)_{VN} \quad \left[\text{and } -P = \left(\frac{\partial U}{\partial V}\right)_{SN}, \mu = \left(\frac{\partial U}{\partial N}\right)_{SV} \right]$$

Can then assemble a complete model of the system behavior.