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Second law

Functions F and G

Property relation

Property relation derived from U , H , F , and G

etc.



Review

2nd law

Entropy as a state function / Carnot cycle

Heat engine

Refrigerator

Heat pumps

Entropy changes in chemical reactions

3rd law



Index of nomenclature

Second Law 第二定律

Entropy 熵

Heat engine 热机

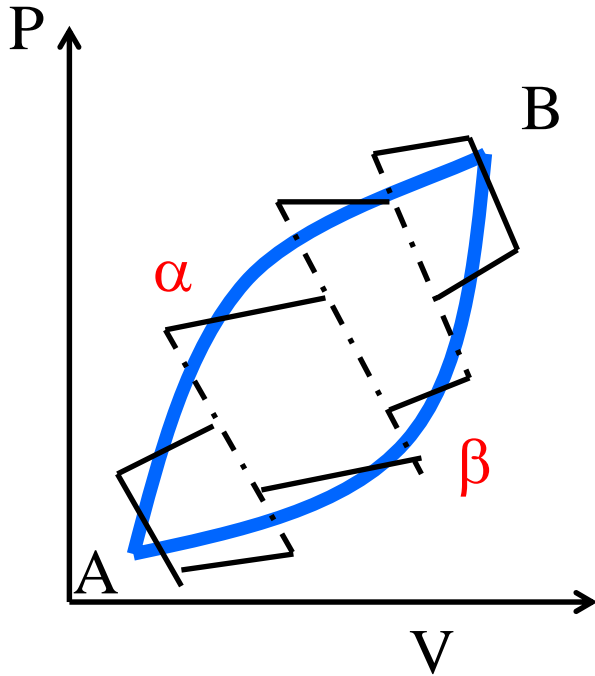
Refrigerator 冰箱

Heat Pump 热泵

Third law 第三定律



Entropy as a State Function(3)



$$\oint \frac{\delta Q_r}{T} = \int_A^B \left(\frac{\delta Q_r}{T} \right)_\alpha + \int_B^A \left(\frac{\delta Q_r}{T} \right)_\beta = 0$$

$$\int_A^B \left(\frac{\delta Q_r}{T} \right)_\alpha = - \int_B^A \left(\frac{\delta Q_r}{T} \right)_\beta = \int_A^B \left(\frac{\delta Q_r}{T} \right)_\beta$$

这一积分的数值与积分的途径无关，代表着某个状态的改变量，定义为熵

For a close system the reversible heat flow divided by the absolute temperature of the system is a state or point function.



第二定律

1842年在热力学第一定律被发现之前，卡诺定理

工作在两个热源之间的热机以卡诺热机的效率最高

卡诺认为：热机是通过把热量从高温热源传到低温热源而作功的，热量本身并没有消耗。犹如水力作功，热质说。

热力学第二定律/否定的方式来阐述的！

Clausius: 不可能把热量从低温物体传到高温物体而不引起其它变化。
。1850年

Kelvin: 不可能从单一热源吸热使之完全变成有用的功而不引起其它的变化；1851年 /第二类永动机机不可能

强调“不引起其它变化”

最终的唯一效果



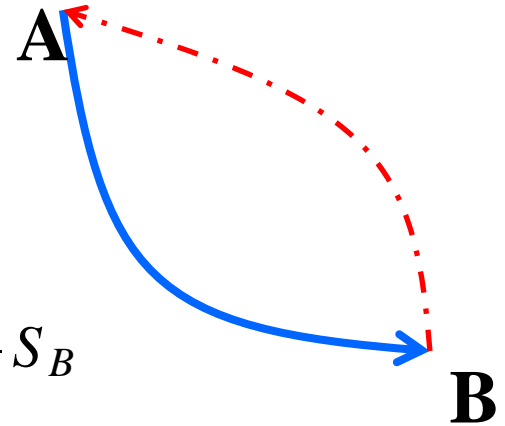
熵增原理—热力学第二定律的普遍描述

$$\oint \frac{\delta Q}{T} \leq 0$$

δQ 为为系统从温度为T的热源吸取的热量

可逆过程的热温商为零，所定义的熵为状态函数

设系统由初态A变为终态B，设系统经过一个设想的可逆过程由状态B回到状态A



$$\int_A^B \frac{\delta Q}{T} + \int_B^A \frac{\delta Q_{rev}}{T} \leq 0$$

$$\int_B^A \frac{\delta Q_{rev}}{T} = S_A - S_B$$

$$S_B - S_A \geq \int_A^B \frac{\delta Q}{T}$$

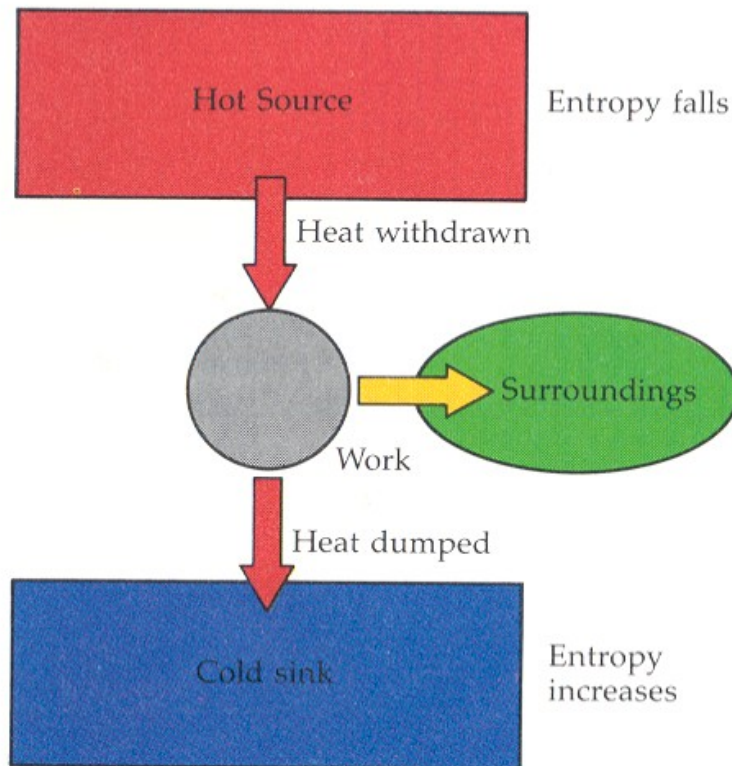
热力学第二定律对过程的限制，违反上述不等式的过程是不可能发生的！

$$S_B - S_A \geq 0$$

绝热条件下



Summary



Some heat must be discarded into a cold sink in order for us to generate enough entropy to overcome the decline taking place in the hot reservoir

Energy stored at a high temperature has a better “quality”: high-quality energy is available for doing work; low-quality energy, corrupted energy, is less available for doing work 冬季取暖/进化

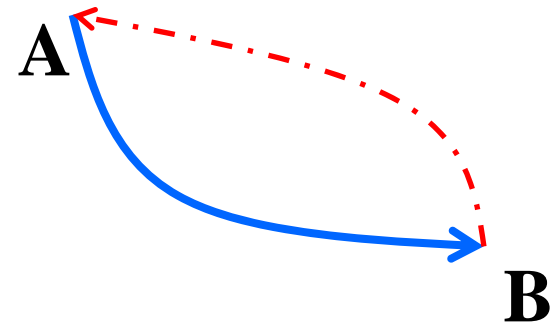


热力学第二定律几点说明！

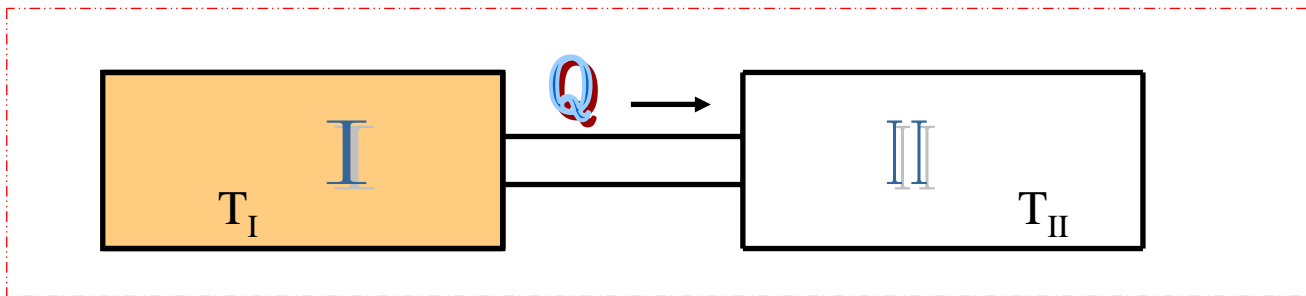
过程

- 不可能的过程
- 可能的过程
 - 可逆
 - 不可逆（自发）过程

研究过程方向问题（任务）《一体系+环境（孤立体系熵增原理）》《一热力学第二定律（基础但不好用）》

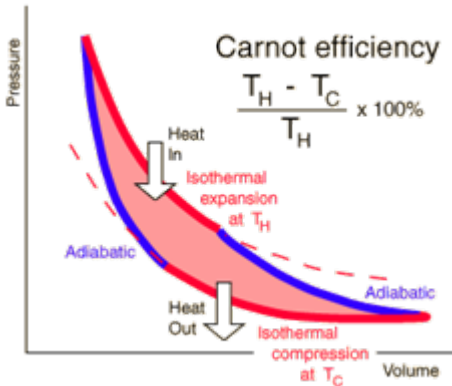
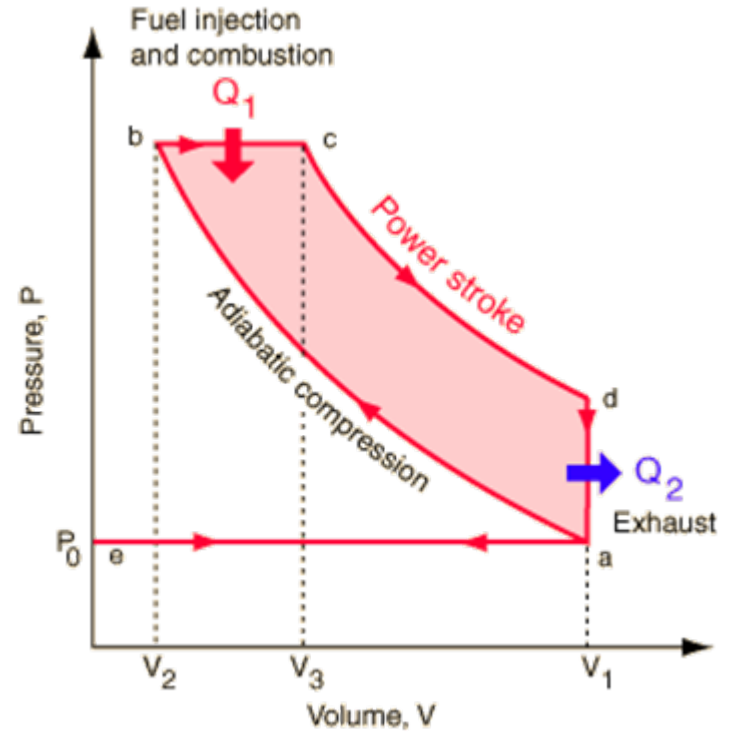
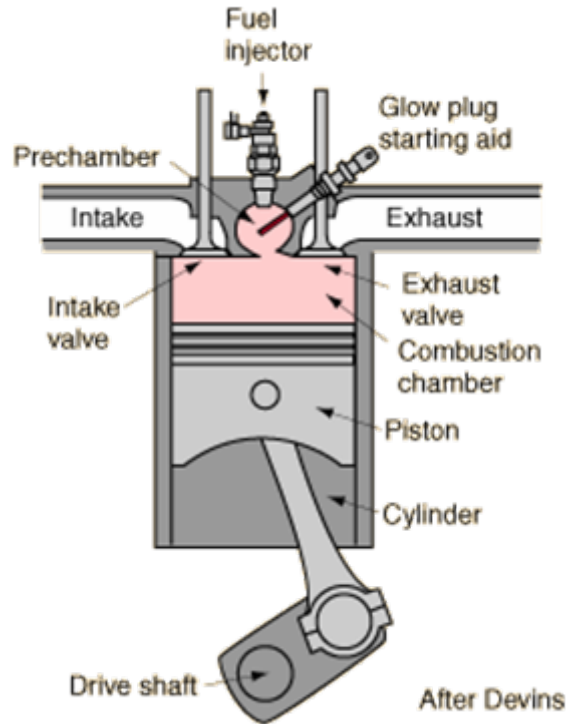


熵为体系的状态函数/ 平衡状态



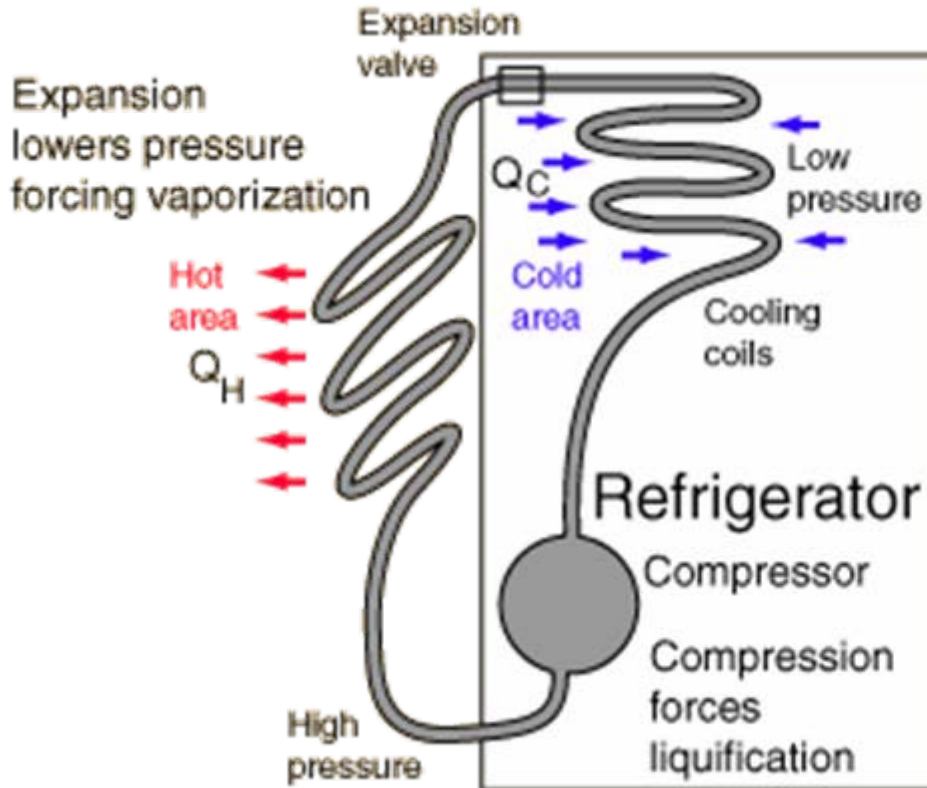


Diescycle

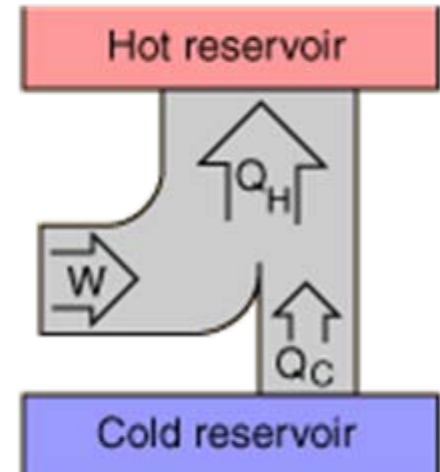




Refrigerator



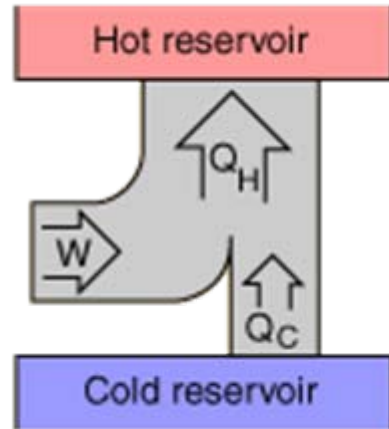
All real refrigerators require work to get heat to flow from a cold area to a warmer area.





Heat Pumps

All real refrigerators and heat pumps require work to get heat to flow from a cold area to a warmer area.



$$\text{Coefficient of Performance} = \frac{Q_H}{W}$$

General definition

$$CP = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_C} \Rightarrow \frac{T_H}{T_H - T_C}$$

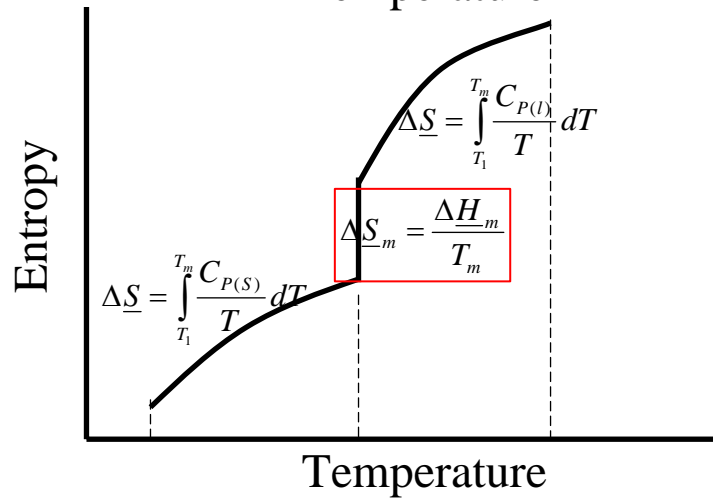
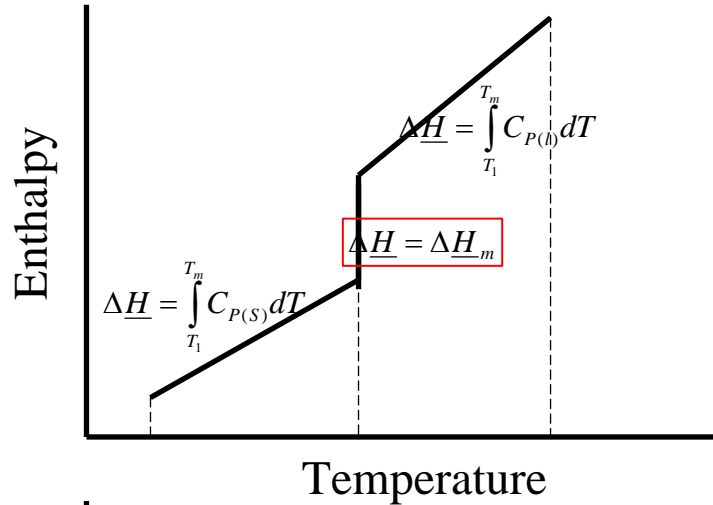
Limit for ideal
Carnot case

Ideal coefficient
of performance



2.9 Entropy Changes (2)

变化过程的熵很重要，所以要计算





2.10 Entropy change in chemical reactions and the third law (1)

S. J. T. U.

Phase Transformation and Applications

The calculation of entropy changes for a chemical reaction is similar to the calculation in the case of enthalpy changes.

One very important difference:

Nernst 1906

The entropy change in any chemical reaction involving only pure, crystalline substances: ZERO at the ABSOLUTE Zero of temperature.

Pure: pure elements and stoichiometrically balanced compounds that are perfectly crystalline.

Planck

The entropy of a pure, perfectly crystalline substances: ZERO at the ABSOLUTE Zero of temperature.

$$\Delta S_0^0 = 0$$

Superscript zero: **standard state, 1 atm**

Subscript zero: temperature ZERO



2.10 Entropy change in chemical reactions and the third law (2)

S. J. T. U.

Phase Transformation and Applications

The third law provides a great simplification in the calculation of entropies of reaction.

$$\Delta S_T^0 = \Delta S_0^0 + \int_0^T \frac{C_P}{T} dT = \int_0^T \frac{C_P}{T} dT$$

The entropy changes near room temperature are often needed in thermodynamic calculations, the integral in above equation has been evaluated for many substance at 298 K.

$$S_{298}^0 = \int_0^{T_m} \frac{C_P}{T} dT + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T_b} \frac{C_P}{T} dT + \frac{\Delta H_b}{T_b} + \int_{T_b}^{298} \frac{C_P}{T} dT$$



Index of nomenclature

Helmholtz free energy (F): 亥姆赫茨自有能

Gibbs free energy (G): 吉布斯自有能

Chemical potential: 化学位



Chap 3 Property Relations

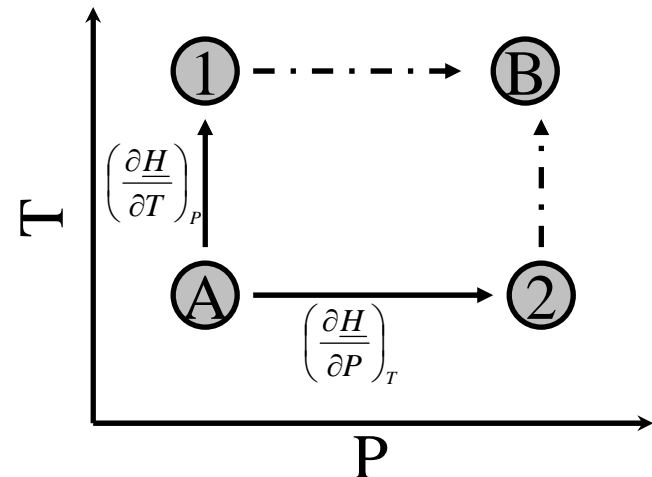
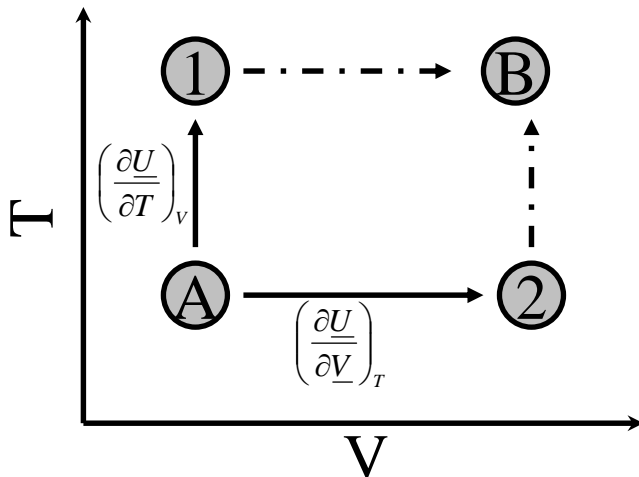
S. J. T. U.

Phase Transformation and Applications

The First Objective: to explore the variation of the energy functions (U and H) with temperature and pressure.

The heat capacities (C_p and C_v) give the change of U and H with temperature, at constant volume and constant pressure, respectively.

The Second Objective: to examine the dependence of properties, such as the internal energy, enthalpy, entropy, and other thermodynamic functions, on temperature, pressure, specific volume, and other intensive variables.





3.1 The property relation

A closed system consisting of a homogeneous material with uniform properties throughout.

$$\text{First law: } dU = \delta Q + \delta W$$

$$\text{Second law: } dS = \frac{\delta Q}{T} - \frac{\delta l w}{T}$$

$$TdS = \underline{\delta Q} - \delta l w$$

$$dU = TdS + \underline{\delta W} + \delta l w = TdS + \underline{\delta W_{rev}}$$

All the work terms:

Surface, electrical, stress effects, etc

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$



3.2 The Functions F and G (1)

S. J. T. U.
Phase Transformation and Applications

F: the Helmholtz free energy

G: the Gibbs free energy

Measures of the work required to change a system from one state to another.

$$dU = TdS + \delta W_{rev}$$

Integrating at constant temperature

$$W_{rev} = \Delta U - T\Delta S = \Delta U - \Delta(TS) = \Delta(U - TS)$$

U-TS is defined as the Helmholtz free energy F

$$W_{rev} = \Delta F$$



3.2 The Functions F and G (2)

S. J. T. U.

Phase Transformation and Applications

G: the Gibbs free energy

The useful work that can be done by the system must be calculated exclusive of the P-V term.

$$\delta W_{rev} = \delta W_{rev}^* - PdV = dU - TdS$$

Integrating at constant temperature and pressure

$$\begin{aligned} W_{rev}^* &= \Delta U + P\Delta V - T\Delta S = \Delta(U + PV - TS) \\ &= \Delta(H - TS) = \Delta G \end{aligned}$$

$$G = H - TS$$

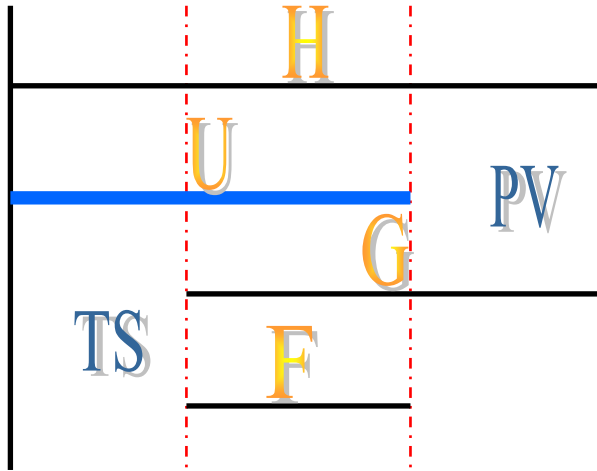
$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$



3.2 The Functions F and G (3)

S. J. T. U.
Phase Transformation and Applications



$$H \equiv U + PV$$

$$G \equiv H - TS$$

$$F \equiv U - TS$$



3.2 The Functions F and G (4)

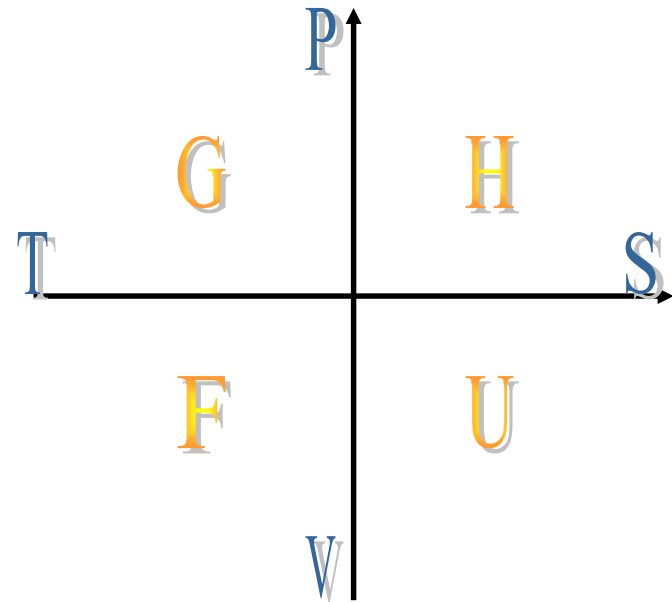
S. J. T. U.
Phase Transformation and Applications

$$dU = TdS - PdV$$

$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$

$$dH = TdS + VdP$$





3.3 Chemical Potentials (1)

S. J. T. U.
Phase Transformation and Applications

Closed systems consisting of a homogeneous material with uniform properties throughout.

$$U = U(S, V)$$

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

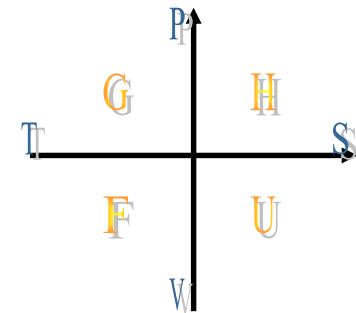
$$dU = TdS - PdV$$

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

$$\left(\frac{\partial F}{\partial T} \right)_V = -S \quad \left(\frac{\partial F}{\partial V} \right)_T = -P$$

$$\left(\frac{\partial G}{\partial T} \right)_P = -S \quad \left(\frac{\partial G}{\partial P} \right)_T = V$$

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





3.3 Chemical Potentials (2)

S. J. T. U.
Phase Transformation and Applications

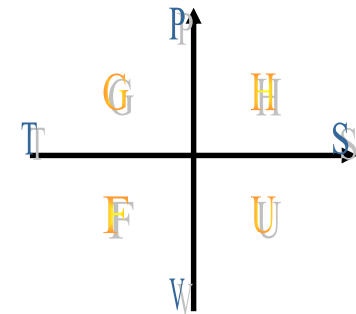
The thermodynamic equations **will be extended to deal with changes in composition through additions of mass.**

The equations are used especially for the treatment of solutions and chemical equilibria, where molar compositions are important. We will denote mass by the letter, n , number of moles.

$$U = U(S, V, n_i)$$

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_i \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j \neq n_i} dn_i$$

$$dU = TdS - PdV + \sum_i \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j \neq n_i} dn_i$$





3.3 Chemical Potentials (3)

S. J. T. U.
Phase Transformation and Applications

$$H = H(S, P, n_i)$$

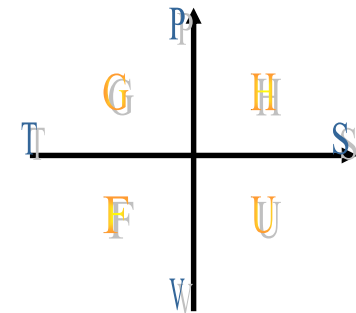
$$dH = \left(\frac{\partial H}{\partial S}\right)_{P, n_i} dS + \left(\frac{\partial H}{\partial P}\right)_{S, n_i} dP + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_j \neq n_i} dn_i$$

$$dH = TdS + VdP + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_j \neq n_i} dn_i$$

$$F = F(T, V, n_i)$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V, n_i} dT + \left(\frac{\partial F}{\partial V}\right)_{T, n_i} dV + \sum_i \left(\frac{\partial F}{\partial n_i}\right)_{T, V, n_j \neq n_i} dn_i$$

$$dF = -SdT - PdV + \sum_i \left(\frac{\partial F}{\partial n_i}\right)_{T, V, n_j \neq n_i} dn_i$$





3.3 Chemical Potentials (4)

S. J. T. U.
Phase Transformation and Applications

$$G = G(T, P, n_i)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq n_i} dn_i$$

$$dG = -SdT + VdP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq n_i} dn_i$$

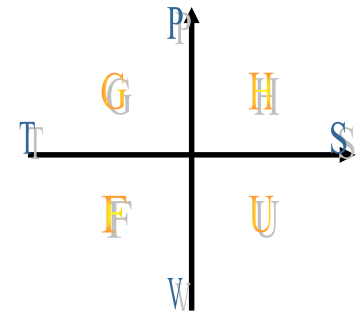
$$G = F + PV$$

$$dG = dF + PdV + VdP$$

$$dG = -SdT + VdP + \sum_i \left(\frac{\partial F}{\partial n_i}\right)_{T, V, n_j \neq n_i} dn_i$$

$$dF = -SdT - PdV + \sum_i \left(\frac{\partial F}{\partial n_i}\right)_{T, V, n_j \neq n_i} dn_i$$

$$\sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq n_i} dn_i = \sum_i \left(\frac{\partial F}{\partial n_i}\right)_{T, V, n_j \neq n_i} dn_i$$





3.3 Chemical Potentials (5)

S. J. T. U.

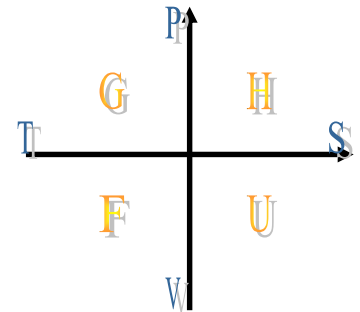
Phase Transformation and Applications

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j \neq n_i}$$

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j \neq n_i} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_j \neq n_i} = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j \neq n_i} = \mu_i$$

μ_i The chemical potential of the component i.

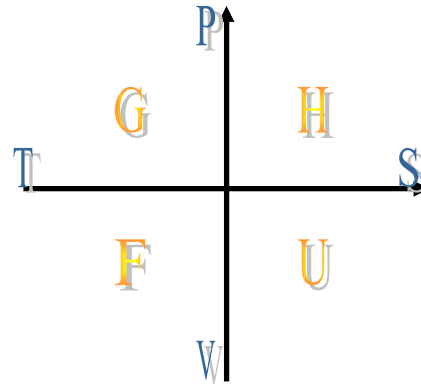
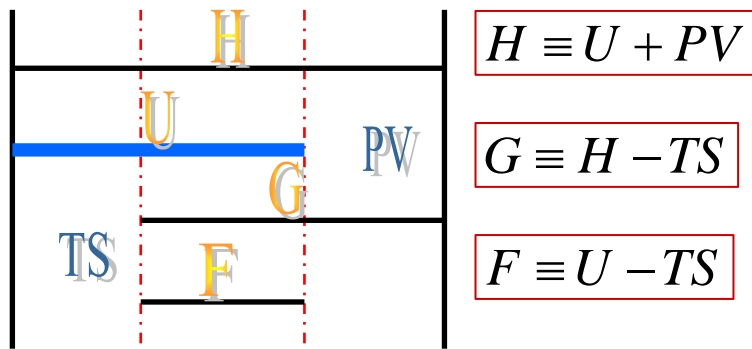
Used extensively in the treatment of the thermodynamics of solutions and of chemical reactions.





Review

当系统由始态I经过某一过程变到终态II后，如能使系统再回到原态，同时也消除了原过程对环境所产生的一切影响，则原来过程称为可逆过程。



$dU = TdS - PdV$

$dF = -SdT - PdV$

$dG = -SdT + VdP$

$dH = TdS + VdP$

μ_i The chemical potential of the component i.

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j \neq n_i} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_j \neq n_i} = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j \neq n_i} = \mu_i$$



Homework

Exercises in Chap 3

P94, 3.2