# Lecture Notes 4

## 1. The Ideal Gas

The ideal gas is a low density gas for which we can ignore the interaction potential energy. We have shown in Lecture Notes 2 that for a monatomic ideal gas U = (3/2)pV. This formula is generalized to diatomic and polyatomic molecules as: U = (i/2)pV where i is the number of degrees of freedom for a molecule. For monatomic gases such as noble gases (He, Ne, Ar, Kr, Xe, Rn) i =3 counting the 3 coordinates. For diatomic gases, such as $N_2$, $O_2$, $H_2$, i = 5, counting the 3 coordinates of the center of mass and the 2 angles that give the direction of the molecular axis. For polyatomic molecules, such as $H_2O$, i = 6.

Since the energy is only kinetic we can estimate the root mean square velocity of such a molecule. For a monatomic gas: $U = (3/2)pV = (3/2)Nk_BT = Nm\langle v^2\rangle/2$, so:

$v_{rms} = \langle v^2\rangle^{1/2} = (3k_BT/m)^{½} = (3RT/M)^{½}$, where M is molar mass.

Example: Compute the rms velocity for Argon at room temperature.

Molar mass is M = 40g/mole and temperature is T = 300K.

$v_{rms} = (3*8.3*300/40*10^{-3})^{1/2} = 432$m/s.

## 2. The Ideal Gas: Fundamental Equation

The ideal gas equation of state relating pressure, volume, temperature and number of molecules is:

$pV = Nk_BT$ or $pv = k_BT$ (1)

The internal energy is:

$U = (i/2)pV = (i/2)Nk_BT$ or $u = (i/2)k_BT$ (2)

In (1) and (2) u = U/N, v = V/N. We start from the molecular form of the 1'st law:

$du = Tds - pdv$ (3)

Next we substitute on right hand side of equation (3): $ds = (\frac{\partial s}{\partial T})_v dT + (\frac{\partial s}{\partial v})_T dv$:

$$du = T(\frac{\partial s}{\partial T})_v dT + (T(\frac{\partial s}{\partial v})_T - p)dv \quad (4)$$

It follows that:

$$c_v = T(\frac{\partial s}{\partial T})_v = (\frac{\partial u}{\partial T})_v = \frac{i}{2}k_B \quad (5)$$

$$T(\frac{\partial s}{\partial v})_T - p = \left(\frac{\partial u}{\partial v}\right)_T = 0 \quad (6)$$

To get the and right hand side of (5) and (6) I used Eq. (2). We rewrite Eq. (6) by using the equation of state Eq. (1):

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{i}{2}\frac{k_B}{T} \qquad (7)$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{p}{T} = \frac{k_B}{v} \qquad (8)$$

We integrate (7) and (8) to get:

$$s - s_0 = \frac{i}{2} k_B \ln\left(\frac{T}{T_0}\right) + k_B \ln\left(\frac{v}{v_0}\right) \qquad (9)$$

The constants of integration represent the values of entropy, molecular volume and temperature in a reference state. In Statistical Physics the integration constants are determined in terms of the fundamental constants: Planck constant h, Boltzmann constant $k_B$, and molecular mass. We can use the equation of state, v ~ T/p, to express s as a function of the intensive variables T and p:

$$s - s_0 = \frac{i+2}{2} k_B \ln\left(\frac{T}{T_0}\right) - k_B \ln\left(\frac{p}{p_0}\right) \qquad (10)$$

<u>Application: Isobaric Specific Heat</u>

Differentiate both sides of Eq. (10) with respect to T at fixed p:

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p = \frac{i+2}{2} k_B \qquad (11)$$

The isochoric specific heat is given in Eq. (5):

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v = \frac{i}{2} k_B \qquad (12)$$

Note $c_p > c_v > 0$. Those inequalities hold true for any material, as they are required by the 2nd Law of Thermodynamics. The ratio of the two specific heats, using Eqs. (11) and (12) is:

$$\gamma = \frac{c_p}{c_v} = \frac{i+2}{i} \qquad (13)$$

We solve for temperature in Eq. (9):

$$\frac{T}{T_0} = \left(\frac{v}{v_0}\right)^{-\frac{2}{i}} \exp\left(\frac{2}{i}\frac{(s-s_0)}{k_B}\right) \qquad (14)$$

We get the fundamental equation of the ideal gas by substituting the temperature from Eq. (14) into the energy Eq. (2):

$$u = u_0 \left(\frac{v}{v_0}\right)^{-\frac{2}{i}} \exp\left(\frac{2}{i}\frac{(s-s_0)}{k_B}\right) \qquad (15)$$

We scale up and get the fundamental equation U = U(S, V, N):

$$U = U_0 \left(\frac{V}{V_0}\right)^{-\frac{2}{i}} \left(\frac{N}{N_0}\right)^{\frac{i+2}{i}} \exp\left(\frac{2}{i}\frac{1}{k_B}\left(\frac{S}{N} - \frac{S_0}{N_0}\right)\right) \quad (16)$$

Application: Adiabatic Process, Poisson Equation

In an adiabatic process the entropy and the amount of material are unchanged: $S = S_0$ and $N = N_0$, and hence $s = s_0$. From Eq. (14) we find:

$$\frac{T}{T_0} = \left(\frac{v}{v_0}\right)^{-\frac{2}{i}} \quad (17)$$

or:

$$Tv^{\gamma-1} = const. \quad (18)$$

where $\gamma - 1 = \frac{2}{i}$. (see Eq. (13).

In view of the equation of state T/v ~ p, Eq. (18) can be written as:

$$pv^{\gamma} = const. \quad (19)$$

$$pT^{-\gamma/(\gamma-1)} = const. \quad (20)$$

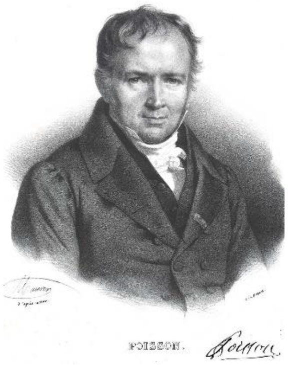


*Figure 1: Simeon Denis Poisson (1781-1840), French physicist, mathematician who contributed to many areas of mathematical physics.*

Equation (19) is known as the Poisson equation.

Application: Adiabatic Compressibility

For adiabatic process we have the Poisson equation. Differentiate both sides of Eq (19) with respect to p:

$$v^{\gamma} + p\gamma v^{\gamma-1}\left(\frac{\partial v}{\partial p}\right)_S = 0$$

$$k_S = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_S = \frac{1}{\gamma p} \quad (21)$$

Remember in Lecture Notes 3 we proved: $k_T = 1/p$. Note $k_T > k_s > 0$. Those inequalities hold true for any material, as they are required by the 2nd Law of Thermodynamics. The ratio of the two compressibilities equals the ratio of the specific heats (this is true for any material):

$$\frac{k_T}{k_S} = \frac{c_p}{c_v} = \gamma = \frac{i+2}{i} \qquad (22)$$

Application: The Speed of Sound

Sound propagates in a material with a speed determined by the strength of the material (bulk modulus) and its density: $v_{\text{sound}} = \sqrt{\frac{B}{\rho}}$ The bulk modulus is the inverse of compressibility: $B = 1/k$. For ideal gases: $B_T = p$ and $B_S = \gamma p$. The sound propagates fast enough that the process is adiabatic rather than isothermal, as discovered by Laplace. The density is:

$\rho = \mathcal{N}M/V = pM/RT$. Then:

$v_{\text{sound}} = \sqrt{\frac{B_S}{\rho}} = \sqrt{\frac{\gamma RT}{M}}$ We estimate the speed of sound in air at room temperature:

$T = 300K$, $M = 29 \cdot 10^{-3}$kg/mole, $R = 8.3$j/K*mole, $\gamma = 1.4$. We find $v_{\text{sound}} = 346$m/s in agreement with the measured value.

*Figure 2: Pierre-Simon Laplace (1749-1827), French physicist, mathematician who contributed to many areas of mathematical physics.*

Interesting enough, Newton calculated the speed using the isothermal bulk modulus. As a consequence of this assumption, that estimate was about 20% lower than the experimental value.

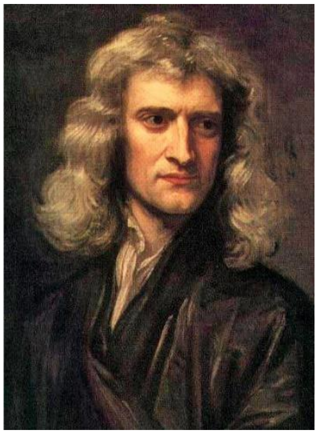


*Figure 3: Isaac Newton (1642-1727), English physicist, mathematician who discovered the laws of mechanics and calculus.*

Application: Adiabatic Atmosphere

We consider a model of the atmosphere in hydrostatic equilibrium and undergoing adiabatic processes.

$$\frac{dp}{dh} = -\rho g \qquad (23)$$

The air density is: $\rho = \mathcal{N}M/V = pM/RT$. Hence Eq. (23) becomes:

$$\frac{d\ln(p)}{dh} = -\frac{Mg}{RT} \qquad (24)$$

For adiabatic processes p and T are related by Eq.(20): $p = p_0(T/T_0)^{\gamma/(\gamma-1)}$,

and $\gamma/(\gamma\text{-}1) = (i+2)/2$. Then: $\ln(p) = \ln(p_0) + [(i+2)/2]\ln(T/T_0)$. We differentiate ln(p) with respect to h to get the left hand side of Eq.(24):

$$\frac{i+2}{2}\frac{1}{T}\frac{dT}{dh} = -\frac{Mg}{RT} \qquad (25)$$

$$\frac{dT}{dh} = -\frac{Mg}{R\frac{i+2}{2}} \qquad (26)$$

But according to Eq. (11) the molar isobaric specific heat is $c_p = \frac{i+2}{2}R$. The quantity on the right hand side of Eq.(26) is called the dry adiabatic lapse rate $\Gamma$:

$$\Gamma = \frac{Mg}{c_p} \qquad (27)$$

Exercise: Air is a diatomic gas i = 5 with molar mass M = 29g/mol. Compute the dry adiabatic lapse rate.

$\Gamma = 29*10^{-3}*9.8/(8.3*3.5) = 9.8*10^{-3}$ °C/m. Hence going up in altitude for 100m, the temperature drops by 1°C.

Integrate Eq. (26):

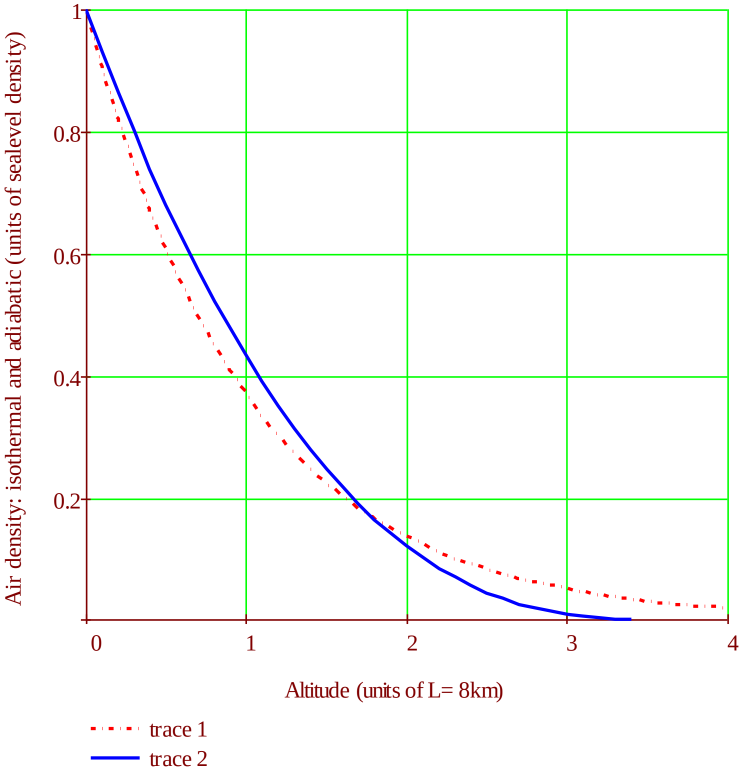
$$T = T_0 - \Gamma h \qquad (28)$$

Pressure dependence on altitude becomes:

$$p = p_0(1 - \Gamma h/T_0)^{(i+2)/2} \qquad (29)$$

Density dependence on altitude is obtained by substituting Eqs. (28), (29) into $\rho = pM/RT$:

$$\rho = \rho_0\left(1 - \frac{\Gamma}{T_0}h\right)^{\frac{i}{2}} \qquad (30)$$



trace 1 isothermal model;
trace 2 adiabatic model

Readings
HRW Ch.19
Callen Ch. 3, Sec 4;
Problem Set 4

# Lecture Notes 5

## 1. The Ideal Gas: Fundamental Equation in Terms of Intensive Variables

We derive the ideal gas fundamental equation relating chemical potential, temperature, and pressure. We start with the equation of state:

$$pv = k_B T \tag{1}$$

The internal energy is:

$$u = (i/2)k_B T \tag{2}$$

The molecular entropy is (see Lecture Notes 4, Eq.10)

$$s - s_0 = \frac{i+2}{2} k_B \ln\left(\frac{T}{T_0}\right) - k_B \ln\left(\frac{p}{p_0}\right) \tag{3}$$

In (1), (2), and (3): $u = U/N$, $v = V/N$, $s = S/N$. We substitute (1), (2), (3) into the molecular form of the Euler equation:

$$u = Ts - pv + \mu \tag{4}$$

We calculate the chemical potential:

$$\mu = \frac{i}{2} k_B T - T s_0 - \frac{i+2}{2} k_B T \ln\left(\frac{T}{T_0}\right) + k_B T \ln\left(\frac{p}{p_0}\right) + k_B T \tag{5}$$

In the reference state:

$$\mu_0 = \frac{i}{2} k_B T_0 - T_0 s_0 + k_B T_0 \tag{6}$$

Combining Eqs (5) and (6) we get:

$$\mu = \frac{\mu_0}{T_0} T - \frac{i+2}{2} k_B T \ln\left(\frac{T}{T_0}\right) + k_B T \ln\left(\frac{p}{p_0}\right) \tag{7}$$

Equation (7) is the fundamental equation of the ideal gas in terms of the intensive variables. All the information about this thermodynamic system is contained in this equation. To calculate entropy, volume we need to remember the Gibbs-Duhem equation (see Lecture Notes 3, Eq. 16) :

$$d\mu = -s\,dT + v\,dp \tag{8}$$

<u>Application:</u>

Compute s(T,p) and v(T,p) starting from Eqs. (7) and (8):

$$s = -\left(\frac{\partial \mu}{\partial T}\right)_p = -\frac{\mu_0}{T_0} + \frac{i+2}{2} k_B \ln\left(\frac{T}{T_0}\right) + \frac{i+2}{2} k_B - k_B \ln\left(\frac{p}{p_0}\right) = s_0 + \frac{i+2}{2} k_B \ln\left(\frac{T}{T_0}\right) - k_B \ln\left(\frac{p}{p_0}\right) \tag{9}$$

$$v = \left(\frac{\partial \mu}{\partial p}\right)_T = \frac{k_B T}{p} \tag{10}$$

Eq (9) is the same as Eq. 10 of Lecture Notes 4 and Eq (10) is the ideal gas equation of state.

## 2. Van der Waals Fluid

The equation of state is:

$$p = \frac{k_B T}{v-b} - \frac{a}{v^2} \qquad (11)$$

The molecular form of the 1'st law: du = Tds – pdv becomes after substituting

ds = $(\frac{\partial s}{\partial T})_v dT + (\frac{\partial s}{\partial v})_T dv$:

$$du = T(\frac{\partial s}{\partial T})_v dT + (T(\frac{\partial s}{\partial v})_T - p)dv \qquad (12)$$

Now we use: $\frac{\partial^2 u}{\partial v \partial T} = \frac{\partial^2 u}{\partial T \partial v}$:

$$T\frac{\partial^2 s}{\partial v \partial T} = (\frac{\partial s}{\partial v})_T + T\frac{\partial^2 s}{\partial T \partial v} - (\frac{\partial p}{\partial T})_v \qquad (13)$$

We get the following Maxwell relation:

$$(\frac{\partial s}{\partial v})_T = (\frac{\partial p}{\partial T})_v \qquad (14)$$

The right hand side of Eq. (14) is obtained from the equation of state Eq (11):

$$(\frac{\partial s}{\partial v})_T = \frac{k_B}{v-b} \qquad (15)$$

Integrating (15) with respect to v we get:

$$s = k_B \ln(v-b) + \Phi(T), \qquad (16)$$

where $\Phi(T)$ is unknown function of temperature. Using Eq(16) we get the isochoric specific heat:

$$c_v = T(\frac{\partial s}{\partial T})_v = T\frac{d\Phi}{dT} \qquad (17)$$

We thus conclude that the isochoric specific heat of van der Waals fluid is a function of temperature only.

<u>Application: The ideal van der Waals fluid</u>

We assume next that the isochoric heat is the same as for the ideal gas: $c_v = \frac{i}{2}k_B$. It follows that: $\Phi(T) = \frac{i}{2}k_B \ln(T)$ + constant. The entropy equation (16) can be written as:

$$s - s_0 = k_B \ln\left(\frac{v-b}{v_0-b}\right) + \frac{i}{2}k_B \ln(\frac{T}{T_0}), \qquad (18)$$

For adiabatic process s = $s_0$ and Eq. (18) gives:

$$(v-b)T^{\frac{i}{2}} = constant \qquad (19)$$

Substituting T from the equation of state in Eq. (19), we get the analog of the Poisson equation:

$$\left(p + \frac{a}{v^2}\right)(v-b)^{\frac{i+2}{i}} = const \qquad (20)$$

We next derive the energy of the ideal van der Waals fluid. We start with the differential du of Eq.(12), and substitute s from Eq.(18) and p from equation of state (11). We find:

$$\left(\frac{\partial u}{\partial T}\right)_v = \frac{i}{2}k_B \qquad (21)$$

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2} \qquad (22)$$

Integrating Eq (21) and (22) we get the molecular energy:

$$u = \frac{i}{2}k_B T - \frac{a}{v} \qquad (23)$$

The contribution term $(i/2)k_BT$ represents the kinetic energy and $-a/v$ is the potential energy associated with the long-range attraction between molecules.

Application: Thermal Expansion and Isothermal Compressibility (Callen problem 3.9.3)

To calculate the thermal expansion we need only the equation of state: $T = (p + a/v^2)(v-b)/k_B$

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{v\left(\frac{\partial T}{\partial v}\right)_p} = \frac{k_B}{v\left[-\frac{2a}{v^3}(v-b)+p+\frac{a}{v^2}\right]} = \frac{k_B}{pv+\frac{a}{v^2}(-v+2b)} \qquad (24)$$

For the isothermal compressibility, we start with the equation of state: $p = k_BT/(v-b) - a/v^2$

$$k_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{-1}{v\left(\frac{\partial p}{\partial v}\right)_T} = \frac{-1}{v\left[\frac{-k_BT}{(v-b)^2}+\frac{2a}{v^3}\right]} = \frac{1}{\left(p+\frac{a}{v^2}\right)\frac{v}{v-b}-\frac{2a}{v^2}} == \frac{v-b}{pv+\frac{a}{v^2}(-v+2b)} \qquad (25)$$

Note that for $a = b = 0$, $\alpha = 1/T$ and $k_T = 1/p$, which are the ideal gas thermal expansion and isothermal compressibility.

Readings

Callen Ch. 3, Sec 4, 5;
Problem Sets 4, 5

# Lecture Notes 6

## 1. The Stirling Engine

The Stirling engine is an external combustion engine. It is also called the hot air engine. In the 19th century it was used to run printing engines. It is also used to generate power from solar energy and in submarines because they are quiet. It was invented and patented in 1860 by Reverend Dr. Robert Stirling.

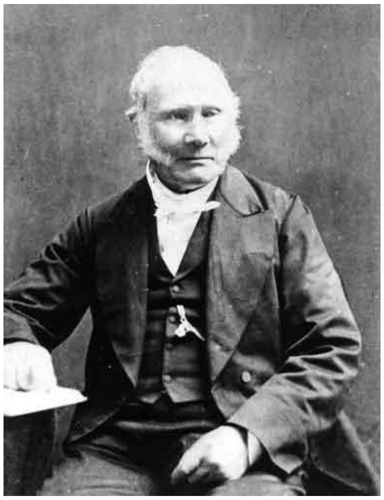


*Figure 1: Robert Stirling (1790 – 1878) was a Scottish clergyman and engineer.*

The four steps of the cycle are: 1 to 2 isothermal (at temperature $T_L$) compression; 2 to 3 isochoric (at volume $v_2$) heating; 3 to 4 isothermal (at temperature $T_H$) expansion when the gas absorbs heat from an external source; 4 to 1 isochoric (at volume $v_1$) cooling.

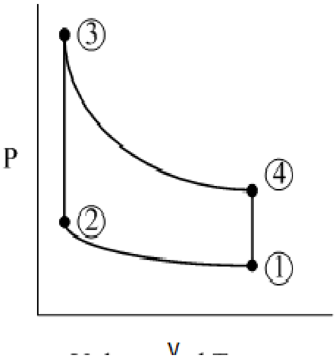


*Figure 2: Stirling cycle*

We will assume that the working fluid is an ideal van der Waals fluid (see Lecture Notes 5) characterized by:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}, \tag{1}$$

$$u = \frac{i}{2}RT - \frac{a}{v} \tag{2}$$

where u is molar energy and v is molar volume. We next calculate the work done on the gas and the heat added to the gas for each step.

1 to 2. Isotherm T = $T_L$

$$W_{12} = -N\int_{v_1}^{v_2} pdv = -NRT_L \ln\left(\frac{v_2-b}{v_1-b}\right) - Na\left(\frac{1}{v_2} - \frac{1}{v_1}\right) \tag{3}$$

$$\Delta U_{12} = -Na\left(\frac{1}{v_2} - \frac{1}{v_1}\right) \tag{4}$$

We get the heat by using the 1st Law:

$$Q_{12} = \Delta U_{12} - W_{12} = NRT_L \ln\left(\frac{v_2-b}{v_1-b}\right) \tag{5}$$

2 to 3. Isochore v = $v_2$

$$W_{23} = 0 \tag{6}$$

$$\Delta U_{23} = N\frac{i}{2}R(T_H - T_L) \tag{7}$$

We get the heat by using the 1st Law:

$$Q_{23} = \Delta U_{23} - W_{23} = N\frac{i}{2}R(T_H - T_L) \tag{8}$$

3 to 4. Isotherm T = $T_H$. This is the gas heating step.

$$W_{34} = -N\int_{v_2}^{v_1} pdv = -NRT_H \ln\left(\frac{v_1-b}{v_2-b}\right) - Na\left(\frac{1}{v_1} - \frac{1}{v_2}\right) \tag{9}$$

$$\Delta U_{34} = -Na\left(\frac{1}{v_1} - \frac{1}{v_2}\right) \tag{10}$$

We get the heat by using the 1st Law:

$$Q_{34} = \Delta U_{34} - W_{34} = NRT_H \ln\left(\frac{v_1-b}{v_2-b}\right) \tag{11}$$

4 to 1. Isochore v = $v_1$

$$W_{41} = 0 \tag{12}$$

$$\Delta U_{41} = N\frac{i}{2}R(T_L - T_H) \tag{13}$$

We get the heat by using the 1st Law:

$$Q_{41} = \Delta U_{41} - W_{41} = N\frac{i}{2}R(T_L - T_H) \tag{14}$$

The total work done on the gas is: $W_{tot} = W_{12} + W_{23} + W_{34} + W_{41}$. We find by using equations: (3), (6), (9), (12):

$$W_{tot} = -NRT_L \ln\left(\frac{v_2 - b}{v_1 - b}\right) - NRT_H \ln\left(\frac{v_1 - b}{v_2 - b}\right)$$

Hence the total work done by the gas is:

$$-W_{tot} = NR(T_H - T_L) \ln\left(\frac{v_1 - b}{v_2 - b}\right) \qquad (15)$$

The efficiency e of the engine is the ratio of the output work $-W_{tot}$ to the input heat $Q_{34}$. Using equations (11) and (15) we find:

$$e = \frac{-W_{tot}}{Q_{34}} = \frac{T_H - T_L}{T_H} \qquad (16)$$

In coming lectures we will discuss the second law of thermodynamics which determines the maximum efficiency of a heat engine, the Carnot cycle efficiency. It so happens that it is equal to the efficiency given above in Eq. (16).

Readings

Callen Ch. 3, Sec. 5;
HRW Ch. 20;
Problem Sets 4, 5, 6.