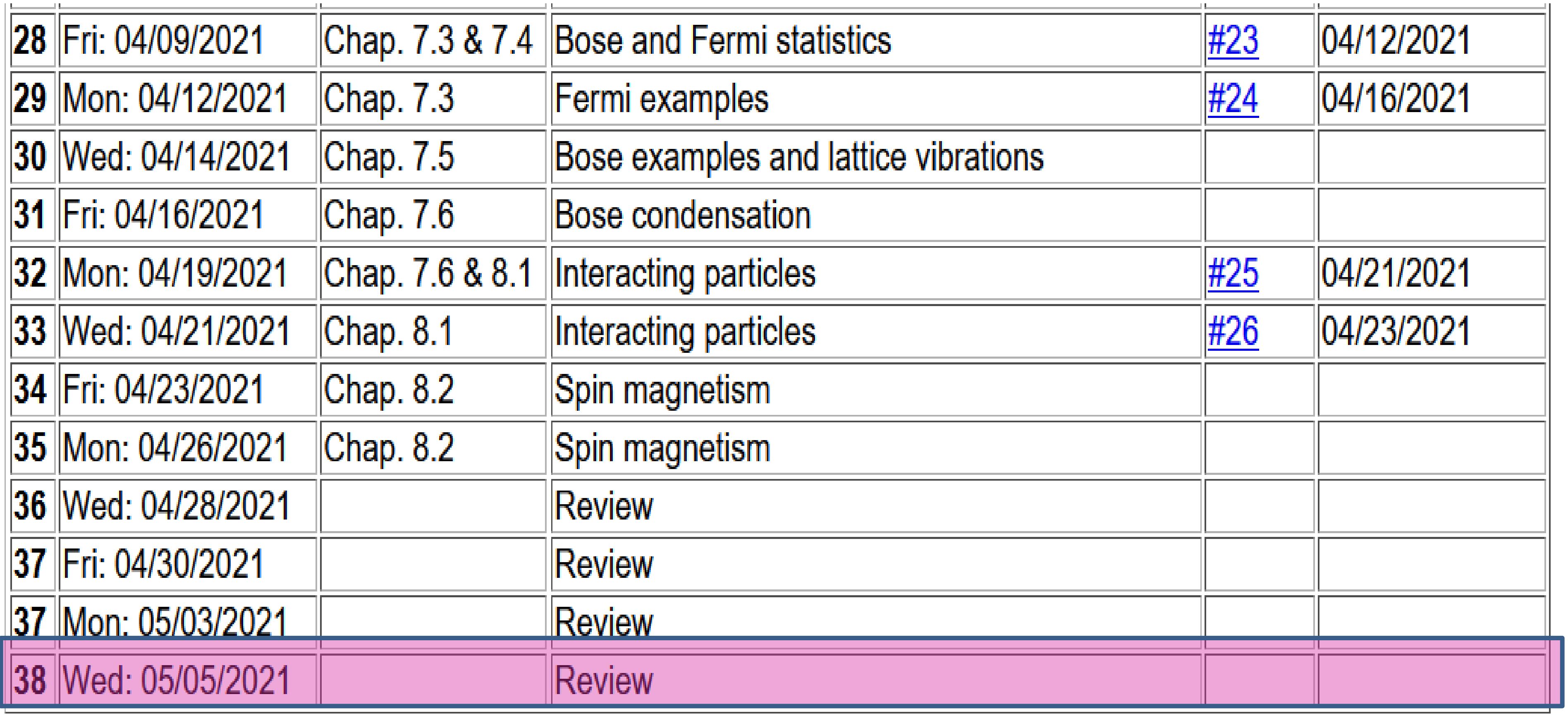
PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 39:

Review Part 4

1. **Advice about problem solving**
2. **Chemical equilibria**
3. **Comment on Bose and Fermi statistics**
4. **Thermodynamic cycles**
5. **Questionnaire**



28	Fri: 04/09/2021	Chap. 7.3 & 7.4	Bose and Fermi statistics	#23	04/12/2021
29	Mon: 04/12/2021	Chap. 7.3	Fermi examples	#24	04/16/2021
30	Wed: 04/14/2021	Chap. 7.5	Bose examples and lattice vibrations		
31	Fri: 04/16/2021	Chap. 7.6	Bose condensation		
32	Mon: 04/19/2021	Chap. 7.6 & 8.1	Interacting particles	#25	04/21/2021
33	Wed: 04/21/2021	Chap. 8.1	Interacting particles	#26	04/23/2021
34	Fri: 04/23/2021	Chap. 8.2	Spin magnetism		
35	Mon: 04/26/2021	Chap. 8.2	Spin magnetism		
36	Wed: 04/28/2021		Review		
37	Fri: 04/30/2021		Review		
37	Mon: 05/03/2021		Review		
38	Wed: 05/05/2021		Review		

Important dates: Final exams available < May 6; due May 14

Outstanding work due May 14

Thursday May 6
4 PM

PHYSICS DEPARTMENT

2021
Honors and Awards Ceremony

Join us May 6th at 4:00 pm as we

HONOR

Theses Presentations by

Noah Meyer
“Materials Simulation and Method Development with Density Functional Theory”

Fernando Rigal
“Effects of Nitric Oxide and Far-red Light on Thrombosis”

CELEBRATE

Graduating Seniors and Graduate Students

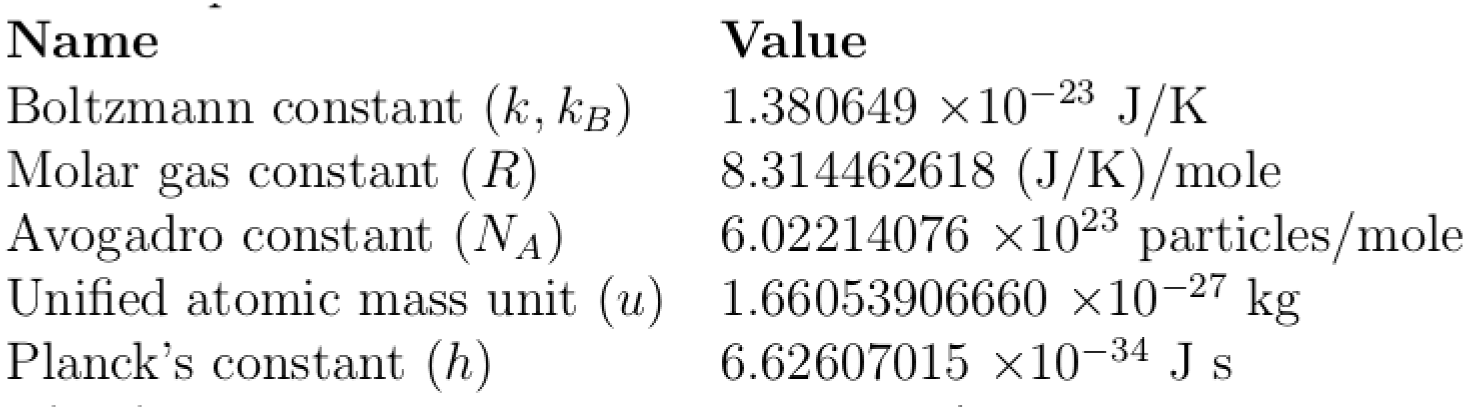
ACKNOWLEDGE

New Physics Majors

New Sigma Pi Sigma Members

Winners of Department Awards
(for extraordinary Dedication and Commitment)

Comment on numerical evaluations – reliable webpage for physical constants -- https://physics.nist.gov/cuu/Constants/index.html



Name	**Value**
Boltzmann constant (k, k_B)	1.380649×10^{-23} J/K
Molar gas constant (R)	8.314462618 (J/K)/mole
Avogadro constant (N_A)	$6.02214076 \times 10^{23}$ particles/mole
Unified atomic mass unit (u)	$1.66053906660 \times 10^{-27}$ kg
Planck's constant (h)	$6.62607015 \times 10^{-34}$ J s

Suppose that you were asked to evaluate the Gibb's free energy:

$$G(T,P,N) = -NkT\left(\ln\left(\frac{kT}{P}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right)\right)$$

$$= -nRT\left(\ln\left(\left(\frac{T}{T_0}\right)^{5/2} \frac{P_0}{P}\right) + \ln\left(\frac{(kT_0)^{5/2}}{P_0}\left(\frac{2\pi u}{h^2}\right)^{3/2}\right) + \frac{3}{2}\ln\left(\frac{m}{u}\right)\right)$$

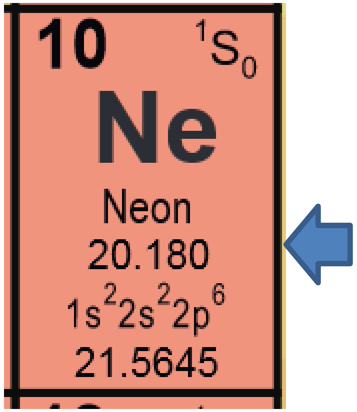
where $n \equiv N / N_A$

Suppose that you were asked to evaluate the Gibb's free energy:

$$G(T,P,N) = -NkT\left(\ln\left(\frac{kT}{P}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right)\right)$$

$$= -nRT\left(\ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + \ln\left(\frac{(kT_0)^{5/2}}{P_0}\left(\frac{2\pi u}{h^2}\right)^{3/2}\right) + \frac{3}{2}\ln\left(\frac{m}{u}\right)\right)$$

where $n \equiv N/N_A$



m/u

For $T_0 = 298K, \quad P_0 = 101325Pa$

$$G(T,P,N) = -nRT\left(\ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + 10.57786319 + \frac{3}{2}\ln\left(\frac{m}{u}\right)\right)$$

For Ne atoms:

$$G_{Ne}(T,P,N) = -nRT\left(\ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + 15.08490121\right)$$

Last lecture, we used these ideal gas relationships to discuss ideal mixing of gases, keeping the assumption of no interactions/reactions.

In the case of reactions between particles, the basic equations still apply, but we cannot ignore particle interactions. However, for the case that the reactions take place in the gas phase, some of the ideas can be extended -- Now, the notion of “internal energy” must be generalized so that we can compare particles of different types. It is convenient to use the energy measure of the heat of formation which is the energy to take a composite particle into its constituents in their “standard” states.

Notion of chemical reactions

$N_2 + 3H_2 \leftrightarrow 2NH_3$

In this case, the reaction of hydrogen and nitrogen gas forming ammonia gas can in principle proceed in either direction, depending on conditions.

Consider the following general reaction with 4 particles A, B, C, D:

$-\nu_A A - \nu_B B \rightleftarrows \nu_C C + \nu_D D$ By convention $\nu_A < 0$ and $\nu_B < 0$

We use N_A, N_B, N_C, N_D to denote the number of each of the particles.

We want to use the Gibbs free energy to analyze the reaction at fixed T and P.

In the case that all of the particles are approximately ideal gasses, we can start with Gibbs free energy of each type of particle. For particle A, for example:

$$G(T,P,N_A) = -N_A kT\left(\ln\left(\frac{kT}{P_A}\left(\frac{2\pi M_A kT}{h^2}\right)^{3/2}\right)\right)$$

$$= N_A\mu_A^0\left(T_0,P_0\right) - N_A kT\ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P_A}\right)$$

For $-\nu_A A - \nu_B B \rightleftarrows \nu_C C + \nu_D D$ it follows that

$dN_A = \nu_A d\chi \qquad dN_B = \nu_B d\chi \qquad dN_C = \nu_C d\chi \qquad dN_D = \nu_D d\chi$

where $d\chi$ measures the "degree of reaction".

It is also useful to define the fraction x_i of each type of particle in terms of the partial pressures $P_i = x_i P$.

Additionally, $N = \sum_i N_i$

In these terms, the Gibbs free energy of the system is

$$G(T,P,\{N_i\}) = -\sum_i N_i kT \left(\ln\left(\frac{kT}{P_i}\left(\frac{2\pi M_i kT}{h^2}\right)^{3/2} \right)\right)$$

$$= \sum_i N_i \mu_i^0\left(T_0,P_0\right) - \sum_i N_i kT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P_i}\right)$$

$$= \sum_i N_i \mu_i^0\left(T_0,P_0\right) - \sum_i N_i kT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + \sum_i N_i kT \ln\left(x_i\right)$$

$$= \sum_i N_i \mu_i^0\left(T_0,P_0\right) - NkT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + kT\sum_i \ln\left(x_i^{N_i}\right)$$

Consider the change in the Gibbs free energy

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

where the chemical potentials are

$$\mu_i = \mu_i^0\left(T_0, P_0\right) - kT\ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + kT\ln\left(x_i\right)$$

Expressed in terms of the degree of reaction:

$$dG = -SdT + VdP + \sum_i \mu_i \nu_i d\chi$$

$$\left(\frac{\partial G}{\partial \chi}\right)_{T,P} = \sum_i \mu_i \nu_i \equiv \boldsymbol{a} \qquad \text{"affinity"}$$

Note that at constant temperature and pressure, when the reactions is at equilibrium $\boldsymbol{a}^0=0$

Summary for reaction:

$$-\nu_A A - \nu_B B \rightleftarrows \nu_C C + \nu_D D$$

Chemical potential:

$$\mu_i = \mu_i^0(T_0, P_0) - kT \ln\left(\left(\frac{T}{T_0}\right)^{5/2} \frac{P_0}{P}\right) + kT \ln(x_i)$$

$$\left(\frac{\partial G}{\partial \chi}\right)_{T,P} = \sum_i \mu_i \nu_i \equiv \boldsymbol{a} \qquad \text{"affinity"}$$

At equilibrium $\boldsymbol{a}^0 = 0$

Off equilibrium $\boldsymbol{a}\, d\chi < 0$

$\Rightarrow$ Reaction proceeding to the right: $d\chi > 0$ and $\boldsymbol{a} < 0$

$\Rightarrow$ Reaction proceeding to the left: $d\chi < 0$ and $\boldsymbol{a} > 0$

$$\boldsymbol{a}(T,P,\chi) = \left(\frac{\partial G}{\partial \chi}\right)_{T,P} = \sum_i \mu_i \nu_i$$

$$\boldsymbol{a}(T,P,\chi) = \sum_i \mu_i \nu_i = \sum_i \nu_i \mu_i^0\left(T_0,P_0\right) - \sum_i \nu_i kT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + \sum_i kT \ln\left(x_i^{\nu_i}\right)$$

At equilibrium: $\boldsymbol{a}(T,P,\chi) = 0$

$$\ln\left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}}\right) = \sum_i \nu_i \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) - \frac{1}{kT}\underbrace{\sum_i \nu_i \mu_i^0\left(T_0,P_0\right)}_{\Delta G(T_0,P_0)}$$

$$\left(\frac{x_C^{\nu_C} x_D^{\nu_D}}{x_A^{|\nu_A|} x_B^{|\nu_B|}}\right)_{T_0 P_0} = e^{-\Delta G(T_0,P_0)/kT_0} \equiv K$$

Consider the gas phase reaction –
$N_2O_4 \leftrightarrow 2NO_2$
$\nu_A=-1 \qquad \nu_C=2$

Ref: L. E. Reichl
A modern course in
Statistical Mechanics

Suppose initially only N_2O_4 is present.

$$N_A = N_0(1-\chi) \qquad\qquad N_C = 2N_0\chi$$

$$x_A = \frac{1-\chi}{1+\chi} \qquad\qquad x_C = \frac{2\chi}{1+\chi}$$

$$\boldsymbol{a}(T,P,\chi) = \sum_i \nu_i \mu_i^0\left(T_0,P_0\right) - \sum_i \nu_i kT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right) + kT\ln\left(\frac{\left(2\chi\right)^2}{\left(1-\chi\right)\left(1+\chi\right)}\right)$$

For our example based on one mole (Avogadro's number of particles) and using $k \rightarrow R$

$$R = 8.315 \text{ J/K}$$

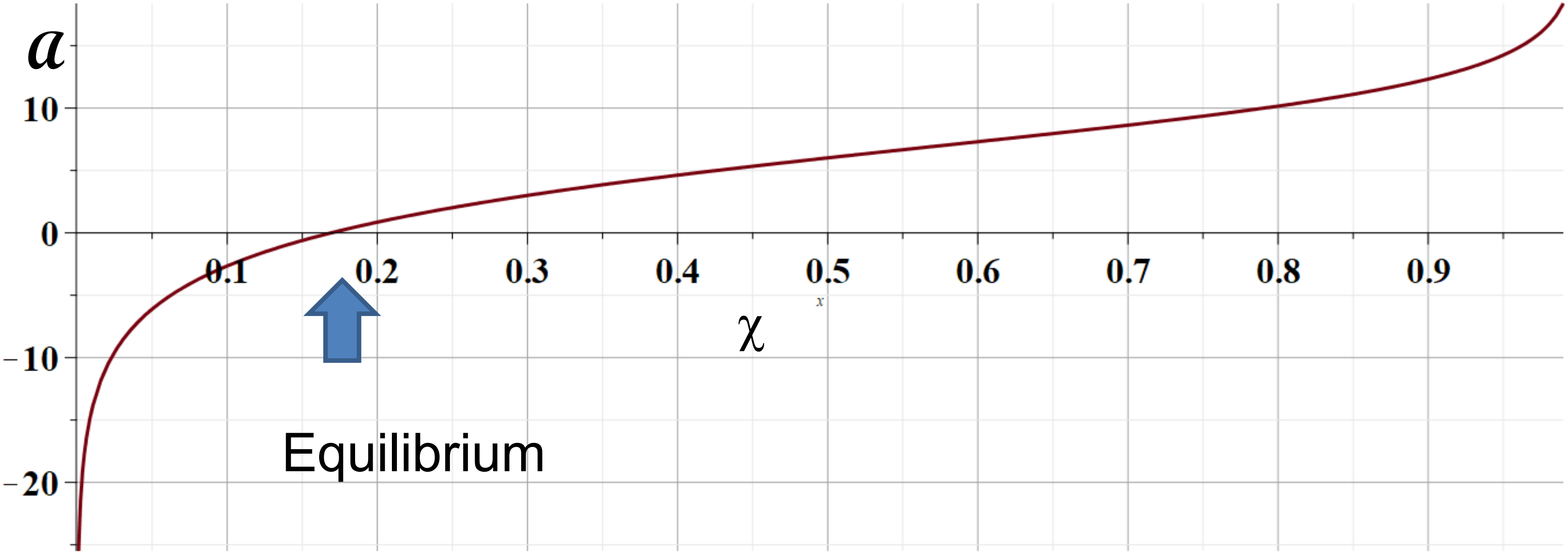
For N_2O_4: $\mu_i^0\left(T_0,P_0\right) = 98.3$ kJ

For NO_2: $\mu_i^0\left(T_0,P_0\right) = 51.8$ kJ

Consider the gas phase reaction –

$N_2O_4 \leftarrow\rightarrow 2NO_2$

$\nu_A=-1$ $\nu_C=2$ At $T_0=298K$ $P_0=1$ atm



Equilibrium

$$x_{N_2O_4} = 0.71 \qquad x_{NO_2} = 0.29$$

Comment on the chemical potential used in the grand partition function, where the summation over s depends on the system.

For Bose particles, the summation over n_s is a geometric sum resulting the analytic form:

$$\ln\left(Z_{GrandBose}(T,\mu)\right) = -\sum_s \ln\left(1 - e^{-\beta(\epsilon_s - \mu)}\right)$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)} - 1} = N$$

If the energy scale is ε≥0 then μ≤0.

For some systems, μ=0 such as photons, lattice vibrations,…

For Fermi particles $n_s=0$ or $n_s=1$ only

$$\ln\left(Z_{GrandFermi}(T)\right) = \sum_s \ln\left(1 + e^{-\beta(\epsilon_s - \mu)}\right)$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)} + 1} = N$$

Example of photon – "black body radiation"

Helmholtz free energy:

$$F_{Bose}(T) = -kT \ln Z_{Bose}(T) = kT \sum_s \ln\left(1 - e^{-\beta\epsilon_s}\right)$$

In practice, the state energies ϵ_s form a continuum

$$\sum_s \to \int d\epsilon \; g(\epsilon) \qquad \text{where } g(\epsilon) \text{ denotes the density of states}$$

$$g(\epsilon) = \frac{8\pi V \epsilon^2}{h^3 c^3}$$

$$F(T) = kT \frac{8\pi V}{h^3 c^3} \int_0^\infty d\epsilon \; \epsilon^2 \ln\left(1 - e^{-\beta\epsilon}\right) = \frac{8\pi V (kT)^4}{h^3 c^3} \int_0^\infty dx \, x^2 \ln\left(1 - e^{-x}\right)$$

$$= -\frac{8\pi V (kT)^4}{h^3 c^3} \frac{\pi^4}{45} = U - TS$$

Bose statistics of blackbody radiation -- continued

$$F(T) = -\frac{8\pi V(kT)^4}{h^3c^3}\frac{\pi^4}{45} = U - TS$$

Further relationships --

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{32\pi Vk^4T^3}{h^3c^3}\frac{\pi^4}{45}$$

$$U = F + ST = \frac{8\pi^5Vk^4T^4}{15h^3c^3}$$

Frequency distribution for microwave “background” radiation --

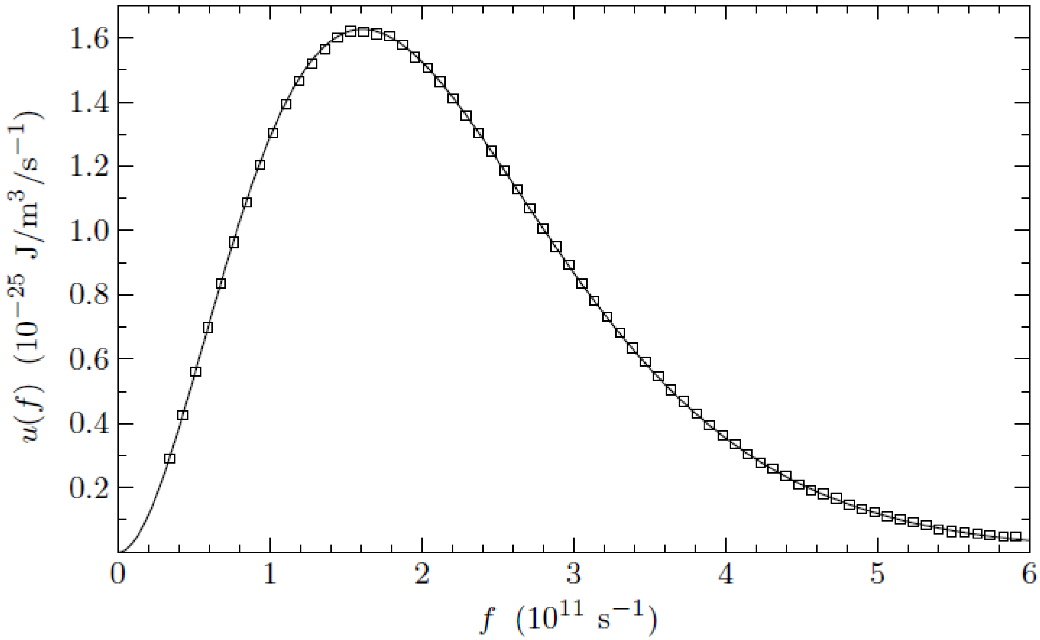
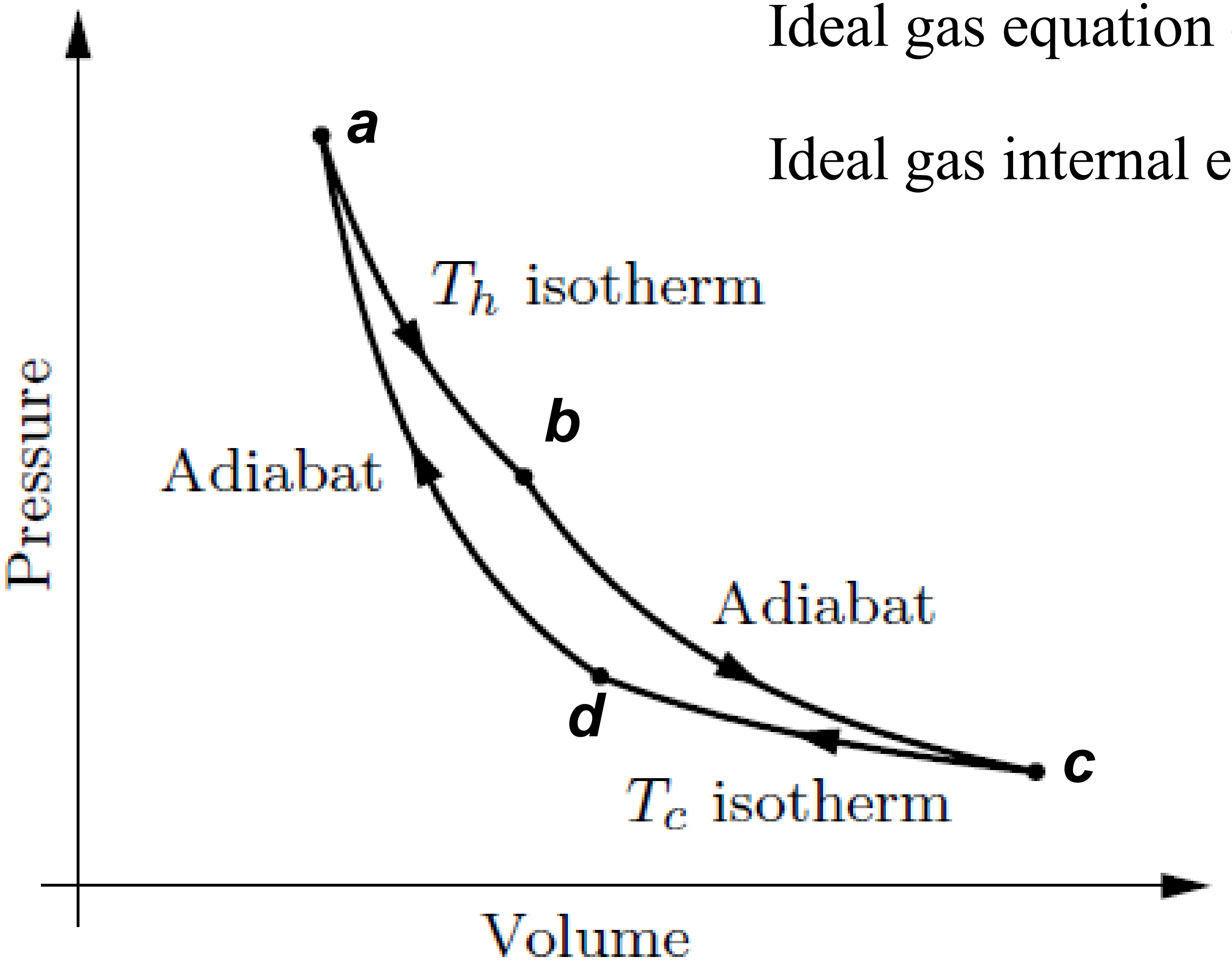


Figure 7.20. Spectrum of the cosmic background radiation, as measured by the *Cosmic Background Explorer* satellite. Plotted vertically is the energy density per unit frequency, in SI units. Note that a frequency of $3 \times 10^{11}\ \mathrm{s}^{-1}$ corresponds to a wavelength of $\lambda = c/f = 1.0$ mm. Each square represents a measured data point. The point-by-point uncertainties are too small to show up on this scale; the size of the squares instead represents a liberal estimate of the uncertainty due to systematic effects. The solid curve is the theoretical Planck spectrum, with the temperature adjusted to 2.735 K to give the best fit. From J. C. Mather et al., *Astrophysical Journal Letters* **354**, L37 (1990); adapted courtesy of NASA/GSFC and the COBE Science Working Group. Subsequent measurements from this experiment and others now give a best-fit temperature of 2.728 ± 0.002 K. Copyright ©2000, Addison-Wesley.

Short review of PV and ST diagrams of cyclic processes

Carnot cycle -- PV diagram from your textbook



Ideal gas relations:

Ideal gas equation of state $PV = Nk_BT$

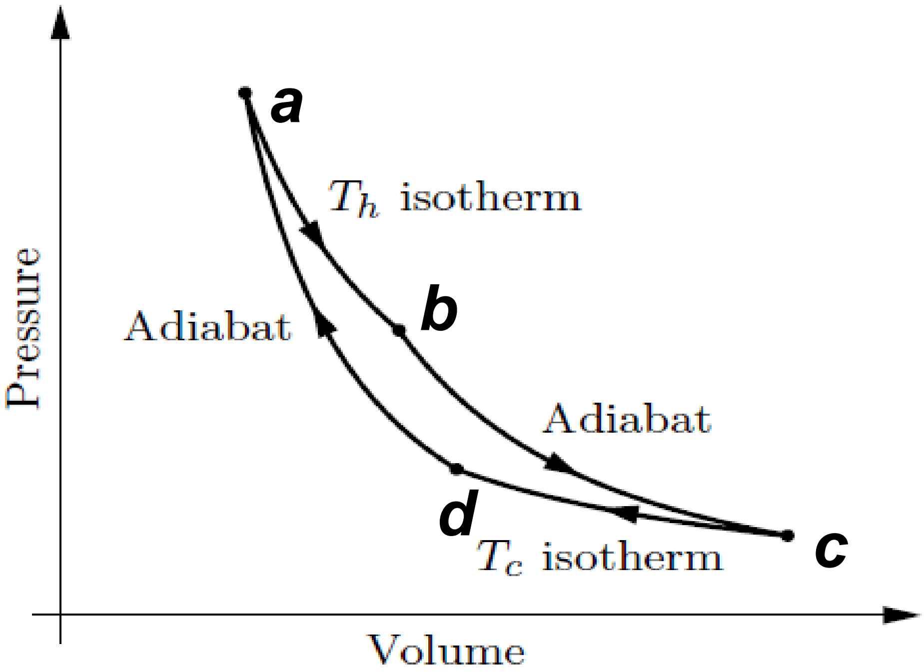
Ideal gas internal energy $U = \frac{Nk_BT}{\gamma - 1}$

Recall that

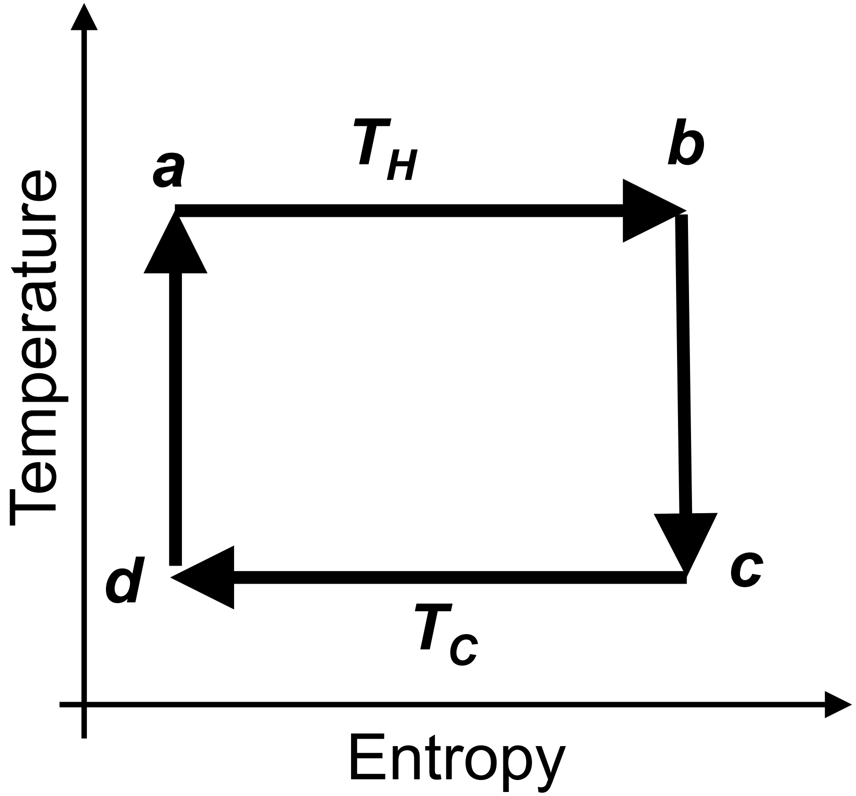
$$\gamma \equiv \frac{C_P}{C_V}$$

γ is an empirically measured quantity related to degrees of freedom of ideal gas

P versus V diagram



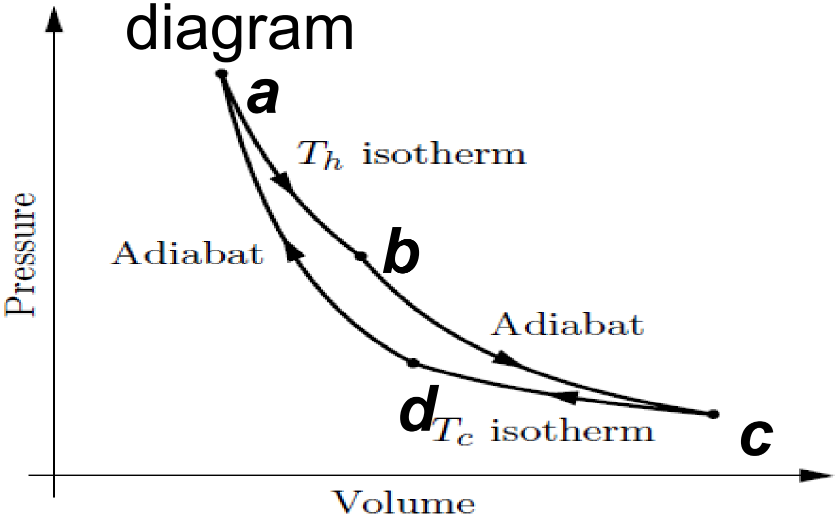
T versus S diagram



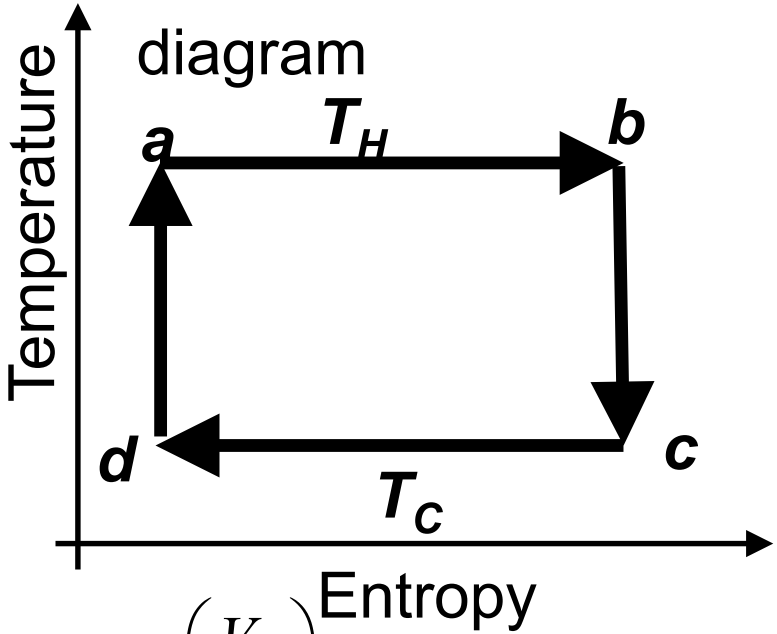
For step a → b: $Q_{ab} = -W_{ab} = Nk_BT_H \ln\left(\frac{V_b}{V_a}\right)$ For step b → c: $Q_{bc} = 0 \quad V_bT_H^{1/(\gamma-1)} = V_cT_C^{1/(\gamma-1)}$

For step c → d: $Q_{cd} = -W_{cd} = Nk_BT_C \ln\left(\frac{V_d}{V_c}\right)$ For step d → a: $Q_{da} = 0 \quad V_dT_C^{1/(\gamma-1)} = V_aT_H^{1/(\gamma-1)}$

P versus V diagram



T versus S diagram

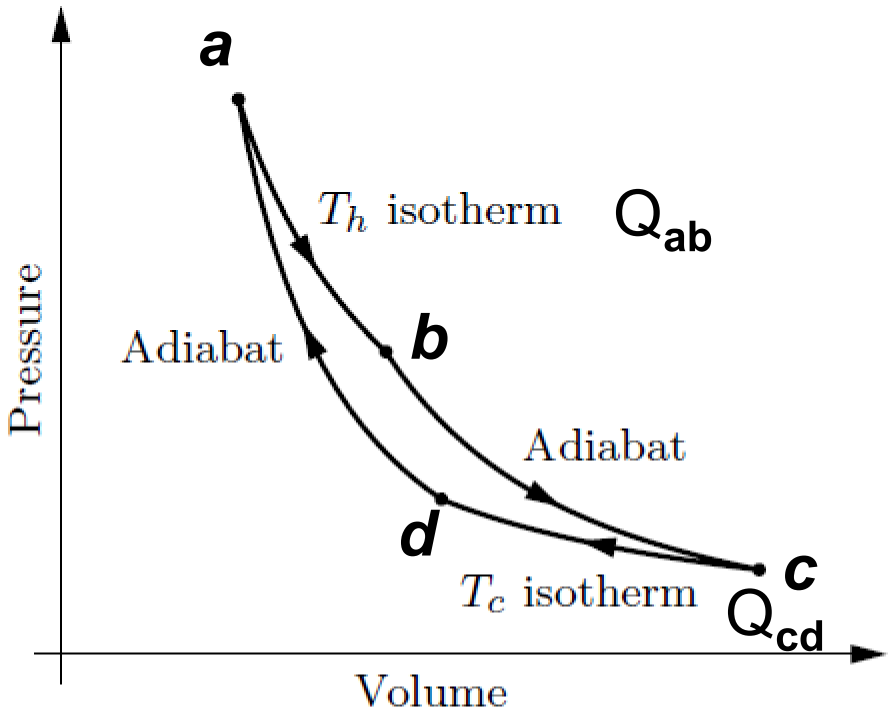


$$Q_{ab} = Nk_B T_H \ln\left(\frac{V_b}{V_a}\right) \qquad Q_{cd} = Nk_B T_C \ln\left(\frac{V_d}{V_c}\right)$$

$$V_b T_H^{1/(\gamma-1)} = V_c T_C^{1/(\gamma-1)} \qquad V_d T_C^{1/(\gamma-1)} = V_a T_H^{1/(\gamma-1)} \quad \Rightarrow \left(\frac{T_H}{T_C}\right)^{1/(\gamma-1)} = \frac{V_c}{V_b} = \frac{V_d}{V_a}$$

$$\Rightarrow \frac{V_b}{V_a} = \frac{V_c}{V_d} \qquad \Rightarrow Q_{cd} = -Nk_B T_C \ln\left(\frac{V_b}{V_a}\right) = -Q_{ab}\frac{T_C}{T_H}$$

Engine efficiency



$$\epsilon \equiv \frac{W_{net}}{Q_{in}} = \frac{Q_{net}}{Q_{in}}$$

$$= \frac{Q_{ab} + Q_{cd}}{Q_{ab}}$$

For the Carnot cycle -- $Q_{cd} = -Q_{ab}\frac{T_C}{T_H}$

$$\epsilon = 1 - \frac{T_C}{T_H}$$

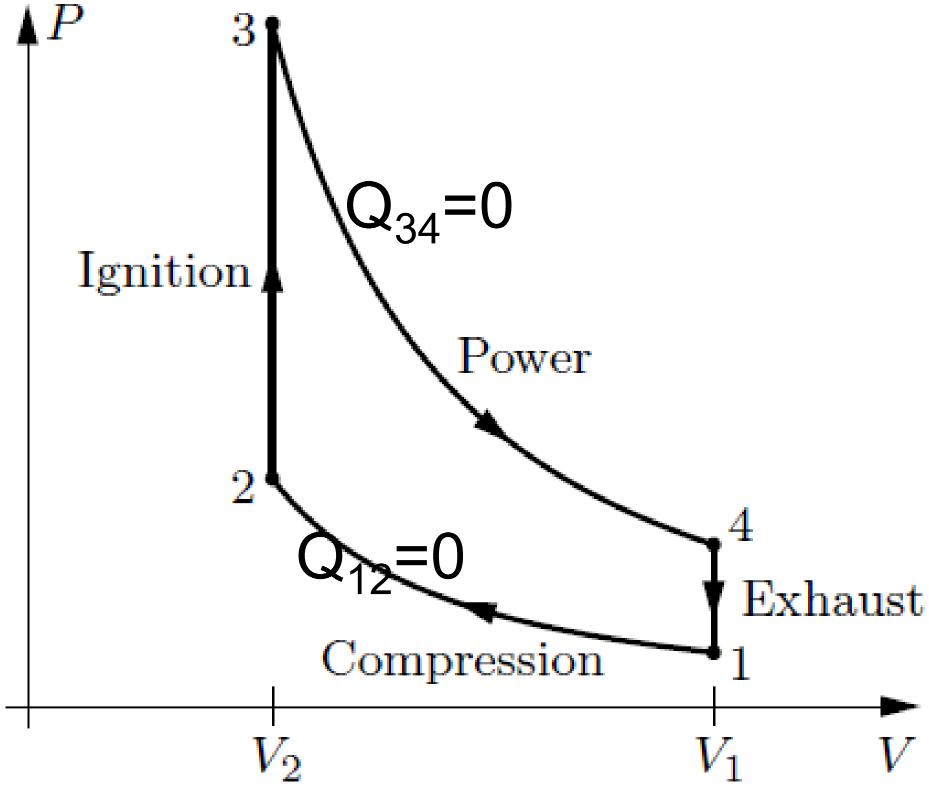
Example: Suppose $T_C = 300K$ and $T_H = 600K$

$$\epsilon = 1 - \frac{300}{600} = 0.5$$

Comment: Here we have assumed that there are no energy losses and that all of the processes are reversible.

Another thermodynamic cycle example

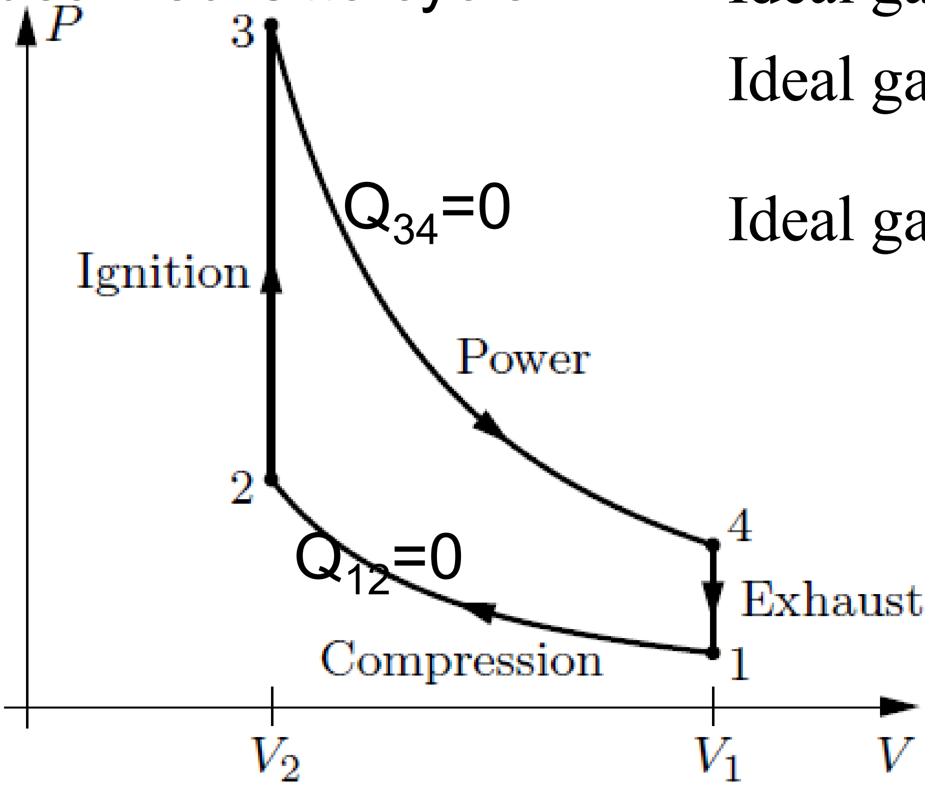
Figure 4.5. The idealized Otto cycle, an approximation of what happens in a gasoline engine. In real engines the compression ratio V_1/V_2 is larger than shown here, typically 8 or 10. Copyright ©2000, Addison-Wesley.



$Q_{34}=0$

$Q_{12}=0$

Idealized Otto cycle



Ideal gas relations:

Ideal gas equation of state $PV = Nk_BT$

Ideal gas internal energy $U = \frac{Nk_BT}{\gamma - 1}$

$$Q_{23} = U_{23} = \frac{Nk_B}{\gamma - 1}(T_3 - T_2)$$

$$Q_{41} = U_{41} = \frac{Nk_B}{\gamma - 1}(T_1 - T_4)$$

$$Q_{12} = 0 \quad V_1T_1^{1/(\gamma-1)} = V_2T_2^{1/(\gamma-1)}$$

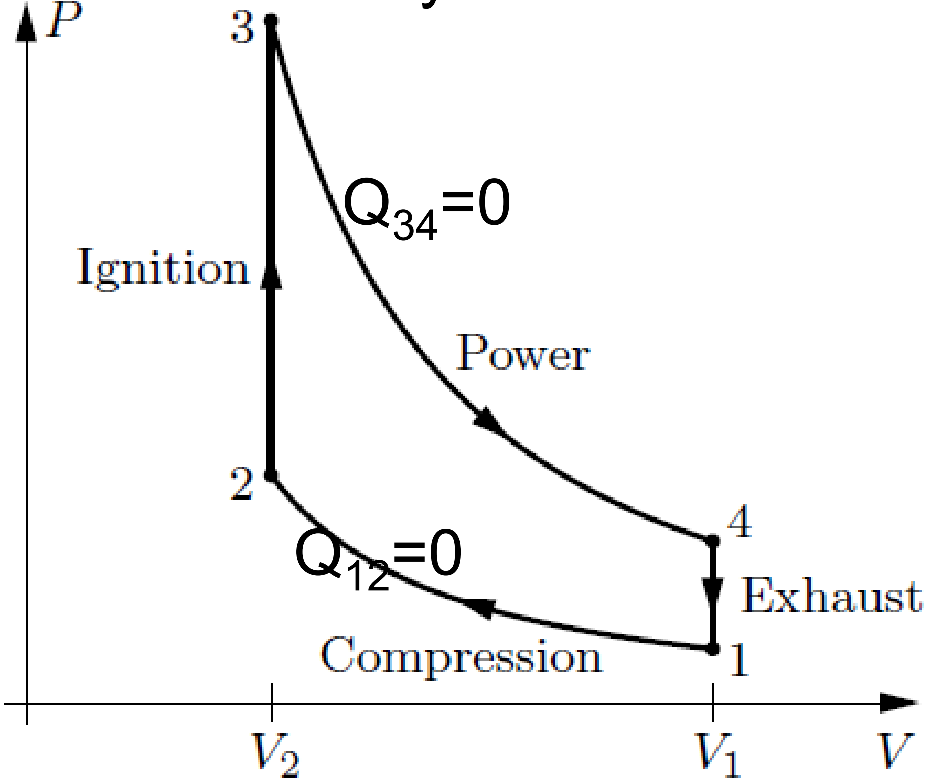
$$Q_{34} = 0 \quad V_2T_3^{1/(\gamma-1)} = V_1T_4^{1/(\gamma-1)}$$

$$\frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{1/(\gamma-1)} = \left(\frac{T_3}{T_4}\right)^{1/(\gamma-1)}$$

$$\epsilon = \frac{Q_{23} + Q_{41}}{Q_{23}} = 1 + \frac{Q_{41}}{Q_{23}}$$

$$= 1 - \frac{T_4}{T_3} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

Idealized Otto cycle



$$\epsilon = \frac{Q_{23} + Q_{41}}{Q_{23}} = 1 + \frac{Q_{41}}{Q_{23}}$$

$$= 1 - \frac{T_4}{T_3} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma - 1}$$

For $\gamma = 1.4$ and $\frac{V_2}{V_1} = \frac{1}{8}$ $\quad \epsilon = 0.56$