PHY 341/641
Thermodynamics and Statistical Physics

Lecture 5

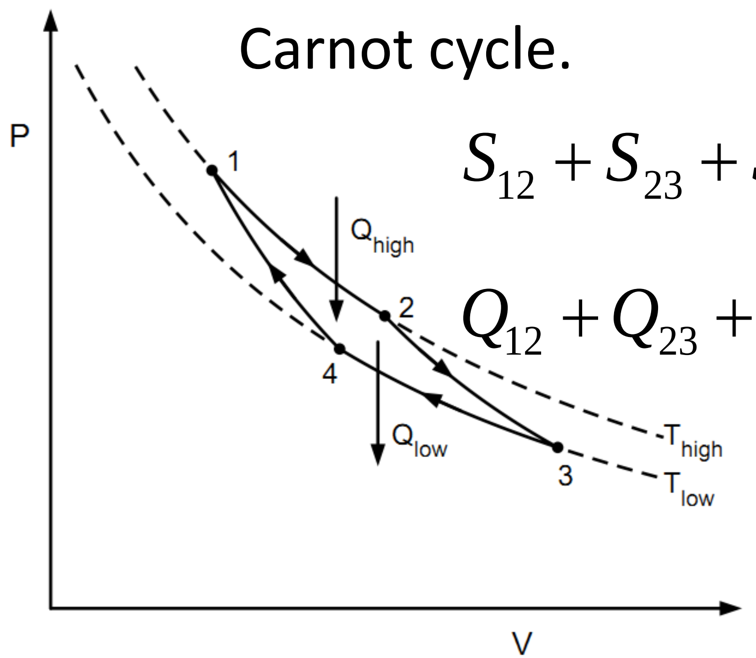
1. Entropy
2. Second law of thermodynamics
3. Variable dependences of thermodynamic relationships

Entropy for a reversible process (quasi-static via continuous changes in the variables):

$$dS = \frac{dQ}{T}$$

Note that *dS* is an "exact differential" *dQ* is not.

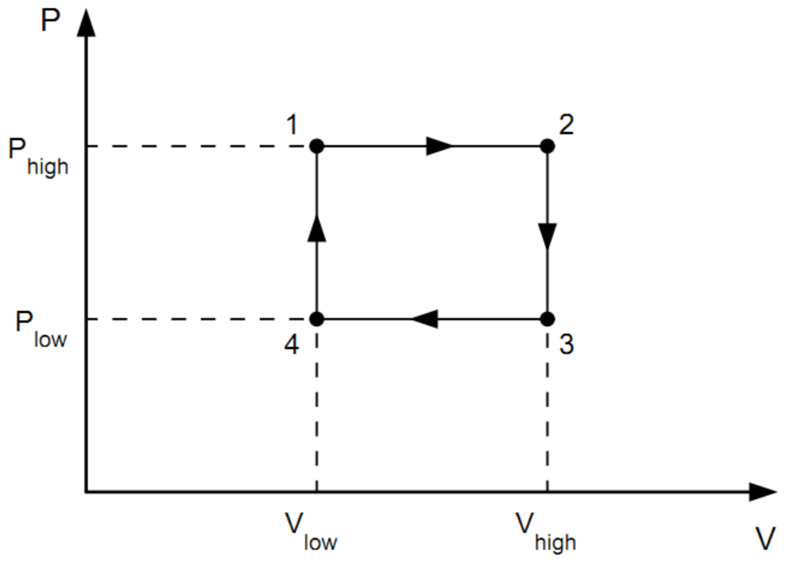
Carnot cycle.



$$S_{12} + S_{23} + S_{34} + S_{41} = 0$$

$$Q_{12} + Q_{23} + Q_{34} + Q_{41} = Nk(T_{high} - T_{low}) \ln \frac{V_2}{V_1}$$

Square cycle:

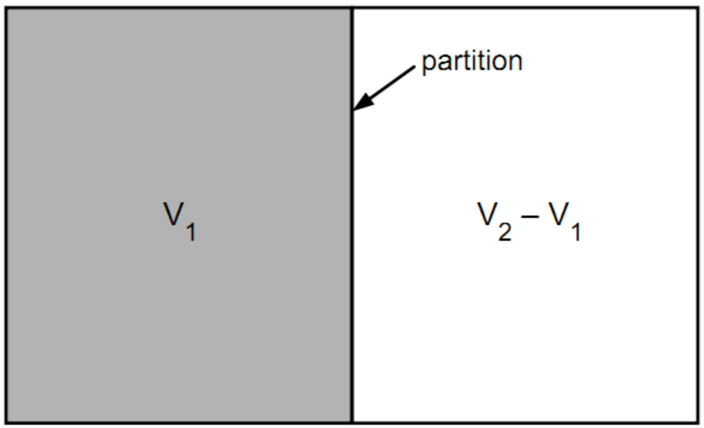


$$S_{12} + S_{23} + S_{34} + S_{41} = 0$$
$$Q_{12} + Q_{23} + Q_{34} + Q_{41} = \left(P_{high} - P_{low}\right)\left(V_{high} - V_{low}\right)$$

Second law of thermodynamics

- Kelvin-Planck: It is impossible to construct an engine which, operation in a cycle, will produce no other effect than the extraction of energy from a reservoir and the performance of an equivalent amount of work.
- Clausius: No process is possible whose sole result is cooling a colder body and heating a hotter body.
- Gould-Tobochnik:There exists an additive function of state known as the entropy S that can never decrease in an isolated system.

Comment on "quasi-static" restrictions



Consider the free expansion of an isolated ideal gas, initially in left chamber at V_1 with vacuum in right chamber and finally occupying full volume V_2.

In order to use the laws of thermodynamics, we must envision a quasi-static process that accomplishes the free expansion

$$dU = TdS - PdV = 0$$

$$\Rightarrow dS = \frac{P}{T} dV = Nk \frac{dV}{V} \qquad \Rightarrow S_{12} = Nk \ln \frac{V_2}{V_1}$$

Variables and functions:

Internal energy	U
Entropy	S
Pressure	P
Volume	V
Temperature	T
Number of particles	N

Assume N constant --

Consider First Law of Thermodyamics --

$$dU = TdS - PdV \quad \Rightarrow \text{suppose} \quad U = U(S,V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

Further relations:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$\left(\frac{\partial}{\partial V}\right)_s \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial U}{\partial V}\right)_S$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Mathematical transformations for continuous functions of several variables & Legendre transforms:

$$z(x,y) \quad \Leftrightarrow \quad x(y,z)???$$

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

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

$$\text{But:} \quad \left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\partial z / \partial y\right)_x}{\left(\partial z / \partial x\right)_y}$$

Mathematical transformations for continuous functions of several variables & Legendre transforms continued:

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

Let $u \equiv \left(\frac{\partial z}{\partial x}\right)_y$ and $v \equiv \left(\frac{\partial z}{\partial y}\right)_x$

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

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

For thermodynamic functions:

$$\text{Internal energy:} \qquad U = U(S,V)$$

$$dU = TdS - PdV$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$\text{Enthalpy:} \qquad H = H(S,P) = U + PV$$

$$dH = dU + PdV + VdP = TdS + VdP = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$\Rightarrow T = \left(\frac{\partial H}{\partial S}\right)_P \qquad V = \left(\frac{\partial H}{\partial P}\right)_S$$

Name	Potential	Differential Form
Internal energy	$E(S,V,N)$	$dE = TdS - PdV + \mu dN$
Entropy	$S(E,V,N)$	$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$
Enthalpy	$H(S,P,N) = E + PV$	$dH = TdS + VdP + \mu dN$
Helmholtz free energy	$F(T,V,N) = E - TS$	$dF = -SdT - PdV + \mu dN$
Gibbs free energy	$G(T,P,N) = F + PV$	$dG = -SdT + VdP + \mu dN$
Landau potential	$\Omega(T,V,\mu) = F - \mu N$	$d\Omega = -SdT - PdV - Nd\mu$

$$\text{Entropy:} \qquad S = S(U,V)$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

$$\text{From First Law:} \qquad dU = TdS - PdV$$

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

$$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$