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

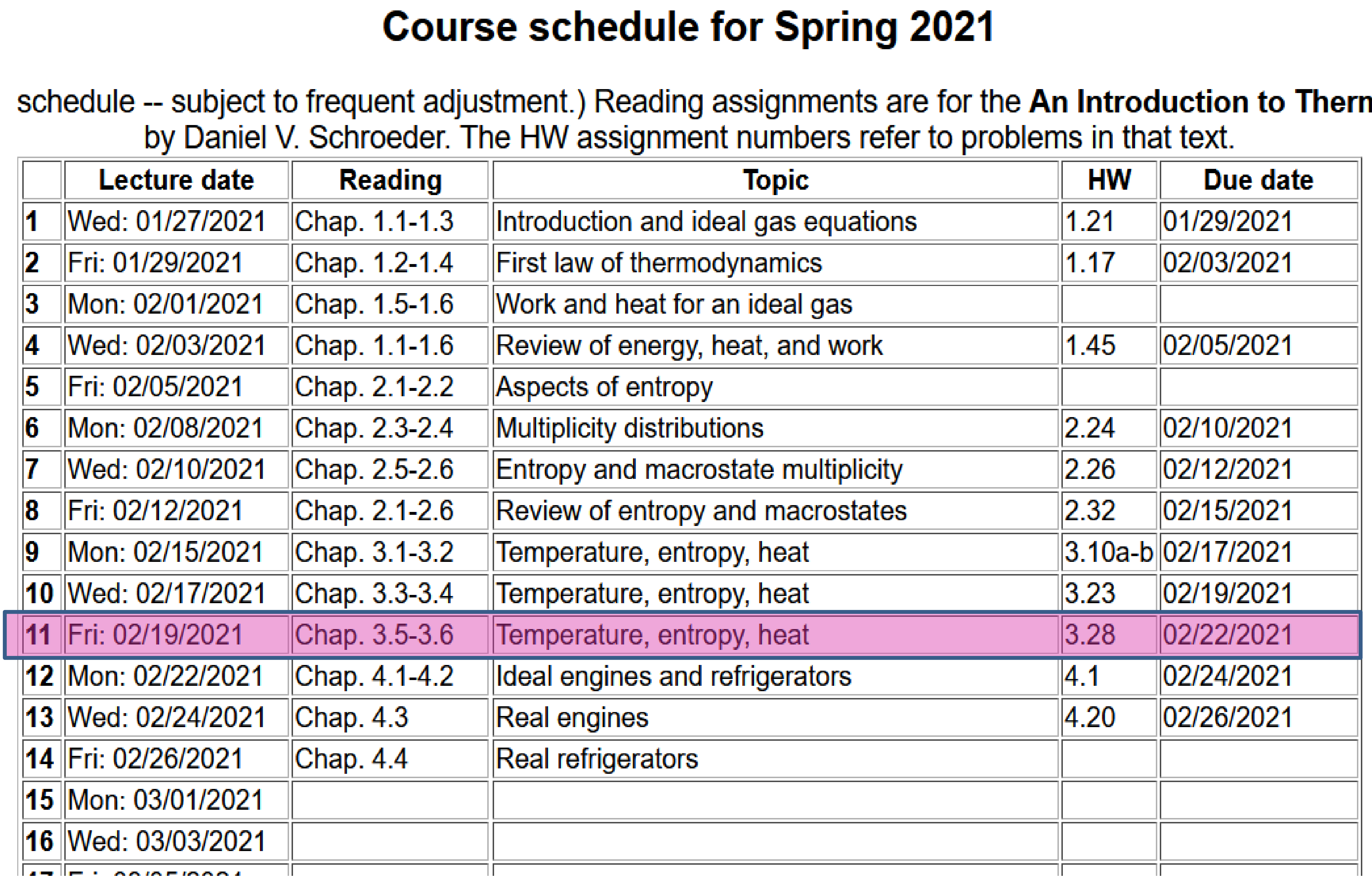
Record!!!

## Discussion for Lecture 11:

### Variations in the number of particles
### Begin discussion of heat engines

**Reading: Chapters 3.5-3.6; 4.1**

1. **Dependence of thermodynamic functions on the number of particle**
2. **Notions of chemical potential**
3. **Cyclic thermodynamic processes; engines**



## Course schedule for Spring 2021

schedule -- subject to frequent adjustment.) Reading assignments are for the **An Introduction to Therm**
by Daniel V. Schroeder. The HW assignment numbers refer to problems in that text.

| | Lecture date | Reading | Topic | HW | Due date |
|---|---|---|---|---|---|
| **1** | Wed: 01/27/2021 | Chap. 1.1-1.3 | Introduction and ideal gas equations | 1.21 | 01/29/2021 |
| **2** | Fri: 01/29/2021 | Chap. 1.2-1.4 | First law of thermodynamics | 1.17 | 02/03/2021 |
| **3** | Mon: 02/01/2021 | Chap. 1.5-1.6 | Work and heat for an ideal gas | | |
| **4** | Wed: 02/03/2021 | Chap. 1.1-1.6 | Review of energy, heat, and work | 1.45 | 02/05/2021 |
| **5** | Fri: 02/05/2021 | Chap. 2.1-2.2 | Aspects of entropy | | |
| **6** | Mon: 02/08/2021 | Chap. 2.3-2.4 | Multiplicity distributions | 2.24 | 02/10/2021 |
| **7** | Wed: 02/10/2021 | Chap. 2.5-2.6 | Entropy and macrostate multiplicity | 2.26 | 02/12/2021 |
| **8** | Fri: 02/12/2021 | Chap. 2.1-2.6 | Review of entropy and macrostates | 2.32 | 02/15/2021 |
| **9** | Mon: 02/15/2021 | Chap. 3.1-3.2 | Temperature, entropy, heat | 3.10a-b | 02/17/2021 |
| **10** | Wed: 02/17/2021 | Chap. 3.3-3.4 | Temperature, entropy, heat | 3.23 | 02/19/2021 |
| **11** | Fri: 02/19/2021 | Chap. 3.5-3.6 | Temperature, entropy, heat | 3.28 | 02/22/2021 |
| **12** | Mon: 02/22/2021 | Chap. 4.1-4.2 | Ideal engines and refrigerators | 4.1 | 02/24/2021 |
| **13** | Wed: 02/24/2021 | Chap. 4.3 | Real engines | 4.20 | 02/26/2021 |
| **14** | Fri: 02/26/2021 | Chap. 4.4 | Real refrigerators | | |
| **15** | Mon: 03/01/2021 | | | | |
| **16** | Wed: 03/03/2021 | | | | |

# Your questions –

From Parker -- what physically is chemical potential, like what does it mean and physically correspond to?

From Kristen -- 1. Could you explain why the total entropy is a maximum at equilibrium? I find this counterintuitive. 2. How can we just add another term into the entropy equation as in formula 3.57? 3. What does diffusive equilibrium actually mean?

From Rich -- Could we discussion equation 3.60 more in class? Since entropy is not in the equation, how could the energy increase from adding the molecules without entropy increasing?

From Chao -- In the real Industry, is this formula still wo need to consider other factors in the industrial production?

$$\mu_{\text{chemistry}} \equiv -T\left(\frac{\partial S}{\partial n}\right)_{U,V},$$

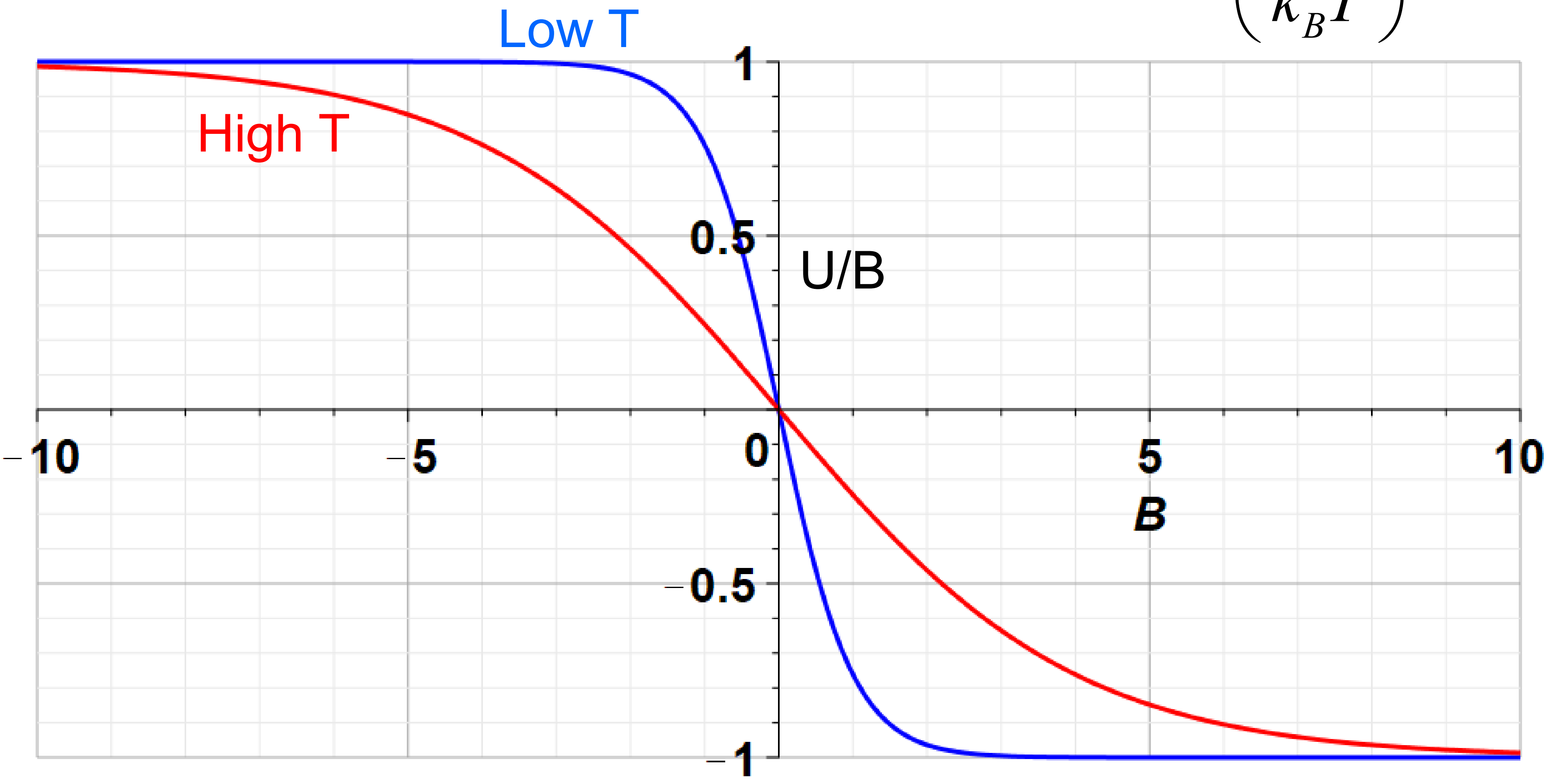
From Annelise -- What is diffusive equilibrium? I am a little confused about what is being exchanged and what is being held fixed?

From Zezhong -- I wonder if there is a definition by word description on chemical potential instead of mathematical formula?

# Correction from Wednesday's lecture --

Plot of (U/B) vs B at fixed T

$$U = -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right)$$



# Variables of thermodynamics

- Temperature – $T \geq 0$ in Kelvin scale
- Volume – V in units of $m^3$
- Pressure – P in units of Pascals (Newtons/$m^2$)
- Entropy – S in units of Joules/K
- Mass – M in units of kg
- Number of particles – N
- Chemical potential – $\mu$ in units of Joules

Recall for the mono atomic ideal gas:

$$PV = Nk_BT$$

$$U = \frac{3}{2}Nk_BT$$

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

Previously we have shown that

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{N,U} = \frac{P}{T}$$

What happens when the number of particles N changes?

$$PV = Nk_BT$$

$$U = \frac{3}{2}Nk_BT$$

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

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = k_B\ln\left(\frac{V}{N}\left(\frac{4\pi MU}{3Nh^2}\right)^{3/2}\right)$$

$$\equiv -\frac{\mu}{T}$$

μ was introduced by Gibbs as the “chemical potential”

# Summary of results for mono atomic ideal gas --

$$PV = Nk_BT \qquad\qquad U = \frac{3}{2}Nk_BT$$

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

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = k_B\ln\left(\frac{V}{N}\left(\frac{4\pi MU}{3Nh^2}\right)^{3/2}\right) \equiv -\frac{\mu}{T}$$

$$\mu = -k_BT\ln\left(\frac{V}{N}\left(\frac{4\pi MU}{3Nh^2}\right)^{3/2}\right) = -k_BT\ln\left(\frac{V}{N}\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\right)$$

Summary --

$$PV = Nk_BT$$

$$U = \frac{3}{2}Nk_BT$$

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

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V}dU + \left(\frac{\partial S}{\partial V}\right)_{N,U}dV + \left(\frac{\partial S}{\partial N}\right)_{U,V}dN$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

# Expressing result in term of the internal energy

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

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

Generalization of first law of thermo

heat

mechanical work

chemical work

Are these equations consistent with each other?

Are they useful?

# Are these equation internally consistent?

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

Suppose $U$ and $V$ are constant; $dU = 0$ and $dV = 0$

$$\Rightarrow 0 = TdS - 0 + \mu dN$$

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

Suppose $S$ and $V$ are constant; $dS = 0$ and $dV = 0$

$$\Rightarrow dU = 0 - 0 + \mu dN$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Note that we will see other relationships with μ that may be more convenient or physical, namely perhaps at constant T and P.

# How might this be useful?

Imagine a chemical reaction

$$\mathrm{H_2O} \rightarrow \mathrm{H_2} + \frac{1}{2}\mathrm{O_2}$$

Associated chemical potentials

$$\mu_{H_2O} \qquad \mu_{H_2} \qquad \mu_{O_2}$$

Generalized relation at constant $S$ and $V$:

$$dU = \sum_i \mu_i dN_i \quad \rightarrow \mu_{H_2} dN_{H_2} + \mu_{O_2} dN_{O_2} + \mu_{H_2O} dN_{H_2O}$$

In practice G (Gibbs free energy) is often more useful than U (internal energy) for analyzing this situation.

Comment – One practical consideration of allowing N to vary, is that we need to relax our focus on “isolated” systems, and to think about particles diffusing --

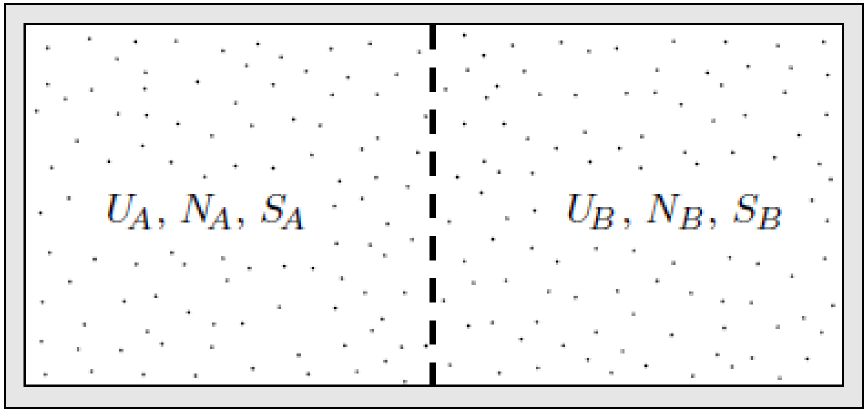


**Figure 3.18.** Two systems that can exchange both energy and particles. Copyright ©2000, Addison-Wesley.

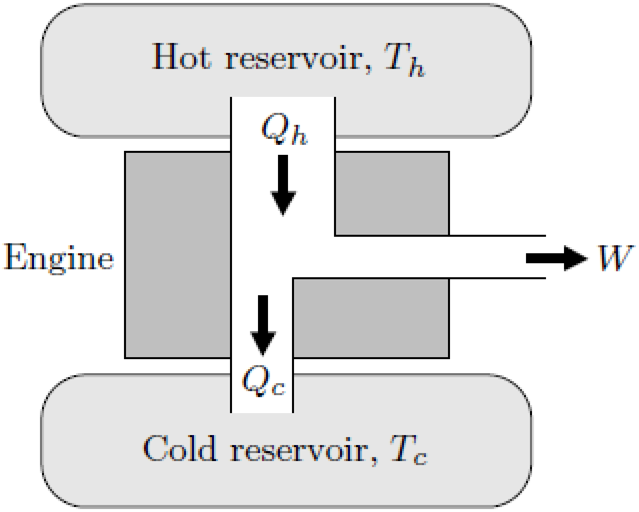
At equilibrium:

$$\left(\frac{\partial S}{\partial N_A}\right)_{U_A,V_A} = \left(\frac{\partial S}{\partial N_B}\right)_{U_B,V_B}$$

$$\mu_A = \mu_B$$

# Introduction to the thermo(statics) of heat engines

Figure 4.1. Energy-flow diagram for a heat engine. Energy enters as heat from the hot reservoir, and leaves both as work and as waste heat expelled to the cold reservoir. Copyright ©2000, Addison-Wesley.



In the engine, the desirable output is the net work while the necessary input is the heat input

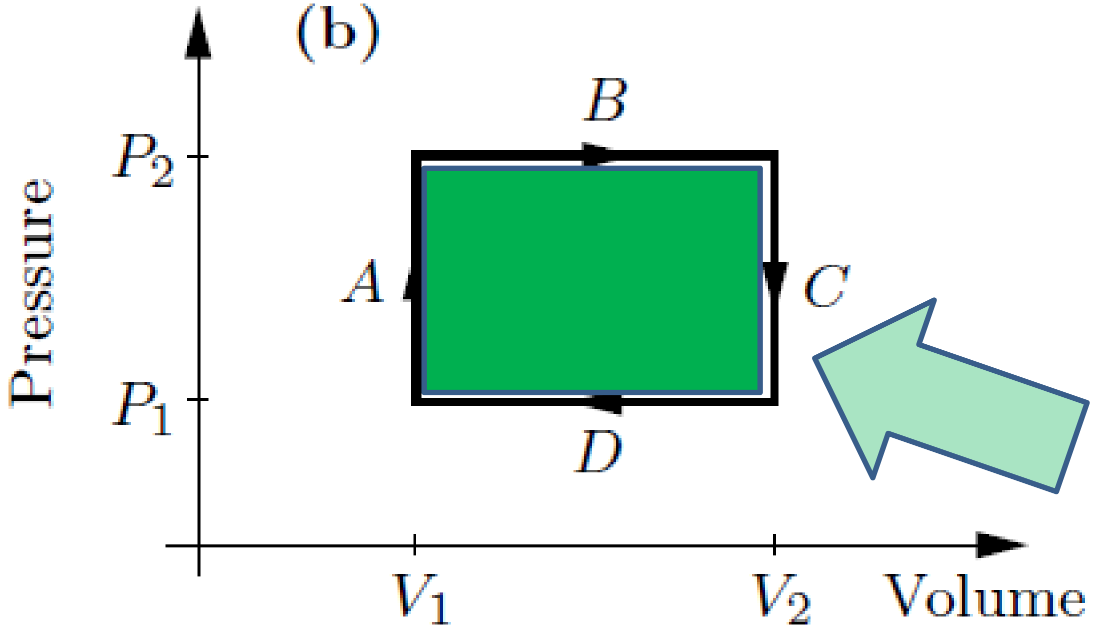
Engine efficiency

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

Note that the net work of interest is the work done **by the system**.

# Net work done in a cyclic process

Consider the following 4 step cycle



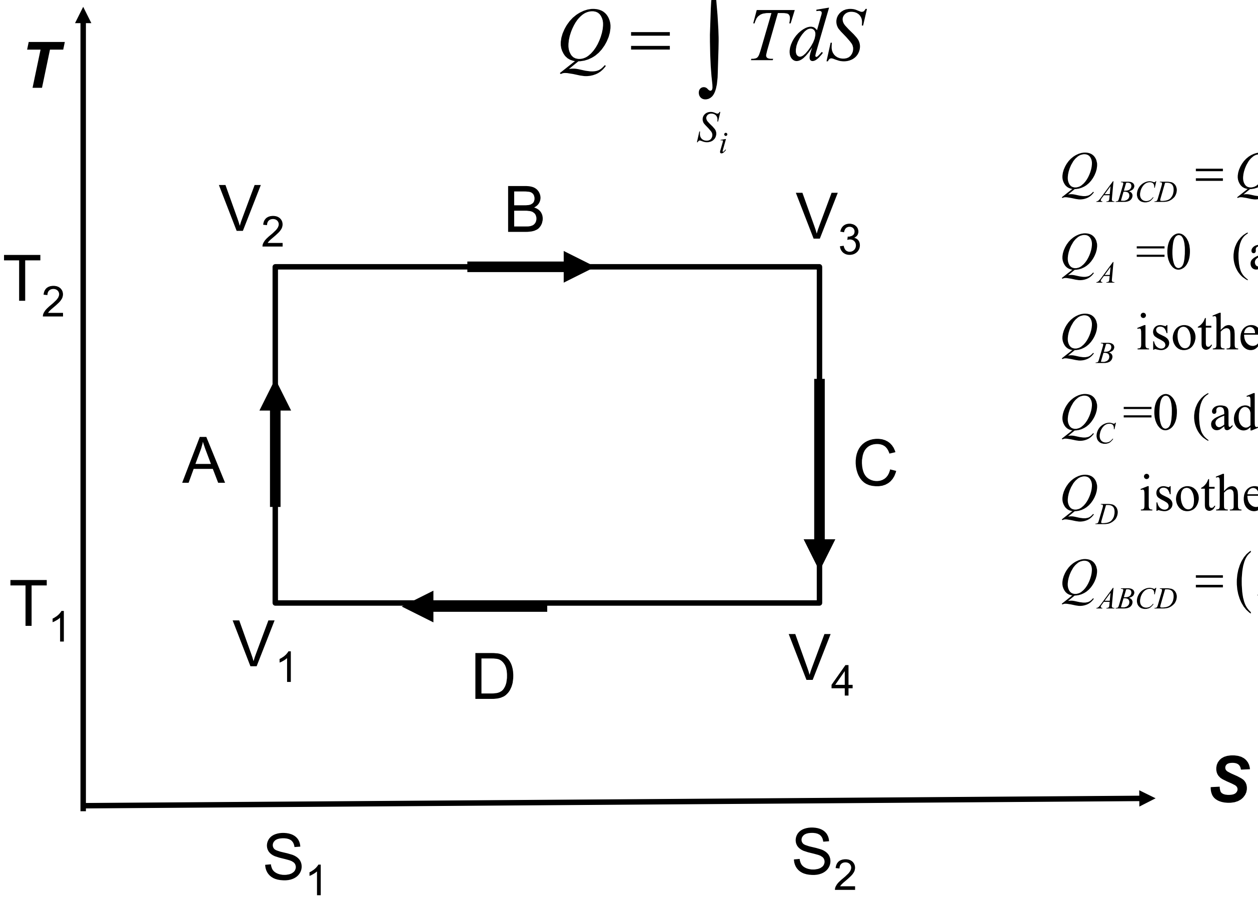
**A** ➔ no work
**B** ➔ **negative work**
**C** ➔ **no work**
**D** ➔ **positive work**

**net work**

$$W_{ABCD} = -(P_2 - P_1)(V_2 - V_1)$$

Carnot invented a very efficient ideal cycle which Clausius further analyzed as “entropy” *S* which is related to heat according to

$$Q = \int_{S_i}^{S_f} T dS$$



$$Q_{ABCD} = Q_A + Q_B + Q_C + Q_D$$

$Q_A$ =0 (adiabatic at $S_1$)

$Q_B$ isothermal at $T_2$

$Q_C$=0 (adiabatic at $S_2$)

$Q_D$ isothermal at $T_1$

$$Q_{ABCD} = (S_2 - S_1)(T_2 - T_1)$$

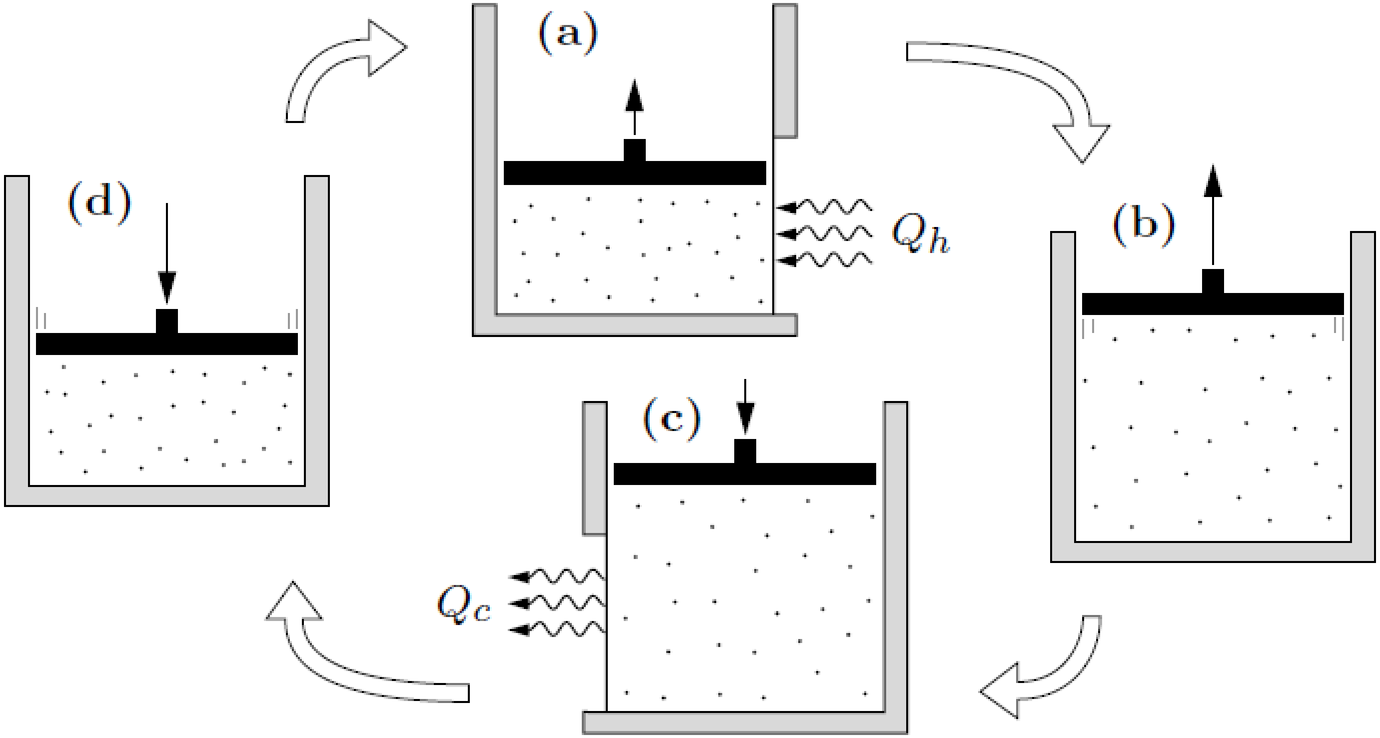


**Figure 4.2.** The four steps of a Carnot cycle: (a) isothermal expansion at $T_h$ while absorbing heat; (b) adiabatic expansion to $T_c$; (c) isothermal compression at $T_c$ while expelling heat; and (d) adiabatic compression back to $T_h$. The system must be put in thermal contact with the hot reservoir during step (a) and with the cold reservoir during step (c). Copyright ©2000, Addison-Wesley.

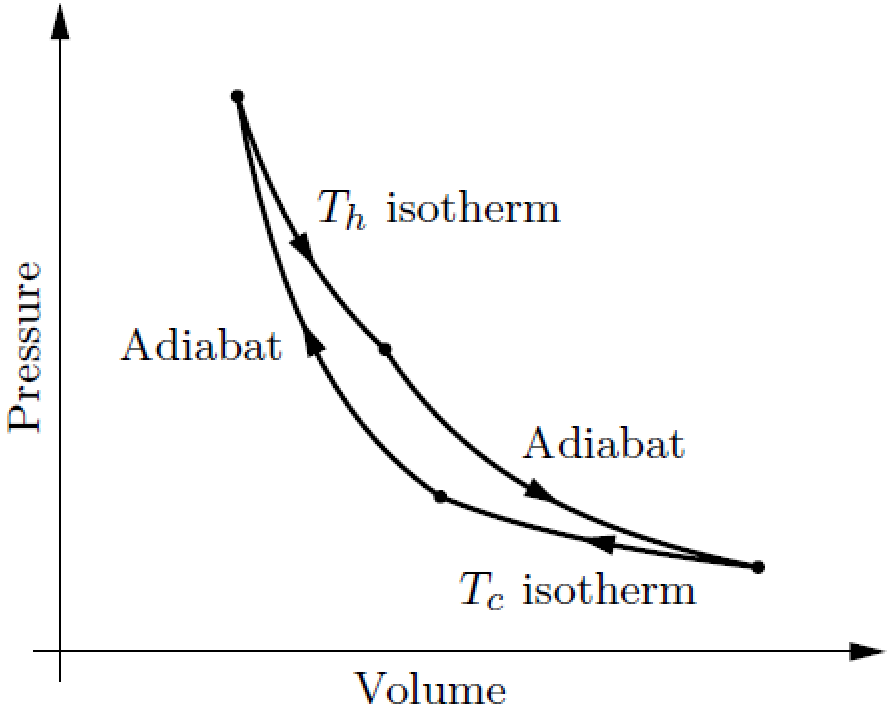
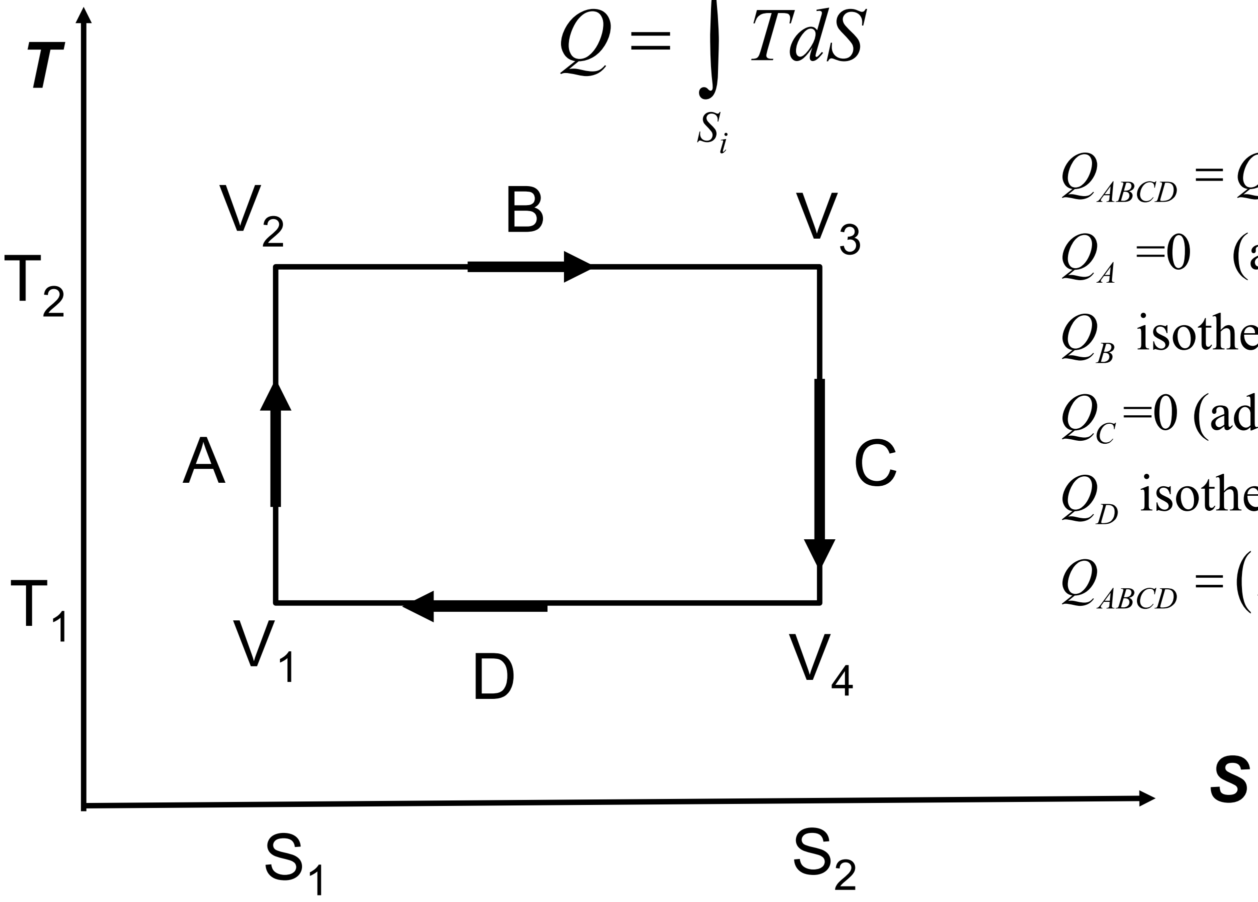


**Figure 4.3.** $PV$ diagram for an ideal monatomic gas undergoing a Carnot cycle. Copyright ©2000, Addison-Wesley.

Some details from Lecture 5 --

Carnot invented a very efficient ideal cycle which Clausius further analyzed as "entropy" *S* which is related to heat according to

$$Q = \int_{S_i}^{S_f} T dS$$



$$Q_{ABCD} = Q_A + Q_B + Q_C + Q_D$$

$$Q_A = 0 \quad \text{(adiabatic at } S_1\text{)}$$

$$Q_B \text{ isothermal at } T_2$$

$$Q_C = 0 \text{ (adiabatic at } S_2\text{)}$$

$$Q_D \text{ isothermal at } T_1$$

$$Q_{ABCD} = \left(S_2 - S_1\right)\left(T_2 - T_1\right)$$

## Some details

Ideal gas equation of state $PV = Nk_BT$

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

First law of thermodynamics

$$\Delta U = Q + W$$

For isothermal process $\Delta U = 0$ and $Q = -W$

$$Q_B = Nk_BT_2 \ln\left(\frac{V_3}{V_2}\right) \qquad Q_D = Nk_BT_1 \ln\left(\frac{V_1}{V_4}\right)$$

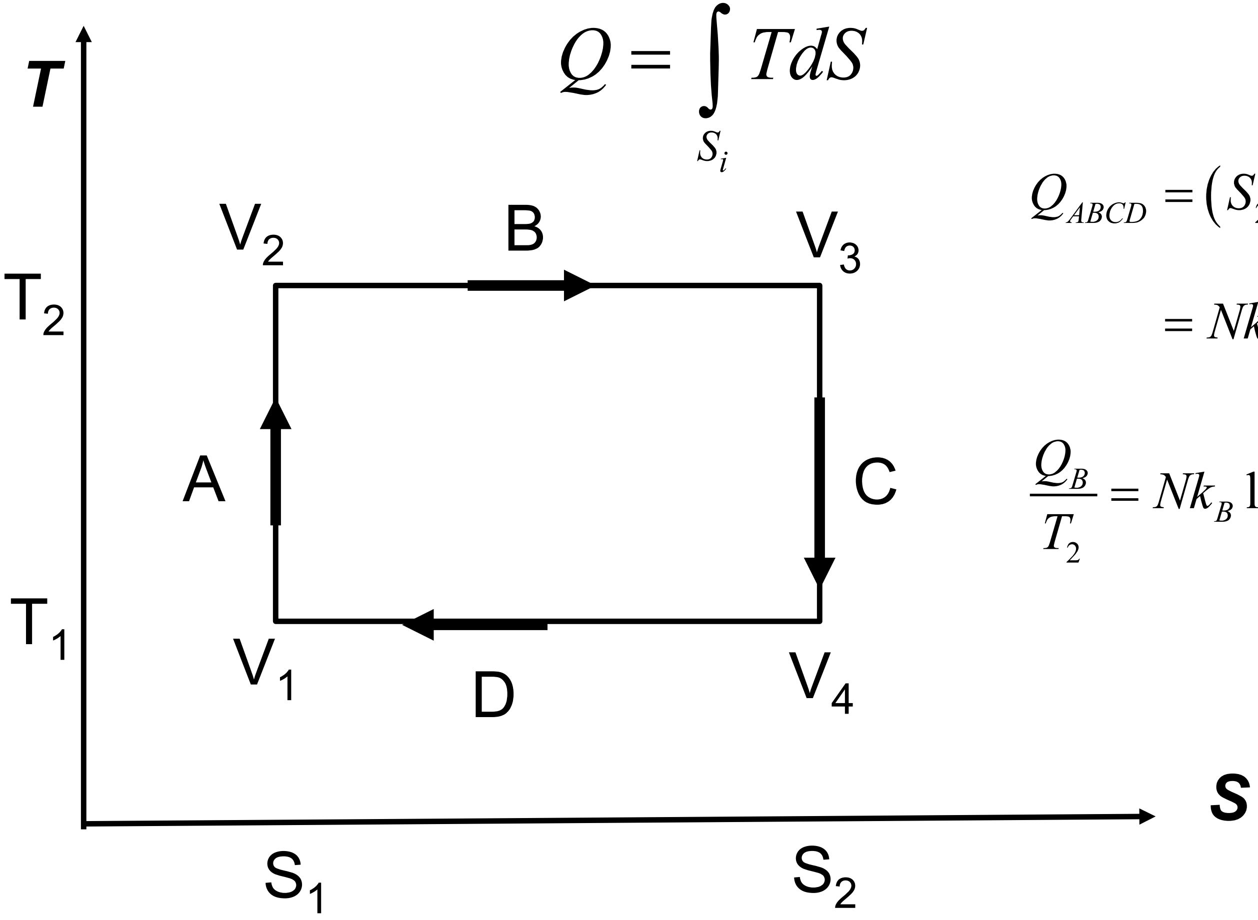
Also note that because of adiabatic ideal gas equations --

$$V_1T_1^{1/(\gamma-1)} = V_2T_2^{1/(\gamma-1)} \quad \text{and} \qquad V_3T_2^{1/(\gamma-1)} = V_4T_1^{1/(\gamma-1)}$$

$$\Rightarrow \frac{V_3}{V_2} = \frac{V_4}{V_1} \qquad \Rightarrow Q_{ABCD} = Nk_B \ln\left(\frac{V_3}{V_2}\right)\left(T_2 - T_1\right)$$

# Summary of results

$$Q = \int_{S_i}^{S_f} T dS$$

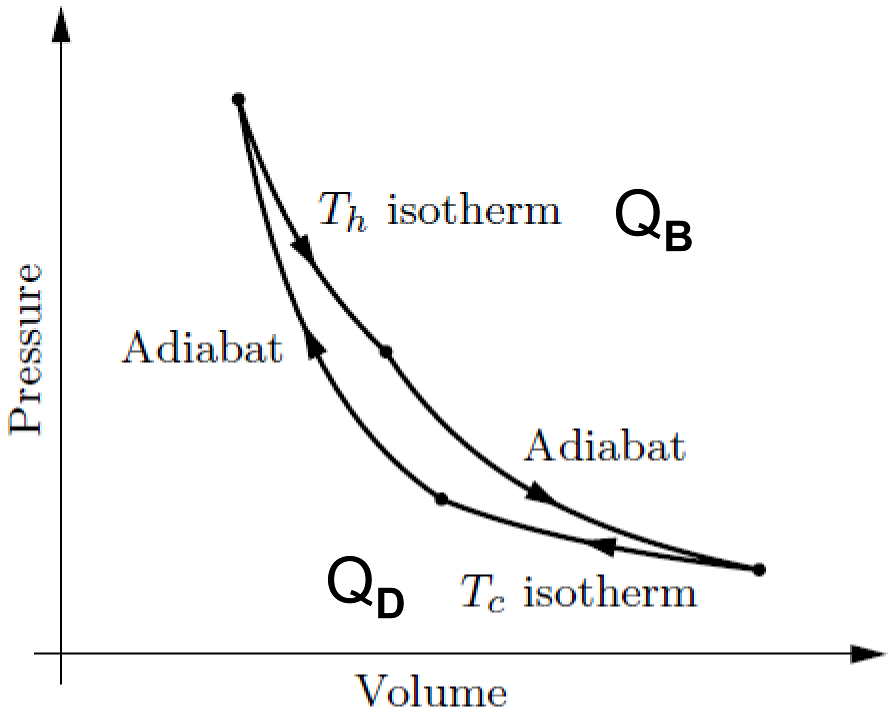


$$Q_{ABCD} = (S_2 - S_1)(T_2 - T_1)$$

$$= Nk_B \ln\left(\frac{V_3}{V_2}\right) \; (T_2 - T_1)$$

$$\frac{Q_B}{T_2} = Nk_B \ln\left(\frac{V_3}{V_2}\right) = -\frac{Q_D}{T_1}$$

# Engine efficiency



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

$$= \frac{Q_D + Q_B}{Q_B}$$

For the Carnot cycle -- $Q_D = -Q_B \frac{T_C}{T_H}$

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