Thermodynamics (Part 2)

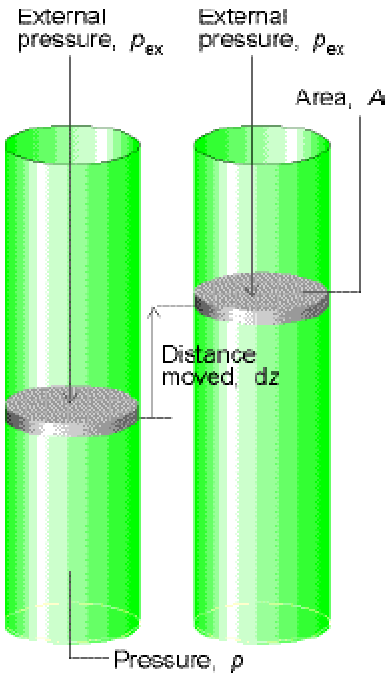
THERMODYNAMIC PROCESSES

- When a state of a thermodynamic system is changed, we say a thermodynamic process occurs in a system. There are a few types of thermodynamic processes.
- **In a cyclic process** the final state is the same as the initial state. The change in any state function for a cyclic process is obviously zero
- **Spontaneous process** takes place without work being done on the system. This process occurs only at the expense of the own energy reserve of the system (without energy entry from the surroundings). It happens naturally: a gas expands to fill the available volume, a hot body cools to the temperature of its surroundings, a body falls from a higher level to a lower one, etc.
- **Nonspontaneous process** must be brought about by doing work to the system: compression a gas to a smaller volume, cools an object with a refrigerator. In closed system every spontaneous process finishes in equilibrium state.

THERMODYNAMIC PROCESSES

- Reversible process in thermodynamics has some other meaning, than in chemistry, where it means only that the process occurred in two opposite directions.
- If we arrange the conditions in such a way that the system is nearly at equilibrium in every moment, and that, consequently, the direction of the process may be reversed by even a very slight change of the initial conditions, the process is called reversible or equilibrium. A reversible process is thus a sequence of (nearly) equilibrium states of a system.

REVERSIBLE PROCESS



The system consists of a gas contained within the piston with cylinder walls. Pmt is a gas pressure and Pext is an external pressure. When Pmt=Pext, the system is in equilibrium. If the Pext above the piston increased by an infinitesimal amount, the gas compressed slightly. If the Pext reduced infinitesimally, then the gas expands slightly, in each increasing of external pressure the volume of the system decreases and the gas pressure increases until the pressure of a system again balances the external pressure. In this process, the difference between the pressures on the two sides of the piston is always infinitesimally small and the system remains infinitesimally close to the state of equilibrium.

REVERSIBLE PROCESS

Reversible process is the one where the system is always infinitesimally close to equilibrium, and infinitesimally changing in external conditions accompanies changing in a process direction, under conditions that direction changing does not accompany changing of the energy in surroundings. For exam-

IRREVERSIBLE PROCESS

The processes in the real world are mostly such that the system is out of equilibrium at least at the beginning. These processes are called irreversible or non-equilibrium (the direction of the process cannot be reversed by any slight change of external conditions, and the process is a sequence of non-equilibrium states). An equilibrium process is thus actually a limiting case of a non-equilibrium process going on at an infinitesimal velocity.

THE SECOND LAW OF THERMODYNAMICS

- In the isolated systems all spontaneous processes take place in the direction of increasing entropy. The change of entropy value (at constant temperature) is equal the ratio of the heat to the absolute temperature.
- heat cannot pass spontaneously from a colder body to a warmer one;
- a process, the only result of which is the transformation of heat into work is impossible;
- it is impossible to construct a machine (a perpetual motion machine of the second order) the only effect of which would be to transform heat taken from the surroundings into work.

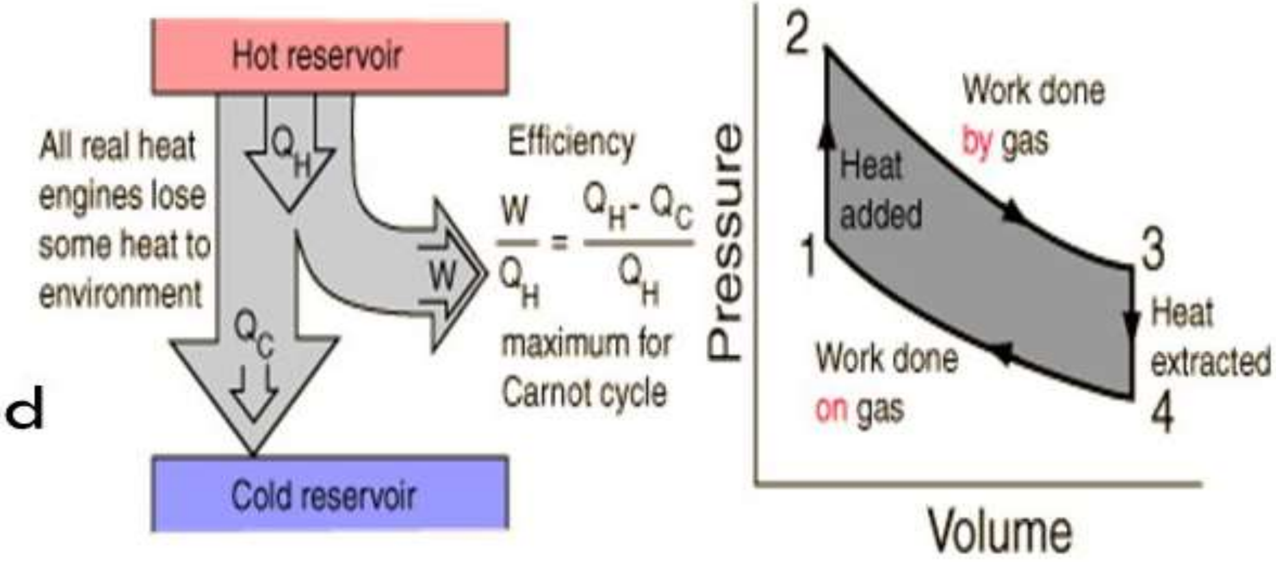
THE SECOND LAW OF THERMODYNAMICS

- Heat cannot be completely converted into work. All the kinds of energy can be transformed into heat, but heat itself cannot be transformed into work completely.

THE CARNOT CYCLE

- Heat engines cannot convert all the input energy.

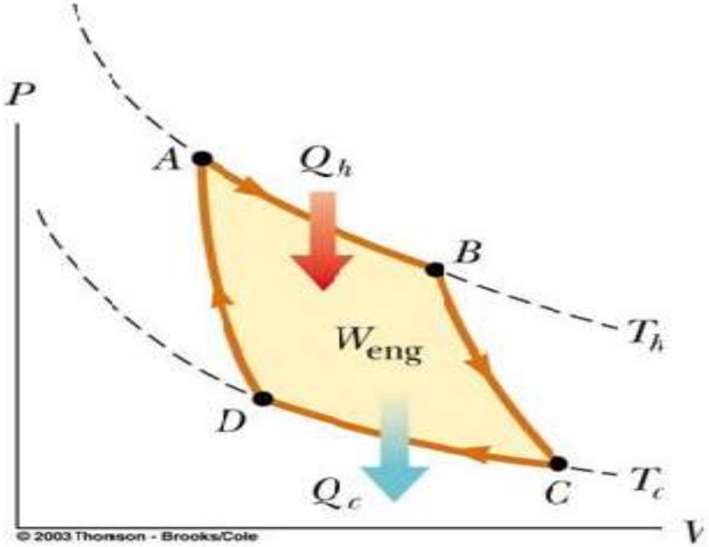
- The fraction converted is called the thermal efficiency



- The maximum possible efficiency of a heat engine is that of a hypothetical (ideal) cycle, called the Carnot Cycle.

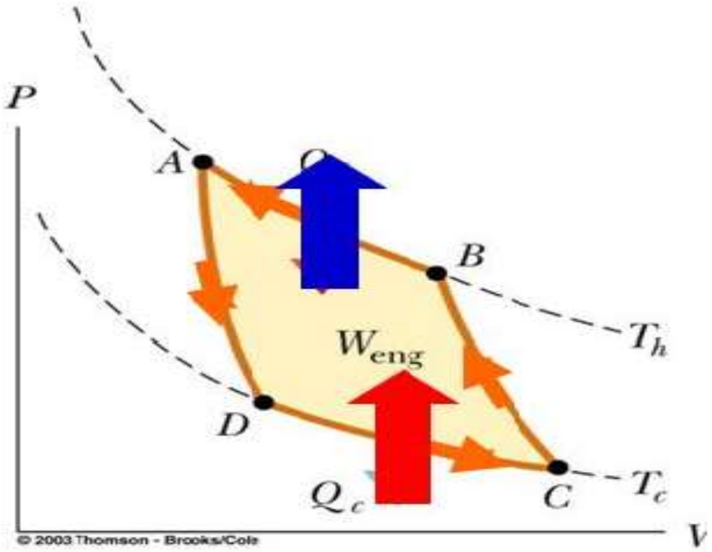
THE CARNOT CYCLE

Carnot cycle



Work done by engine: W_{eng}
$W_{eng}=Q_{hot}-Q_{cold}$
efficiency: $1-T_{cold}/T_{hot}$

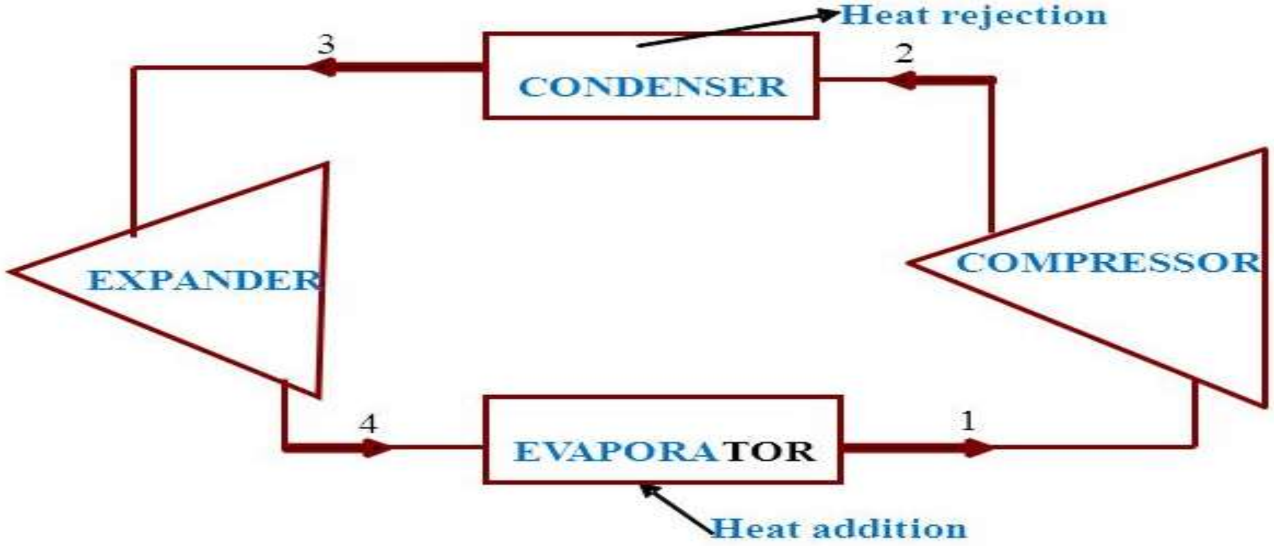
inverse Carnot cycle



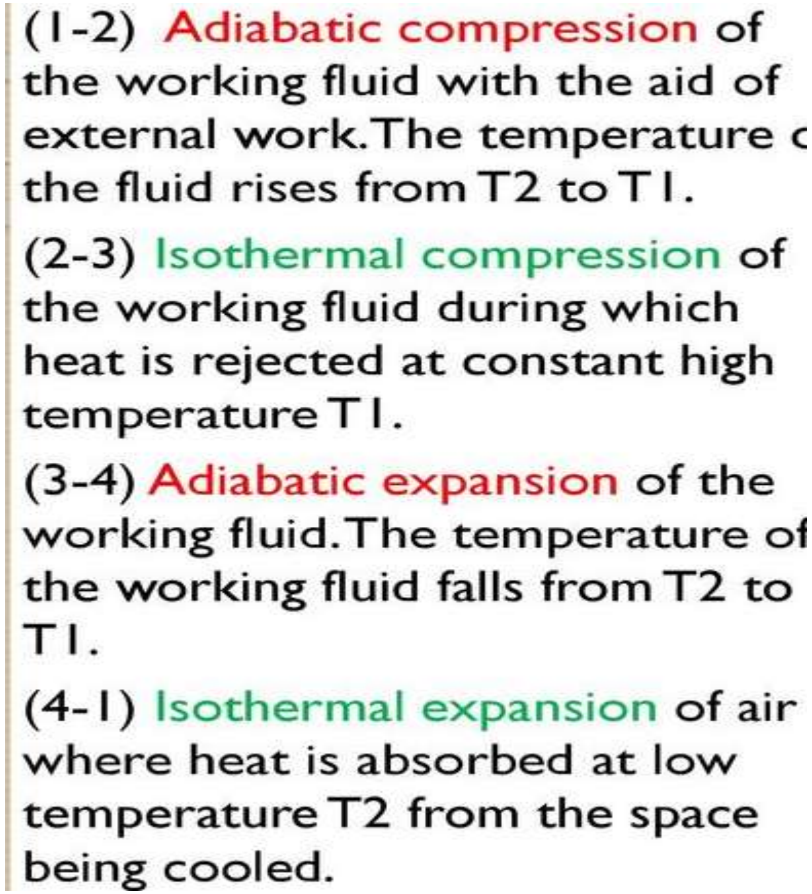
A heat engine or a fridge!
By doing work we can
transport heat

THE CARNOT REFRIGERATION CYCLE

The Carnot refrigeration cycle performs the reverse effect of the heat engine, because it transfers energy from a low level of temperature to a high level of temperature.



REVERSED CARNOT CYCLE

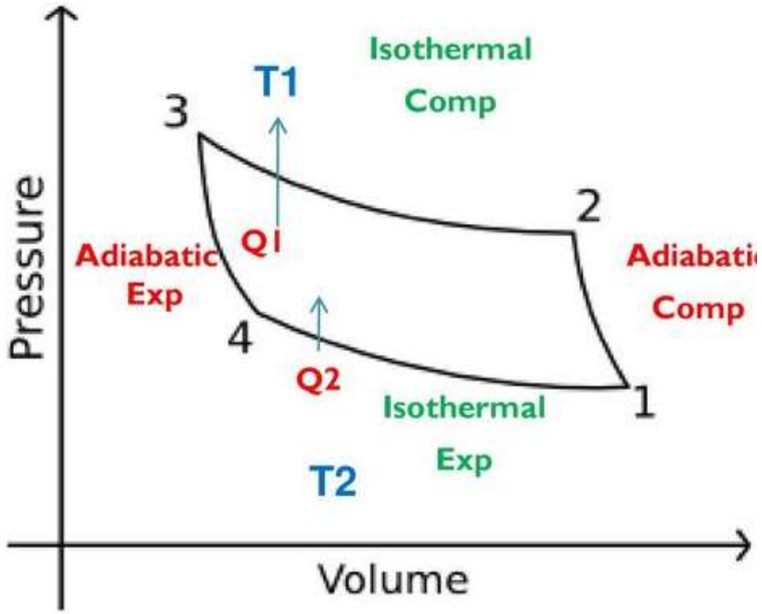


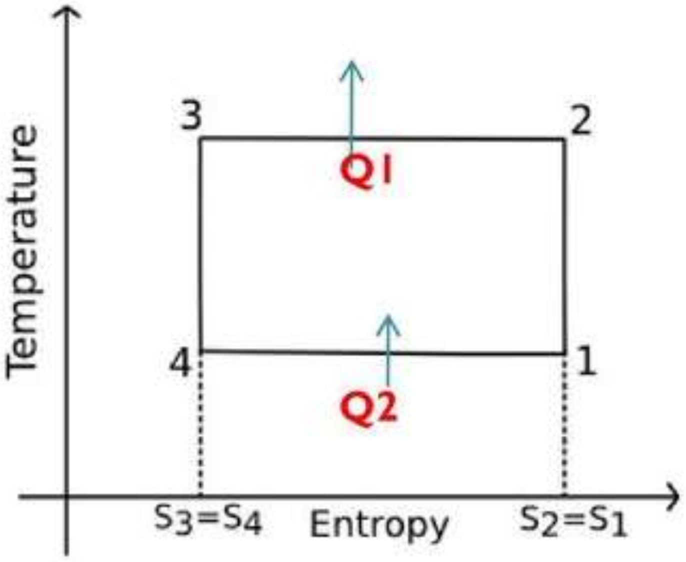
(1-2) Adiabatic compression of the working fluid with the aid of external work. The temperature c the fluid rises from T2 to T1.

(2-3) Isothermal compression of the working fluid during which heat is rejected at constant high temperature T1.

(3-4) Adiabatic expansion of the the working fluid. The temperature of the working fluid falls from T2 to T1.

(4-1) Isothermal expansion of air where heat is absorbed at low temperature T2 from the space being cooled.

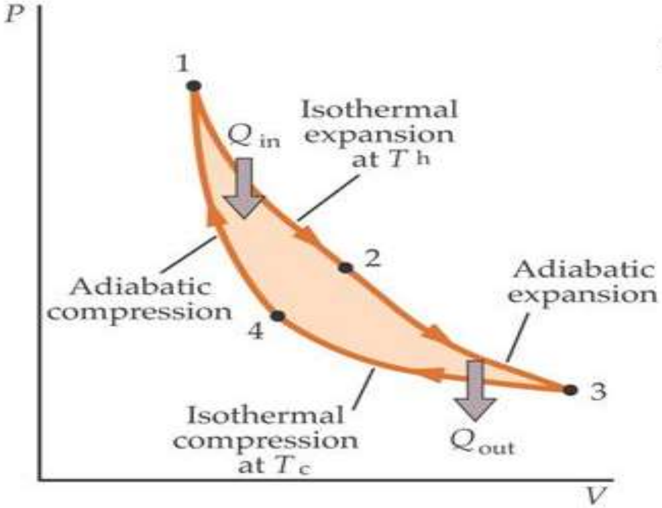




THE CARNOT CYCLE

Carnot cycle is a reversible cycle between two heat reservoirs

$$\varepsilon = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$



Isothermal processes

$$Q_h = W_{by\ gas} = \int_{V_1}^{V_2} P\,dV = nRT_h \ln\frac{V_2}{V_1}$$

$$Q_c = W_{on\ gas} = -\int_{V_3}^{V_4} P\,dV = nRT_c \ln\frac{V_3}{V_4}$$

Adiabatic processes

$$\left.\begin{array}{l} T_h V_2^{\gamma-1} = T_c V_3^{\gamma-1} \\ T_h V_1^{\gamma-1} = T_c V_4^{\gamma-1} \end{array}\right\} \frac{V_2^{\gamma-1}}{V_1^{\gamma-1}} = \frac{V_3^{\gamma-1}}{V_4^{\gamma-1}} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\frac{Q_c}{Q_h} = \frac{T_c \ln\frac{V_2}{V_1}}{T_h \ln\frac{V_3}{V_4}} = \frac{T_c}{T_h} \longrightarrow \boxed{\varepsilon = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}}$$

ENTROPY

All the reversible cycle can be divided into an infinite number of infinitesimal strips, and for each strip

$$1-\frac{q_c}{q_h}=1-\frac{T_c}{T_h}\quad or\quad \frac{q_h}{T_h}-\frac{q_c}{T_c}=0$$

In this equation, dq is an infinitesimal portion of the heat transferring along the reversible cycle and Tis the temperature at which this heat transfer occurs. The sum of these infinitesimal transfers is a line integral around the cycle,

$$\oint\frac{dq_{rev}}{T}=0$$

ENTROPY

- Since such integral of any reversible cycle is zero, it follows, that the value of the line integral is independent of the path of the process and depends only on the initial and final states. Hence. dq/T is the state function. Clausius discovered this state function in 1854 and called it entropy. (S), which is related to the transformation of heat to work.
- Entropy is an extensive state function. The commonly used units of S are J/(mol K) or cal/(mol K).
- **Entropy** is a measure of the disorder of the system

AN ANALYTICAL EXPRESSION OF THE SECOND LAW

$$dS = \frac{dq_{rev}}{T}$$

This equation is right only for ideal reversible spontaneous processes.

AN ANALYTICAL EXPRESSION OF THE SECOND LAW

- This equation is right only for ideal reversible spontaneous processes. For irreversible process dS is not equal dirre/T, because in such process a part of energy is lost in the surroundings as heat (exept amount of heat absorbed by cold sink).

$$\frac{dq_{rev}}{T} \rangle \frac{dq_{irrev}}{T} \qquad dS \rangle \frac{dq_{irrev}}{T}$$

AN ANALYTICAL EXPRESSION OF THE SECOND LAW

$$dS \geq \frac{dq}{T}$$

STATISTICAL OR MOLECULAR INTERPRETATION OF SECOND LAW

Entropy is a measure of the molecular disorder of a system: entropy increasing means increasing of molecular disorder. The statistical nature of the second law supposes that it is applicable only to the systems composed of a very great number of particles. This nature of entropy was first demonstrated in the works of L Boltzmann in 1896.

$$\mathbf{S=klgW}$$

where k is called Boltzmann's constant, lgW thermodynamic probability of the given state of the system, and ω is the total number of microstates for the system of certain energy level by which the microstate of the system could be realized.

DIRECTION OF THE SPONTANEOUS PROCESS

Change of entropy **(ΔS)** indicates a direction of the spontaneous process. Thus, the entropy of an isolated system must increase in any irreversible spontaneous process: **$\Delta S>0$**: Since the spontaneous process is finished in the state of equilibrium, so the equilibrium is a state with maximal entropy: **S=max.**

ΔS FOR SOME PROCESSES

The entropy of phase transition

$$\Delta S_{trs} = \Delta H/T$$

The entropy of a gas expansion

$$\Delta S = \frac{dW}{T} = \frac{RT\ln\frac{V_2}{V_1}}{T}$$ from which

$$\Delta S = Rln\frac{V_2}{V_1} = Rln\frac{P_1}{P_2}$$

The variation of entropy with temperature

$$\Delta S = \frac{CdT}{T} = C\int_{T_1}^{T_2}\frac{dT}{T}$$ from which

$$\Delta S = C_p \ln\frac{T_2}{T_1}$$ and $$\Delta S = C_v \ln\frac{T_2}{T_1}$$

THE THIRD LAW OF THERMODYNAMICS

- ***The entropy of a perfect crystalline material is zero at absolute zero temperature.***

THERMODYNAMIC POTENTIALS

Consider a system in thermal equilibrium with its surroundings at temperature T. When a change in the system occurs and there is a transfer of energy as heat between the system and its surrounding, total entropy change is the sum of the entropy changes both the system and its surroundings and an equation dSsyst + **$dSsur \geq 0$**. Because **$dSsur = -dq_{sur}/T$**, and **$dq_{sur} = -dq_{syst}$** (the heat that enters into the system comes from surroundings) it follows that for any change

THE HELMHOLTZ FREE ENERGY

$$dS_{syst} - \frac{dq_{syst}}{T} \geq 0$$

At constant volume dq=dU , so

$$dS - \frac{dU}{T} \geq 0$$

$$TdS \geq dU \quad \text{or} \quad dU - TdS \leq 0$$

The function **(U – TS)** is called the **Helmholtz free energy** and is denoted by the symbol **A**:

$$A = U - TS$$

For infinitesimal changes it is in the form

$$dA = dU - TdS$$

For constant volume–temperature processes

$$dA \leq 0$$

GIBBS ENERGY

For processes carried out at constant pressure, when **dq=dH**, we obtain another thermodynamic quantity **– the Gibbs energy**, which is defined as

$$dG = dH - TdS$$

For constant pressure–temperature processes

$$dG \leq 0$$

GIBBS ENERGY

- If G decreases (**$\Delta G<0$**) as the reaction proceeds, then the reaction has a **spontaneous tendency** to convert reactants into products.
- If G increases (**$\Delta G>0$**), then the **reverse reaction** is spontaneous.
- If **$\Delta G=0$** – **equilibrium state**

EXPRESSIONS, FOR REVERSIBLE PROCESS IN CLOSED SYSTEM, WHEN ONLY *P-V WORK IS OCCURED*

$$dU = TdS - pdV$$

$$dH = TdS - Vdp$$

$$dA = -SdT - pdV$$

$$dG = -SdT + Vdp$$