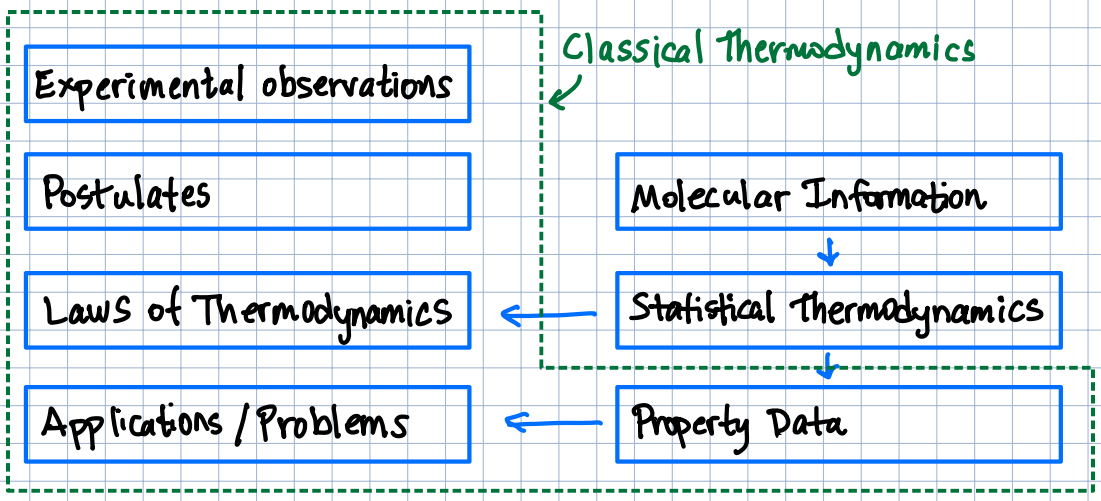
Lecture 21 - The postulates and Laws of Thermodynamics

A. What is Thermodynamics?

Thermodynamics is the study of energy, its transformations, and the principles governing equilibrium and spontaneous change. It started as a field that dealt with extraction of mechanical work from heat. It evolved to provide a general framework for analyzing and organizing a large body of experimental observations, information, and data that involve mechanical, thermal, and chemical processes and systems.



Postulates

i. Existence of Energy

ii. Existence of Equilibrium States

iii. Existence of Entropy

Postulates given between stars.

What are postulates?

These are the foundational assumptions or logical starting point upon which our theory is built. The basis of postulates are often based on repeated observation (empirical) or reason, i.e. "we hold these truths

to be self-evident." Usually, engineers learn thermodynamics from a "historical" approach. It is useful the second time through to take the "postulate" approach (see e.g. Callen). Physicists love postulate-based theories. We have seen several already: classical mechanics, quantum mechanics, and statistical thermodynamics.

B. Existence of Energy Postulate

* Energy, E, is a conserved quantity of a system. This means that E is a state function — a property of the state of the system and not the process that reached that state. * This postulate is a restatement of what we know from mechanics. There is nothing "new" here beyond mechanics.

* The change in energy for a closed system (no matter moves across the boundary of the system) is given by the 1st law of thermodynamics. *

$$dE = \delta Q + \delta W \qquad W: \text{Work (on system)} \quad Q: \text{heat}$$

$$dE = \delta Q - \delta W \qquad W: \text{Work (by system)}$$

the quantities δQ and δW are inexact differentials. Q and W are not state functions. they are path-dependent quantities.

↖ see Appendix for more details.

Energy is composed of mechanical and internal energy.

$$E = E_k + E_p + U$$

E_k: kinetic energy — motion of whole system

E_p: potential energy — energy in an external field, e.g. gravity (mechanical)

U: internal energy — other energy, associated with "internal" degrees of freedom (molecular motion, chemical state, etc.)

Often E_K and E_P are not important. They are usually much smaller than U for many thermodynamic problems. Or they can be considered separately.

Work is defined in mechanics as the energy resulting from the application of a force along a displacement.

$$\delta W = \underline{F} \cdot d\underline{X}$$

$\underline{F}$: force (gradient of a potential)

$\underline{X}$: displacement (extensive)

There are many types of work:

Type	"$\underline{F} \cdot d\underline{X}$"	
Pressure-volume	$-P dV$	
Stress-strain	$V \underline{\underline{\sigma}} : d\underline{\underline{\varepsilon}}$	$\underline{\underline{\sigma}}$: Cauchy stress, $\underline{\underline{\varepsilon}}$: true strain
Surface Deformation	$\gamma\, dA$	γ: surface energy
chemical	$\mu_i\, dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V}$, chemical potential
Electric polarization	$V \underline{E} \cdot d\underline{D}$	E: Electric Field, D: Dielectric Displacement
Magnetic polarization	$V \underline{H} \cdot d\underline{B}$	H: Magnetic Field, $\underline{B}$: Magnetic Induction

Quantities that relate these conjugate variables are called "constitutive laws." These are things like Hooke's law for a solid or a Curie Magnet. these are material specific! (Static Force-Displacement relationships)

↖ Dynamic ones in transport phenomena

Example:

Hooke's law: $\underline{\underline{\sigma}} = 2G\,\underline{\underline{\varepsilon}} + \lambda\, tr(\underline{\underline{\varepsilon}})\,\underline{\underline{I}}$ (istotropic), $\underline{\underline{\sigma}} = \underline{\underline{\sigma}}(\underline{\underline{\varepsilon}})$

Curie's law: $\underline{H} = \frac{1}{\mu_0 (1+\chi)} \underline{B}$ χ: susceptibility

μ_0: magnetic permeability of free space

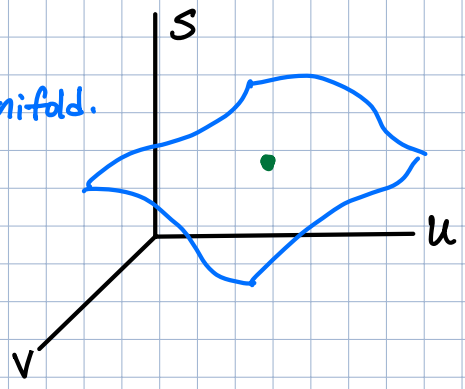
Heat accounts for the remaining modes of energy transfer that cannot be

expressed as $\underline{F} \cdot d\underline{X}$. These turn out to be microscopic work interactions between the system and the surroundings.

C. Existence of Equilibrium States

* Isolated systems spontaneously evolve towards static/steady states characterized by a small set of macroscopic variables (state functions). These states are reproducible and independent of process history. *
The energy and displacements ($\underline{X}$) completely specify the equilibrium state. We will see that $S = S(E, \underline{X})$ only. For example, in the case where E_p, E_k are neglible and we are looking at a single component fluid, $S = S(U,V)$.

Equilibrium states live on this manifold.
U,V completely specify our state.



Equilibrium Criteria. How do we know we are at equilibrium? 1) We don't for sure. 2) The system is independent of time and history. 3) No flows/gradients of energy or matter.

Let's be a bit more precise about the latter point. We will empirically say we are at equilibrium when the intensive variables are spatially uniform.

$T = \text{const}$	Thermal equilibrium	$(U \leftrightarrow T)$
$P = \text{const}$	Mechanical equilibrium	$(P \leftrightarrow V)$
$\mu_i = \text{const}$	Chemical equilibrium	$(\mu_i \leftrightarrow n_i)$

Reversibility

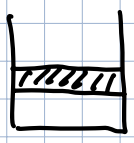
A reversible process is one that proceeds quasi-statically, with the system passing through a continuous sequence of equilibrium states. At every instant the system is uniform (no gradients of intensive variables T, P, μ) and the intensive variables differ from the surrounding only infinitesimally. Because each intermediate state is at equilibrium, the process generates no entropy — there is no dissipation.

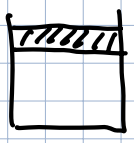
Note that even in reversible processes Q & W are still path dependent (depends on process, not just end point). Only state functions (S, U, V) depend solely on the state. Path dependence does not imply irreversibility. Irreversibility adds an additional feature of dissipation. All irreversible processes are path dependent, but not all path dependent processes are irreversible.

Path Dependence
Irreversibility

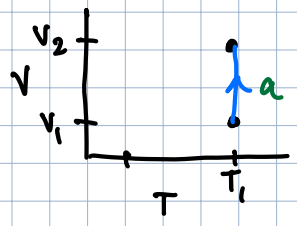
Example: Expansion of a monoatomic ideal gas

$$U = \frac{3}{2}nRT \qquad PV = nRT \qquad \Delta U = \Delta Q - \Delta W_{by} \qquad \Delta W_{by}: \text{ by gas}$$

State 1: T_1, V_1  $U_1 = \frac{3}{2}nRT_1$

State 2: T_1, V_2  $U_2 = \frac{3}{2}nRT_2$, $\Delta U_{12} = 0$

Isothermal Path:



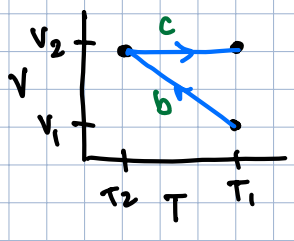
$$\Delta W_a = \int_1^2 dW = \int_1^2 -P\,dV = -\int_1^2 \frac{nRT_1}{V}\,dV = -nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta W_a = -nRT_1 \ln(V_2/V_1)$$

$$\Delta U_a = 0 = -\Delta W_a + \Delta Q_a$$

$$\Delta Q_a = -nRT_1 \ln(V_2/V_1)$$

Adiabatic expansion followed by (reversible) thermal equilibrium:



b) $\Delta Q_b = 0 \quad \Delta U_b = -\Delta W$

$\Delta U_b = \frac{3}{2} nR(T_2 - T_1) \quad \Delta W_b = -\frac{3}{2} nR(T_2 - T_1)$

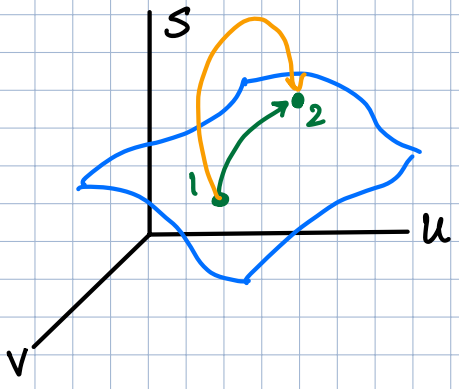
c) $\Delta W_c = 0$ (no ΔV) $\quad \Delta U_c = \Delta Q_c$

$\Delta U_c = \frac{3}{2} nR(T_1 - T_2) \quad \Delta Q_c = \frac{3}{2} nR(T_1 - T_2)$

$\Delta W_{bc} = \Delta W_b + \Delta W_c = \frac{3}{2} nR(T_1 - T_2)$

$\Delta Q_{bc} = \Delta Q_b + \Delta Q_c = \frac{3}{2} nR(T_1 - T_2)$

Geometric Interpretation



Reversible path on manifold from 1→2

Irreversible path off manifold from 1→2.

Excursion off surface to non-equilibrium states, followed by relaxation back to equilibrium manifold.

D. Existance of Entropy

* There is a quantity we will call entropy, S, that is a state function. Entropy is conserved for a reversible process. *

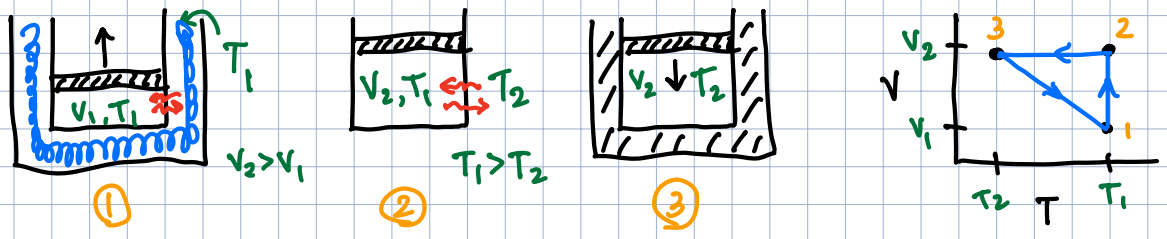
Clausius discovered that during a reversible process, the quantity $\delta Q/T$ was conserved. In other words, $\delta Q_{rev}/T$ is a state function. We call it the entropy,

$$dS = dQ_{rev}/T .$$

The change in entropy for a reversible cycle is zero,

$$\oint \frac{dQ_{rev}}{T} = \oint_{rev} dS = 0 .$$

Example: Reversible Cycle of an Ideal Gas



$\Delta U = \Delta Q - \Delta W$ $\quad U = \frac{3}{2} nRT$ $\quad$ Remember $T_1 > T_2$ & $V_1 < V_2$

$dS = {}^{dQ_{rev}}/_{T}$ $\quad C_V = \frac{3}{2} nR \rightarrow dU = C_V\, dT$

1→2: Isothermal Expansion

$\Delta U_{12} = 0 = \Delta Q - \Delta W$

$\Delta W_{12} = -nRT_1 \ln\left({}^{V_2}/_{V_1}\right)$ ← from above $\quad \Delta Q_{12} = -nRT_1 \ln\left({}^{V_2}/_{V_1}\right)$

$\Delta S_{12} = {}^{\Delta Q_{12}}/_{T_1} = -nR \ln\left({}^{V_2}/_{V_1}\right)$

2→3: Heat transfer $\quad$ state 2: T_1 $\quad$ state 3: T_2

$\Delta U_{23} = \frac{3}{2} nR(T_2 - T_1) = \Delta Q - \Delta W \rightarrow dU = dQ_{rev}$

$\Delta W_{23} = 0 \quad \Delta Q_{23} = -\frac{3}{2} nR(T_1 - T_2)$

$\Delta S_{23} = \int_2^3 \frac{1}{T} dQ_{rev} = \int_{T_1}^{T_2} \frac{1}{T} C_V dT = C_V \ln\left({}^{T_2}/_{T_1}\right) = -C_V \ln\left({}^{T_1}/_{T_2}\right)$

3→1: Adiabatic Compression

$\Delta U_{31} = \frac{3}{2} nR(T_1 - T_2) = \Delta Q - \Delta W$

$\Delta Q_{31} = 0 \quad \Delta W_{31} = -\frac{3}{2} nR(T_1 - T_2)$

$\Delta S_{31} = \int_3^1 \frac{1}{T} \underbrace{dQ_{rev}}_{0} = 0$

$dQ = dU + dW = C_V dT + P dV = C_V dT + \frac{nRT}{V} dV$

Note that V_1/V_2 and T_1/T_2 are not independent.

I cannot pick any combination I want.

$dU = \underbrace{dQ_{rev}}_{0} + dW_{rev} \Rightarrow 0 = dU - dW_{rev} \Rightarrow 0 = C_V dT + P dV$

$0 = \frac{3}{2} nR\, dT + \frac{nRT}{V} dV \Rightarrow 0 = \frac{3}{2} \frac{dT}{T} + \frac{1}{V} dV$

$$\int_2^1 -\tfrac{3}{2}\, d\ln T = \int_2^1 d\ln V \Rightarrow -\tfrac{3}{2}\ln\left(\tfrac{T_1}{T_2}\right) = \ln\left(\tfrac{V_1}{V_2}\right) \Rightarrow \boxed{\ln\left(\tfrac{V_2}{V_1}\right) = \tfrac{3}{2}\ln\left(\tfrac{T_1}{T_2}\right)}$$

Cycle:

$$\Delta U = \Delta U_{12} + \Delta U_{23} + \Delta U_{31} = 0 + \tfrac{3}{2}nR(T_1 - T_2) + \tfrac{3}{2}nR(T_2 - T_1) = 0 \checkmark$$

$$\Delta W = \Delta W_{12} + \Delta W_{23} + \Delta W_{31} = -nRT_1\ln(V_2/V_1) + 0 - \tfrac{3}{2}nR(T_1 - T_2)$$

$$= -nR\left[\tfrac{3}{2}(T_1 - T_2) + T_1\ln(V_2/V_1)\right]$$

$\Delta W < 0$ (work in)

$$= -\tfrac{3}{2}nR\left[(T_1 - T_2) + T_1\ln(T_1/T_2)\right]$$

$$\Delta Q = \Delta Q_{12} + \Delta Q_{23} + \Delta Q_{31} = -nRT_1\ln(V_2/V_1) - \tfrac{3}{2}nR(T_1 - T_2) + 0$$

$$= -nR\left[\tfrac{3}{2}(T_1 - T_2) + T_1\ln(V_2/V_1)\right]$$

$\Delta Q < 0$ (heat out)

$$= -\tfrac{3}{2}nR\left[T_1 - T_2 + T_1\ln(T_1/T_2)\right]$$

$\Delta Q - \Delta W = 0$ ✓ (1st law obeyed)

$$\Delta S = \Delta S_{12} + \Delta S_{23} + \Delta S_{31} = -nR\ln(V_2/V_1) - C_V\ln(T_1/T_2)$$

$$= -nR\left[\ln(V_2/V_1) + \tfrac{3}{2}\ln(T_1/T_2)\right]$$

$$= -nR\left[-\tfrac{3}{2}\ln(T_1/T_2) + \tfrac{3}{2}\ln(T_1/T_2)\right]$$

$$= 0!$$

S is a state function like U!

What happened?

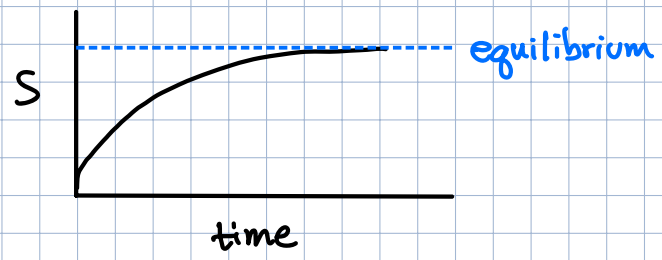
- Moved heat from reservoir at T_1 to reservoir at T_2 $\quad \Delta Q < 0$
- Surroundings did work on the gas in the piston (system). $\Delta W_{sys} < 0$
- Q_{rev} and W_{rev} were both path dependent.
- S is path independent! $\oint dQ_{rev}/T = \oint dS = 0$
- Ours is just an example, but this always works! Amazing!

Geometric interpretation: It is the same as when we talked about state functions above. $S(u, v)$ is a well defined surface.

E. The 2nd Law

We need to know two more things about entropy to complete our postulates.

* First, an isolated system (i.e., no heat or mass transfer with surroundings) will maximize its entropy as it proceeds to equilibrium. *



This postulate can be stated as the 2nd law of thermodynamics,

$\Delta S \geq 0$ isolated system

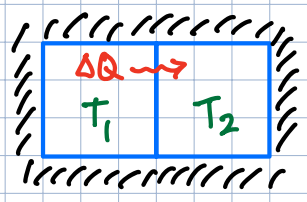
$\Delta S = 0$ when reversible

$\Delta S > 0$ when irreversible (dissipative)

Note: this can be a little confusing. S is a state function and is only defined at equilibrium. You cannot directly calculate S for an irreversible path unless you are doing a detailed transport calculation (local equilibrium with spatial gradients). But when the system relaxes back to the equilibrium manifold, you can construct a reversible path and get it.

The 2nd law sets the spontaneous direction of energy transfer. It also shows us that entropy characterizes energy dispersal.

Example: Direction of Heat Transfer



$$\Delta S_1 = \frac{-\Delta Q}{T_1} \qquad \Delta S_2 = \frac{\Delta Q}{T_2}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{\Delta Q}{T_2} - \frac{\Delta Q}{T_1}$$

Heat is flowing from 1 → 2.

Reversible: $T_1 = T_2$, $\Delta S = 0$

Irreversible: $\Delta S > 0$ iff $T_1 > T_2$ Heat flows from hot → cold.

* Second, entropy is continuous, differentiable, and a monotonically increasing function of U. *

$$\left(\frac{\partial S}{\partial U}\right)_{\underline{X}} > 0$$

This property of entropy lets us define the thermodynamic temperature as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{\underline{X}} \quad \text{or} \quad T = \left(\frac{\partial U}{\partial S}\right)_{\underline{X}}$$

monotonically increasing ensures $T > 0$.

How do we know this is the temperature? We know that if we bring two systems together, at thermal equilibrium $T_1 = T_2$. The entropy will be a maximum in this case.

$$S = S_1 + S_2 \qquad U = U_1 + U_2 \qquad S_1 = S_1(U_1) \qquad S_2 = S_2(U_2)$$

$$\mathcal{L} = S + \alpha(U - U_1 - U_2)$$ Lagrangian

$$\frac{\partial \mathcal{L}}{\partial U_i} = 0$$ entropy is maximized for constant U

$$\frac{\partial \mathcal{L}}{\partial U_1} = \frac{\partial S}{\partial U_1} - \alpha = 0 \qquad \frac{\partial S}{\partial U_1} = \alpha$$

$$\frac{\partial \mathcal{L}}{\partial U_2} = \frac{\partial S}{\partial U_2} - \alpha = 0 \qquad \frac{\partial S}{\partial U_2} = \alpha$$

So, at equilibrium,

$$\frac{\partial S}{\partial U_1} = \frac{\partial S}{\partial U_2} \quad \Rightarrow \quad \frac{1}{T_1} = \frac{1}{T_2}$$

Temperature equilibrates the internal energy

Analogous derivations for $S(V)$ and $S(N)$ find that pressure and chemical potential are the equilibrium criteria respectively.

X. Appendix: the math of state functions

Suppose I have a function $F(X,Y)$. It is unique. For a given X and Y, there is only one value of F. This is a state function. Functions have total derivatives,

$$dF = \frac{\partial F}{\partial X} dX + \frac{\partial F}{\partial Y} dY = M(X,Y)\,dX + N(X,Y)\,dY$$

$$= \nabla F \cdot d\underline{R} \qquad \underline{R} = [X,Y]^T \qquad \nabla F = [M,N]^T$$

The second derivatives of F are symmetric,

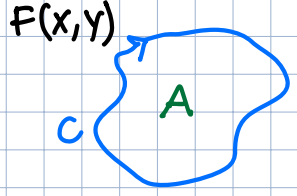
$$\frac{\partial^2 F}{\partial X \partial Y} = \frac{\partial^2 F}{\partial Y \partial X} \quad \Rightarrow \quad \frac{\partial M}{\partial Y} = \frac{\partial N}{\partial X}$$

This means that a closed path integral of dF must be zero.

$$\oint_C dF = \oint M(X,Y)\,dX + \oint N(X,Y)\,dY$$

$$M = \int \frac{\partial M}{\partial Y} dY \qquad N = \int \frac{\partial M}{\partial X} dX$$

$$= \iint_A \frac{\partial M}{\partial Y} dX\,dY + \iint_A \frac{\partial N}{\partial X} dX\,dY$$



Intuitive, but lazy (wrong). Need to do area carefully. Doing so gives,

$$\oint_C dF = \iint_A \left(\underbrace{-\frac{\partial M}{\partial Y} + \frac{\partial N}{\partial X}}_{\frac{\partial M}{\partial Y} = \frac{\partial N}{\partial X}} \right) dX\,dY = 0$$

Green's theorem

Alternatively

$$\oint \nabla F \cdot d\underline{R} = 0$$

Gradient theorem (curl-free vector field)

In physics, we call state functions a "potential!" Just like gravitational potential energy. ∇F are conservative forces.

By contrast, inexact differentials do not have this property.

$$đG = M(X,Y)\,dX + N(X,Y)\,dY \qquad \frac{dM}{dY} \neq \frac{dN}{dX}$$

Now, if we want the quantity G, we must integrate it along some path.

$$G = \int_C đG = \int_C M\,dX + \int_C N\,dY$$

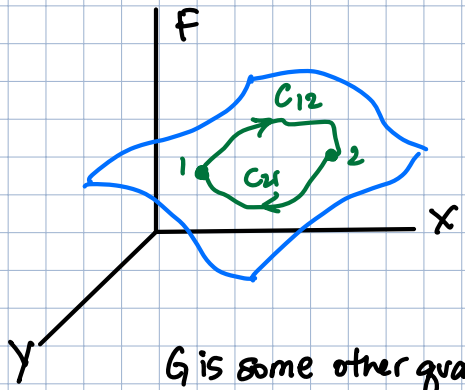
G is not a state function. I cannot write it as $G(X,Y)$. The closed path integral is not zero,

$$\oint đG \neq 0$$

Different paths give different values.

$$\int_{C_1} đG \neq \int_{C_2} đG$$

Think of F(X,Y) as some potential surface,



$$\oint_C dF = \int_{C_{12}} dF + \int_{C_{21}} dF = F(2) - F(1) + F(1) - F(2)$$

$$= \oint_C \nabla F \cdot d\underline{R} = 0$$

G is some other quantity. The integral of G along both paths are different. $\int_{C_{12}} đG \neq -\int_{C_{21}} đG$.