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Carnot Cycles: Traditional and Stefan Boltzmann, and the First Planck Argument

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I. TRADITIONAL CARNOT ENGINE USING GASES

The first semester p-chem course traditionally centers on thermodynamics, and therefore usually includes the Second Law. This Second Law is usually introduced with Carnot Engines working on ideal gas fluids, accepting heat from a high temperature reservoir at T_{high} and emitting that heat into a lower temperature reservoir whose temperature is T_{low} , accompanied by the emission of some work. We illustrate (for memory revival purposes) this traditional Carnot cycle in Figure 1. The drawing is made to highlight the full nature of the cycle, rather than the traditional drawing shown in most texts.

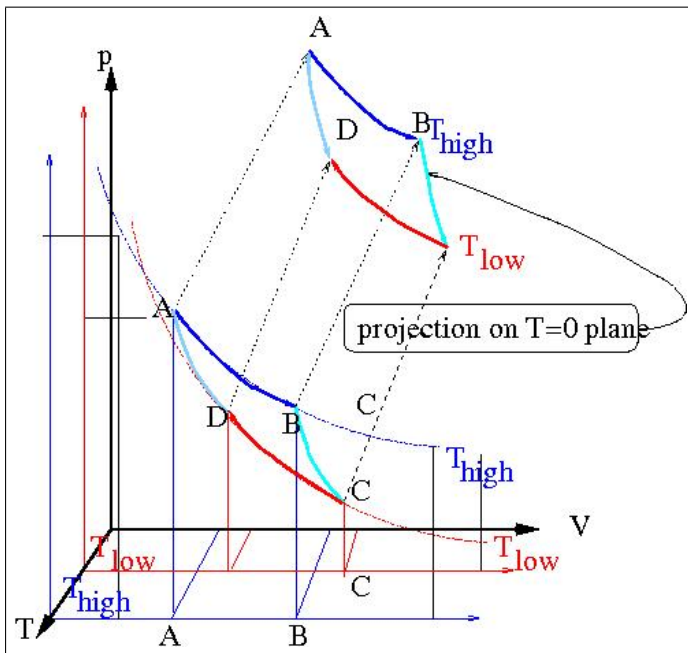


FIG. 1: A Traditional Carnot Cycle for a Gas

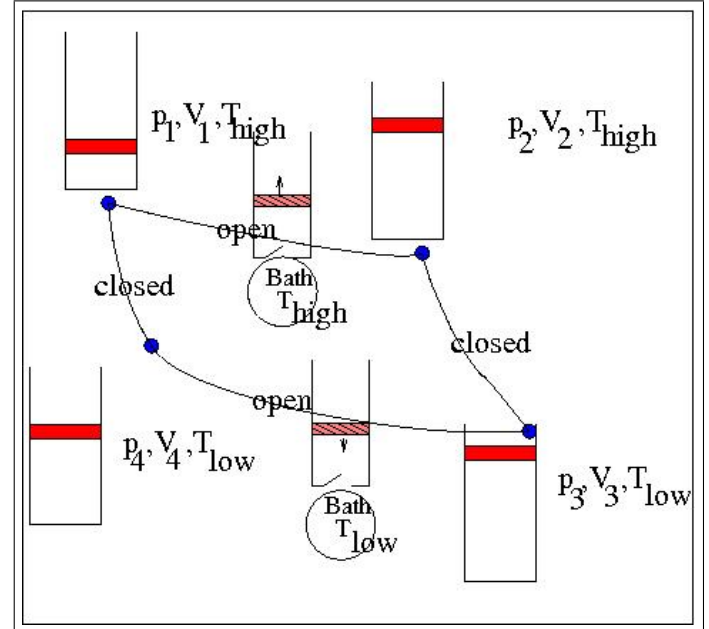


FIG. 2: A Carnot Cycle for a Radiation Gas

II. NON-TRADITIONAL CARNOT ENGINE USING RADIATION

We employ a Carnot engine with a working fluid which is electromagnetic radiation [1]. Walls, base, and the piston itself are assumed to be perfectly reflecting. There is a trap door in the base; when open, radiation comes from the accompanying bath into the cylinder, or goes out from the cylinder to the bath. There are two baths, B_{high} and B_{low} at temperatures T_{high} and T_{low} . The Carnot steps are

1. fill the cylinder with radiation from B_{high} until the piston and bath are at equilibrium. Then ψ_1 is the radiation density both in the piston and in the cylinder. The pressure in the cylinder is $p_1 = \frac{1}{3}\psi_1$ [2].
2. With the piston at p_1 allow the piston to rise reversibly to p_2 . The volume increases from V_1 to V_2 . the radiation density will remain constant since the trap door is held *open* during the expansion. $\psi_1(V_2 - V_1)$ is the amount of radiation which must have entered the cylinder during this expansion.

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The total energy after expansion is

$$\frac{1}{3}\psi_1(V_2 - V_1) + \psi_1(V_2 - V_1) = \frac{4}{3}\psi_1(V_2 - V_1)$$

This is equal to the amount of heat supplied, so that the process could remain isothermal.

3. Close the trap door, expand to P_3 . Energy density goes down from ψ_1 to ψ_2 . The pressure goes down. The temperature decreases to T_{low} . The process is adiabatic. If T_{low} differs only slightly from T_{high} then the difference in temperatures is just dT and the corresponding change in energy density is $d\psi$. Since $p = \frac{1}{3}\psi$ we know that

$$dp = \frac{1}{3}d\psi$$

4. open the trap door, apply external force to reduce the volume to V_4 , with the piston now at P_4 . Radiation leaves the cylinder into bath B_{low} .
5. Close the trap door, and close the cycle adiabatically.

The net work is

$$dw \approx (V_2 - V_1)dp = \frac{1}{3}(V_2 - V_1)d\psi$$

Therefore

$$\frac{dw}{\text{heat in}} = \frac{T_{high} - T_{low}}{T_{high}} = \frac{dT}{T_{high}} = \frac{\frac{1}{3}(V_2 - V_1)d\psi}{\frac{4}{3}(V_2 - V_1)\psi}$$

which means

$$\frac{d\psi}{\psi} = 4 \frac{dT}{T}$$

which yields

$$\psi = aT^4$$

III. FIRST PLANCK ARGUMENT

Planck wrote

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3}E(\nu, T) \quad (3.1)$$

where $E(\nu, t)$ is the average energy of a simple harmonic oscillator (of the wall) in equilibrium with black body radiation.

From the first law one has

$$dE = TdS - pdV$$

so

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$$

means

$$\left(\frac{\partial^2 S}{\partial E \partial T}\right)_V = -\frac{1}{T^2}$$

which becomes, employing the chain rule in reverse

$$\left(\frac{\partial E}{\partial T}\right) \left(\frac{\partial^2 S}{\partial E^2}\right)_V = -\frac{1}{T^2}$$

and, dividing by $\left(\frac{\partial E}{\partial T}\right)$ we obtain

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_V = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E}\right) = -\frac{1}{T^2 \left(\frac{\partial E}{\partial T}\right)} \quad (3.2)$$

Substituting Wien's formula:

$$\rho(\nu, T) = \alpha\nu^3 e^{-\beta\nu/T}$$

into Planck's starting formula (Equation 3.1)

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3}E(\nu, T) = \alpha\nu^3 e^{-\beta\nu/T}$$

we get

$$E(\nu, T) = \frac{\alpha\nu c^3}{8\pi e^{\beta\nu/T}} = \frac{\alpha\nu c^3}{8\pi} e^{-\beta\nu/T}$$

so, taking the derivative explicitly, we have

$$\frac{\partial E}{\partial T} = \frac{\beta\nu}{T^2}E$$

and therefore substituting into Equation 3.2 we obtain

$$\frac{\partial^2 S}{\partial E^2} = -\frac{1}{\beta\nu E} = -\frac{1}{CE} \quad (3.3)$$

where C is independent of the temperature. Since Wien's formula is itself wrong, for at high temperatures and low frequencies ($\lambda \uparrow$), $\rho(T) \sim T$ and therefore one has, approximately, $E(T) \sim T$ i.e., $E(T) = a \text{ constant} \times T$ and

$$\frac{\partial E}{\partial T} \sim \text{constant} \rightarrow K$$

so, if $E=KT$ then $T=E/K$ and $T^2 = \frac{E^2}{K^2}$ so we have using Equation 3.2

$$\frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2 \frac{\partial E}{\partial T}} \sim -\frac{1}{KT^2} = -\frac{1}{K'E^2} \quad (3.4)$$

At high frequency is (using Equation 3.3)

$$\frac{\partial^2 S}{\partial E^2} \sim -\frac{1}{E}$$

at low frequencies (using Equation 3.4)

$$\frac{\partial^2 S}{\partial E^2} \sim -\frac{1}{E^2}$$

Planck saw that one equation filled the bill, i.e.,

$$\frac{\partial^2 S}{\partial E^2} = -\frac{1}{E(a+E)}$$

If this is true then

$$\frac{\partial S}{\partial E} + b' = -\int \frac{dE}{E(a+E)}$$

which we decompose into

$$= -\int \left(\frac{1}{aE} - \frac{1}{a(a+E)} \right) dE$$

which is

$$= -\frac{1}{a} \ln E + \frac{1}{a} \ln(a+E)$$

or

$$= \frac{1}{a} \ln \left(\frac{a+E}{E} \right)$$

so

$$\frac{\partial S}{\partial E} = \frac{1}{a} \ln \left(\frac{a+E}{E} \right) = \frac{1}{T}$$

As $T \rightarrow \infty$, $E \rightarrow \infty$ but $\frac{1}{T} \rightarrow 0$, so

$$\frac{1}{a} \ln \left(\frac{a+E}{E} \right) + b = \frac{1}{T}$$

Therefore, $b=0$ and

$$\ln \left(\frac{a+E}{E} \right) = \frac{a}{T}$$

so

$$\frac{a+E}{E} = e^{a/T}$$

$$a+E = Ee^{a/T}$$

$$a = -E + Ee^{a/T}$$

$$E = \frac{a}{e^{a/T} - 1}$$

and finally

$$\rho(\nu, T) = \frac{8\pi}{c^3} \left(\frac{a\nu^2}{e^{a/T} - 1} \right)$$

but, from Wien, we know that $a(\nu)$ should go as ν^3 and we have $a\nu^2$ in the formula, so we should make a be a constant $\times \nu^3$ i.e., i.e. we should have $a = h\nu$, so that

$$\rho(\nu, T) = \frac{8\pi}{c^3} \left(\frac{h\nu^3}{k(e^{h\nu/kT} - 1)} \right)$$

[1] F. K. Richtmeyer and E. H. Kennard, "Introduction to Modern Physics", Fourth Edition, McGraw-Hill Book Co., Inc., 1947, page 149

[2] It is beyond the scope of these notes to show why this is true. See Richtmeyer and Kennard, *loc. cit.*, page 147-148