PHY 341/641 Thermodynamics and Statistical Mechanics

MWF: Online at 12 PM & FTF at 2 PM

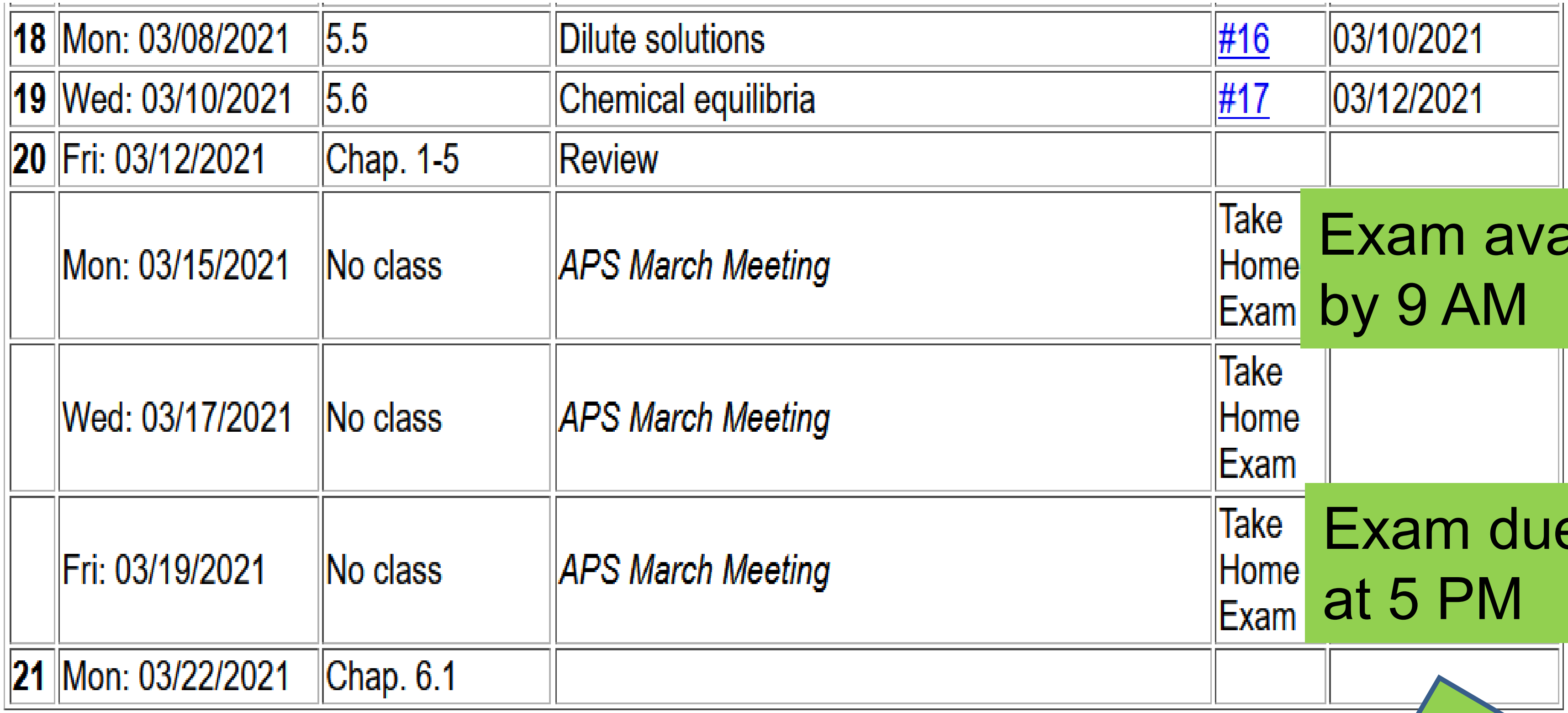
Record!!!

Discussion for Lecture 20:

Review of Chapters 1-5

1. Comment on schedule and exam
2. Your questions
3. Some review

Schedule --



18	Mon: 03/08/2021	5.5	Dilute solutions	[#16](#)	03/10/2021
19	Wed: 03/10/2021	5.6	Chemical equilibria	[#17](#)	03/12/2021
20	Fri: 03/12/2021	Chap. 1-5	Review		
	Mon: 03/15/2021	No class	*APS March Meeting*	Take Home Exam	
	Wed: 03/17/2021	No class	*APS March Meeting*	Take Home Exam	
	Fri: 03/19/2021	No class	*APS March Meeting*	Take Home Exam	
21	Mon: 03/22/2021	Chap. 6.1			

Exam available by 9 AM

Exam due at 5 PM

Note that mid term grades are due at 12 noon on Monday, March 22, 2021

“Due” means receiving your exam submission electronically by that time. If you prefer paper submission, please slide the exam under my office door and let me know that you have done so.

Comments about exam –

According to the honor code, your exam submission must be your own work. In completing this take-home exam, you may consult your textbook, and other course materials, particularly those posted on the class webpage. You may consult other texts (within reason) as long as these are acknowledged and documented. Should questions arise about the exam, please email natalie@wfu.edu **but no one else**.

Exams will be graded on the basis of correct reasoning as well as correct answers. It is expected that you will use Maple, Mathematica, or Wolfram and these should be included in your exam submission.

Your questions –

From Rich -- I tried using k*T on the homework, but I could not get the right answer without using R*T. Why is this the case? -Does the constant of reactivity still work when comparing across different measurements, like pressure and molality?

From Annie -- For tomorrow's review can we do some example problems? I have a difficult time applying all the formulas we derive- like any problems showing us how to do stuff with H,S,G, Cp,Cv,U,V,F,n. For the most part I understand where these equations come from, but I just don't know what to do with them.
Also, is the exam going to be derivation oriented or more problem solving? Because if it is derivations, please disregard the suggestion I made above, and instead possibly review how the variables relate to each other when certain elements are fixed and stuff like that.

From Kristen – 1. How to find Cv and Cp, I know we take the derivative of Q but how does f come in? 2. The important takeaways from the sections on phase transformations. 3. The most important key ideas to know about the tendencies of a system and why they happen (ex: the tendency to go to a state of lowest Gibbs free energy).

From – Michael -- 1) Could you please explain how the change in entropy can be negative and how this isn't in violation of the second law of thermodynamics? 2) How does the formula (T = To + (KbTo^2)/L for saltwater not give us a number above freezing if To is 273K, shouldn't (KbTo^2)/L always be positive? 3) Last lecture you mentioned that to estimate nB we need to double 0.6 to 1.2, why is that again?

General comments –

For numerical questions, please make sure that your units are consistent. For example, many of our discussions mention N as the number of particles, but since we are typically talking about 10^{23} particles, it is more convenient to use moles

$$Nk_BT \leftrightarrow nRT$$

Materials properties are often listed per kg or per liter. If we know the mass density of the material, it is possible to convert to consistent units.

Some mathematical tools

Mathematical representation –

Thermodynamics involves a lot of functions and a lot of variables which can be nicely modeled using concepts of multivariable functions. Here we need to use the concept of partial derivatives and total derivatives.

Suppose that we have a function f which has variables q and p and t. In turn, $q = q(t)$ and $p = p(t)$. If we know that $f = f(q, p, t)$, the total differential is given by $df = \left(\frac{\partial f}{\partial q}\right)_{p,t} dq + \left(\frac{\partial f}{\partial p}\right)_{q,t} dp + \left(\frac{\partial f}{\partial t}\right)_{q,p} dt$

For example, the total derivative with respect to time is

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial q}\right)_{p,t} \frac{dq}{dt} + \left(\frac{\partial f}{\partial p}\right)_{q,t} \frac{dp}{dt} + \left(\frac{\partial f}{\partial t}\right)_{q,p}$$

Notion of partial derivatives continued --

Example

$f(q,p,t) = qp^2t^3$ where $q(t) = e^{-t}$ $p(t) = e^{-2t}$

Evaluate $\frac{df}{dt}$ in two ways, using partial derivatives and after direct substitution. Do you get the same answer?

Notion of the Legendre transformation

General notions of mathematical transformations for continuous functions of several variables and Legendre transforms --

Consider: $z(x,y) \Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

Let $u \equiv \left(\frac{\partial z}{\partial x}\right)_y$ and $v \equiv \left(\frac{\partial z}{\partial y}\right)_x$ $\quad dz = udx + vdy$

Define new function

$$w(u,y) \Rightarrow dw = \left(\frac{\partial w}{\partial u}\right)_y du + \left(\frac{\partial w}{\partial y}\right)_u dy$$

For $w = z - ux,$ $\quad dw = dz - udx - xdu = udx + vdy - udx - xdu$

$$dw = -xdu + vdy$$

$$\Rightarrow \left(\frac{\partial w}{\partial u}\right)_y = -x \qquad \left(\frac{\partial w}{\partial y}\right)_u = \left(\frac{\partial z}{\partial y}\right)_x = v$$

Desired thermodynamic functions --

Internal energy $U = U(S,V,N)$ $dU = TdS - PdV + \mu dN$

Entropy $S = S(U,V,N)$ $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$

Enthalpy $H = H(S,P,N)$

Helmholtz free energy $F = F(T,V,N)$

Gibbs free energy $G = G(T,P,N)$

Using the Legendre transformation method:

$$H(S,P,N) = U + PV \qquad dH = TdS + VdP + \mu dN$$

$$F(T,V,N) = U - ST \qquad dF = -SdT - PdV + \mu dN$$

$$G(T,P,N) = F + PV \qquad dG = -SdT + VdP + \mu dN$$

Summary of thermodynamic functions

Internal energy	$U=U(S,V,N)$	$dU=TdS-PdV+\mu dN$
Entropy	$S=S(U,V,N)$	$dS=\frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dN$
Enthalpy	$H=H(S,P,N)$	$dH=TdS+VdP+\mu dN$
Helmholtz free energy	$F=F(T,V,N)$	$dF=-SdT-PdV+\mu dN$
Gibbs free energy	$G=G(T,P,N)$	$dG=-SdT+VdP+\mu dN$

Various first derivative relationships

Some first derivative relationships --

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

$$S=-\left(\frac{\partial F}{\partial T}\right)_{V,N}=-\left(\frac{\partial G}{\partial T}\right)_{P,N} \qquad V=\left(\frac{\partial H}{\partial P}\right)_{S,N}=\left(\frac{\partial G}{\partial P}\right)_{T,N}$$

$$\mu=\left(\frac{\partial U}{\partial N}\right)_{V,S}=\left(\frac{\partial H}{\partial N}\right)_{P,S}=\left(\frac{\partial F}{\partial N}\right)_{V,T}=\left(\frac{\partial G}{\partial N}\right)_{T,P}$$

Some concepts to remember

First "law" of thermodynamics

$$\Delta U = Q + W$$

Here Q is heat added to system and W is work added to system.

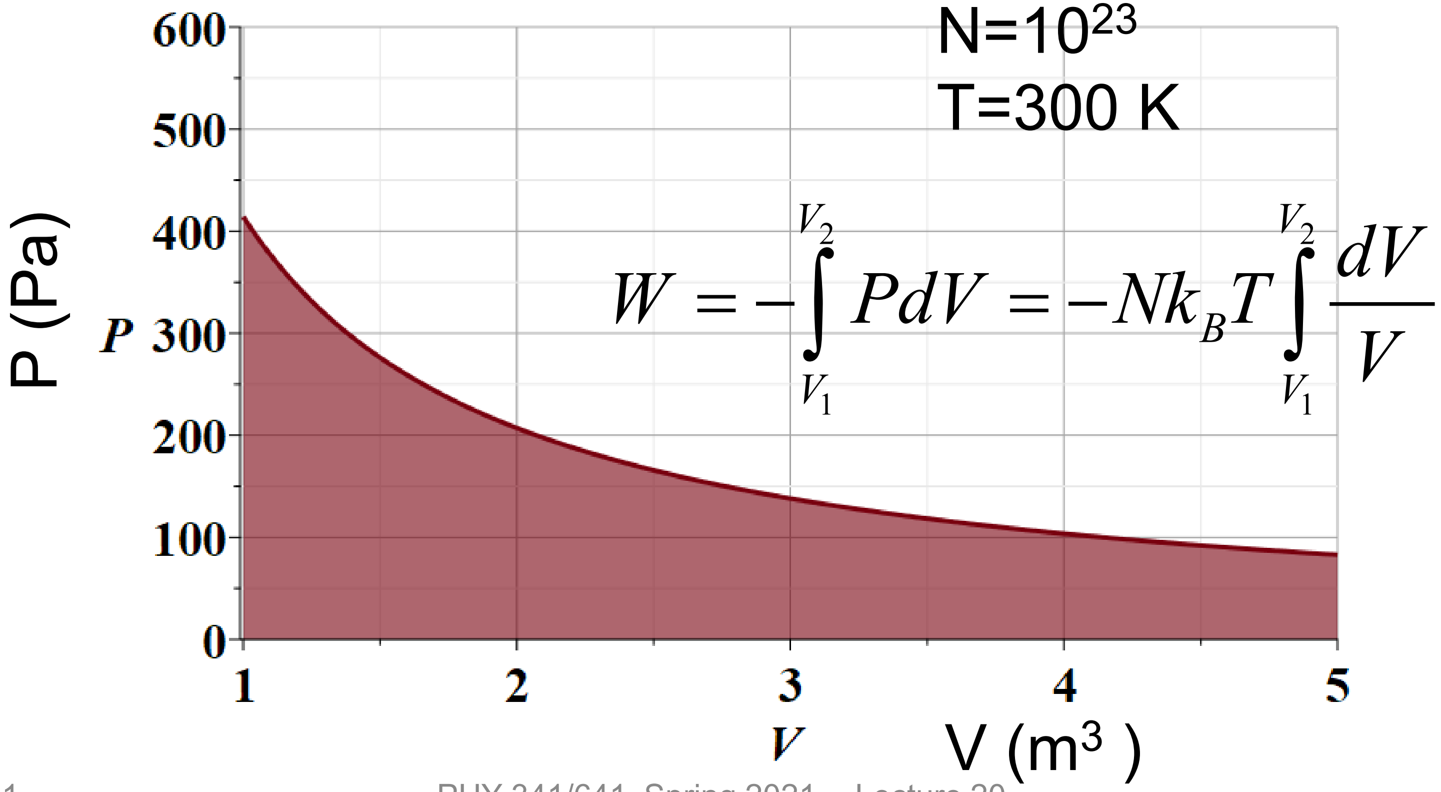
Under quasi static conditions: $Q \rightarrow dQ \rightarrow TdS$
$W \rightarrow dW \rightarrow -PdV$

Work for various processes for an ideal gas

$$W = -P\Delta V \qquad PV = Nk_BT$$

Now consider an isothermal process

In order to evaluate *W*, it is useful to consider a plot of *P* versus *V*



N=10^{23}

T=300 K

$$W = -\int_{V_1}^{V_2} PdV = -Nk_BT\int_{V_1}^{V_2} \frac{dV}{V}$$

Special properties for an ideal gas

General formula for internal energy of an ideal gas

$$U = \frac{f}{2} N k_B T = \frac{1}{\gamma - 1} N k_B T$$

For a mono atomic ideal gas *f*=3 and γ=5/3

Entropy for a mono atomic ideal gas
Sackur-Tetrode equation --

$$S(N,V,U) \approx N k_B \left(\ln\left(\frac{V}{N} \left(\frac{4\pi M U}{3 N h^2} \right)^{3/2} \right) + \frac{5}{2} \right)$$

Some details about entropy on the basis of Boltzmann's analysis

Boltzmann's idea was to use the multiplicity function to calculate the entropy --

$$S = k_B \ln(\Omega(N,V,U))$$

The multiplicity function Ω for a "micro canonical ensemble" counts the number of microstates for which the macroscopic variables (such as N, V, U) are measured.

Measurements of heat

Heat capacity

$$C = \frac{dQ}{dT}$$

Under conditions of constant volume:

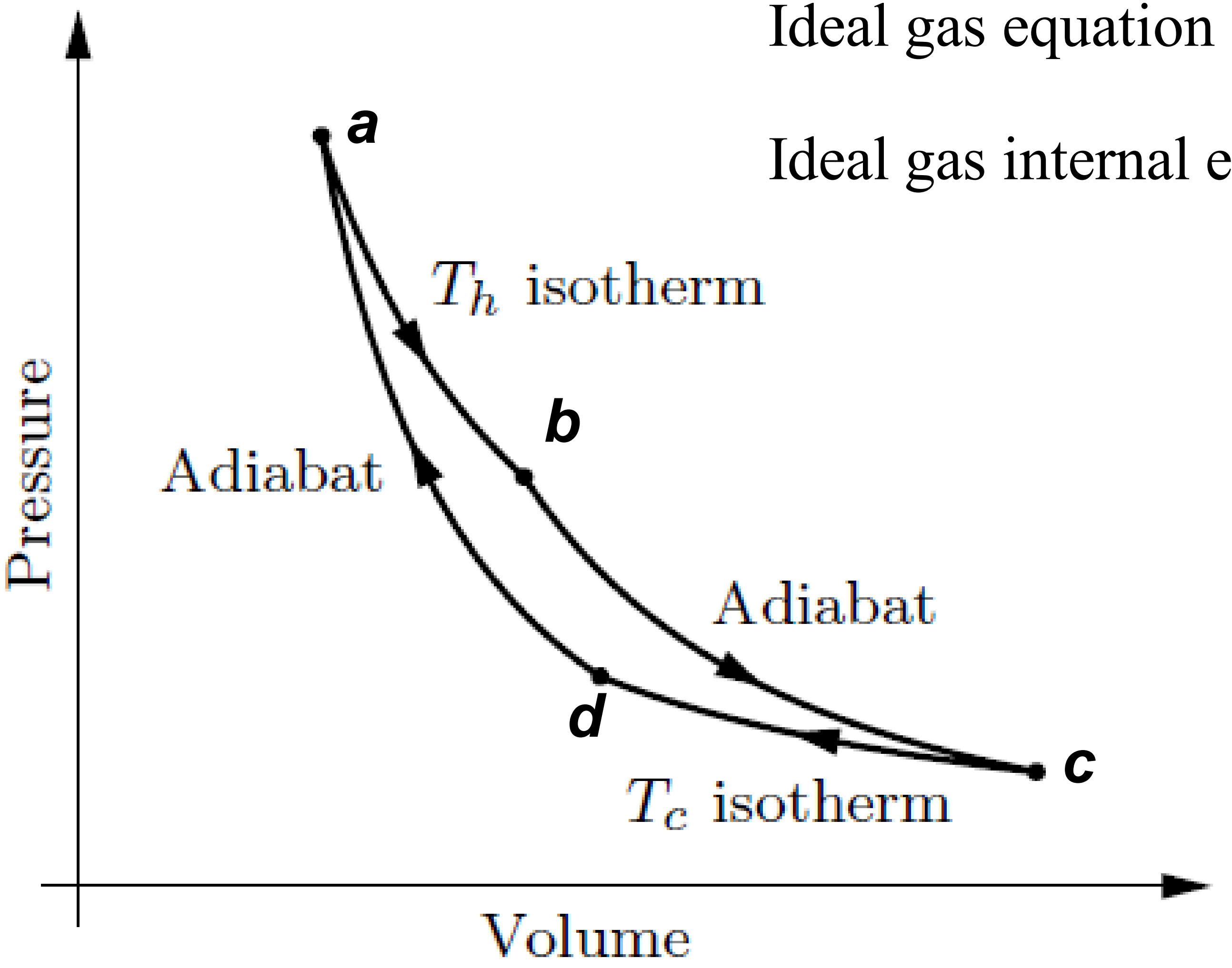
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Under conditions of constant pressure:

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

Note that, generally $C_P > C_V$

Analysis of cyclic processes – Carnot cycle
PV diagram from your textbook



Ideal gas relations:

Ideal gas equation of state $PV = Nk_BT$

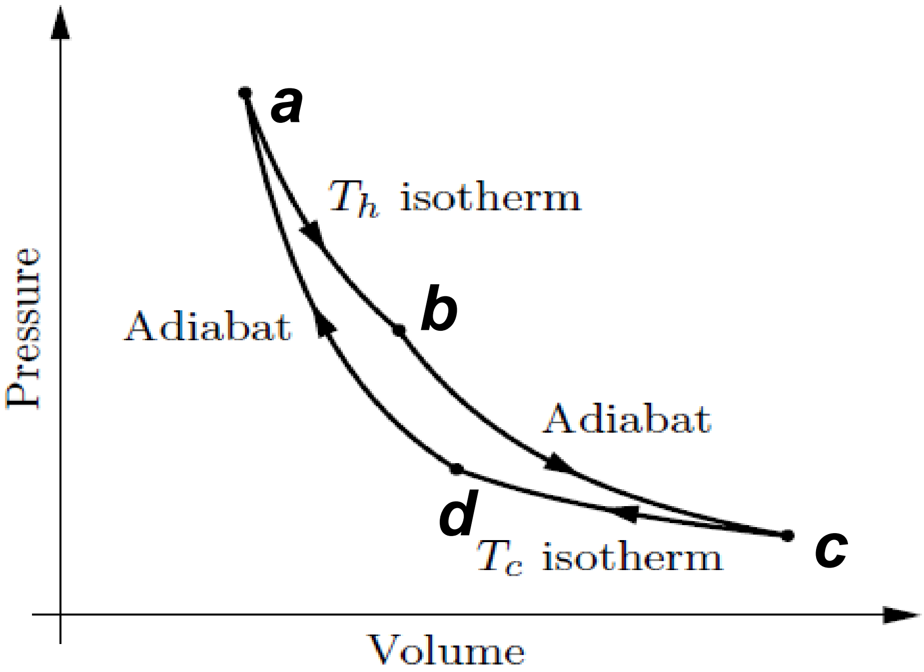
Ideal gas internal energy $U = \frac{Nk_BT}{\gamma - 1}$

Recall that

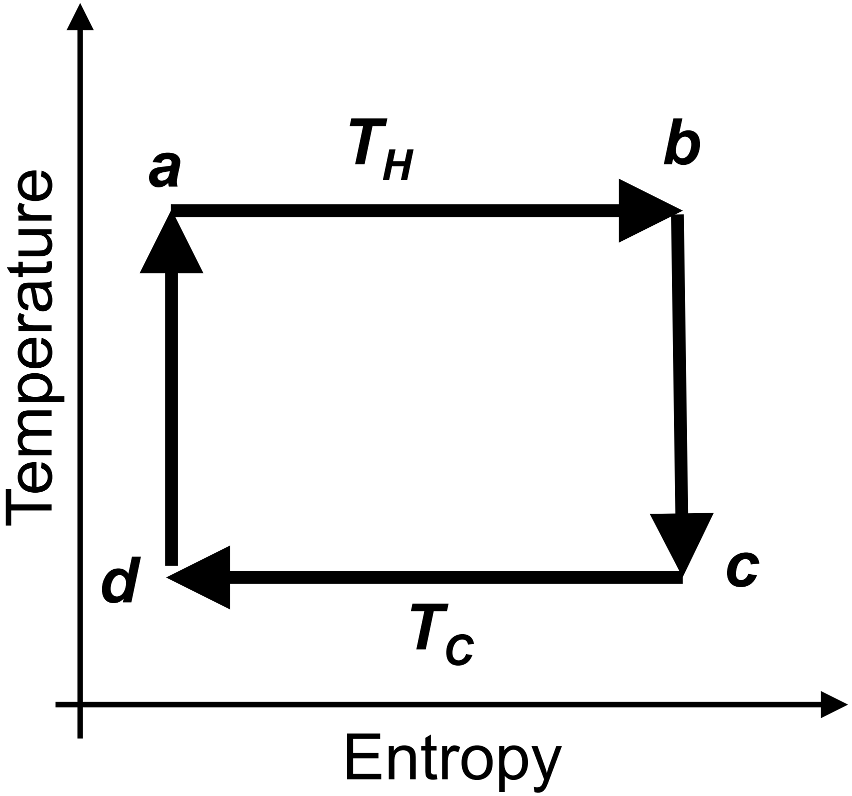
$$\gamma \equiv \frac{C_P}{C_V}$$

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

P versus V diagram



T versus S diagram



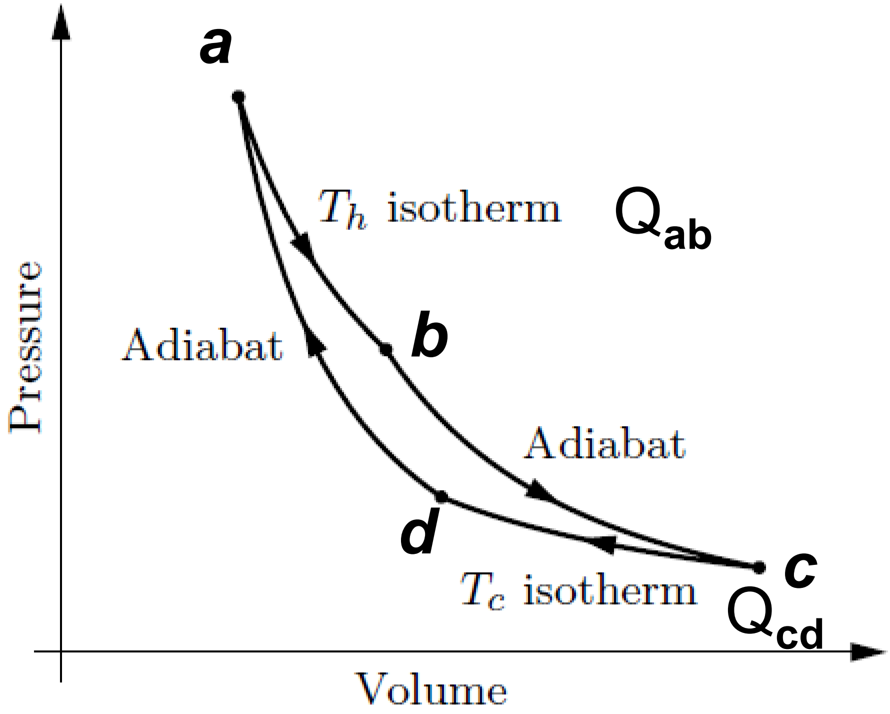
For step a → b: $Q_{ab} = -W_{ab} = Nk_B T_H \ln\left(\frac{V_b}{V_a}\right)$

For step b → c: $Q_{bc} = 0 \quad V_b T_H^{1/(\gamma-1)} = V_c T_C^{1/(\gamma-1)}$

For step c → d: $Q_{cd} = -W_{cd} = Nk_B T_C \ln\left(\frac{V_d}{V_c}\right)$

For step d → a: $Q_{da} = 0 \quad V_d T_C^{1/(\gamma-1)} = V_a T_H^{1/(\gamma-1)}$

Engine efficiency



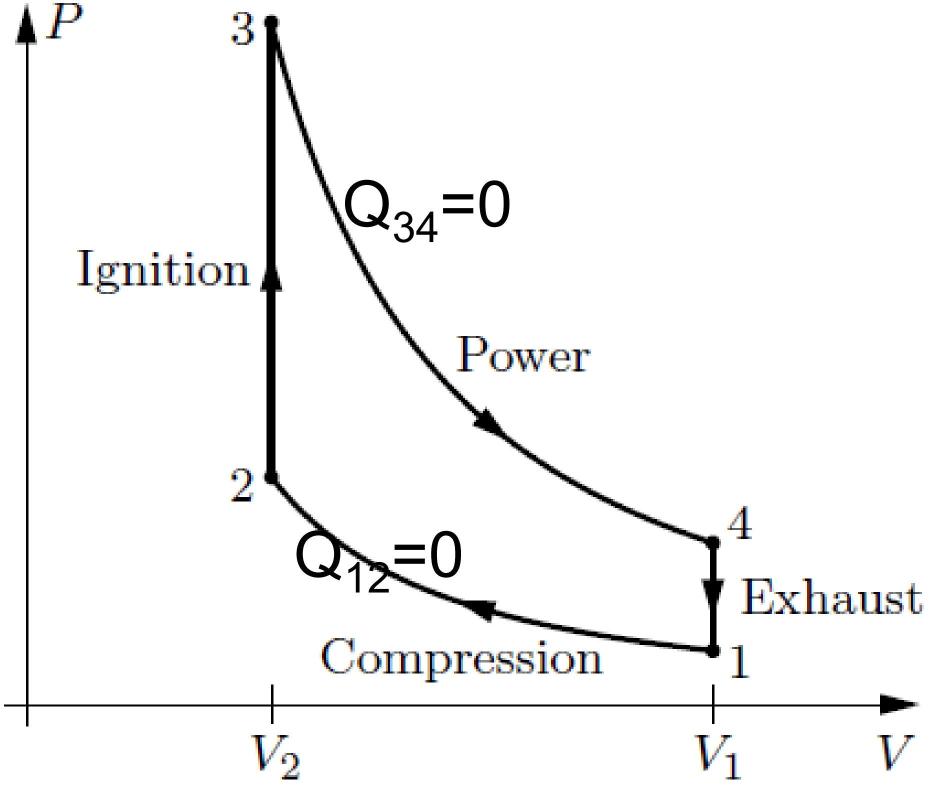
$$\epsilon \equiv \frac{W_{net}}{Q_{in}} = \frac{Q_{net}}{Q_{in}}$$

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

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

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

Other cyclic processes such as the 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 $\frac{V_2}{V_1} = \frac{1}{8}$ $\epsilon = 0.56$