第二章

热力学定律和热力学基本方程

物理化学多媒体课堂教学软件 V1.0版

上一页　下一页　返回目录

2-1 引 言

物理化学多媒体课堂教学软件 V1.0版

热现象与力学现象

热力学—研究自然界中与热现象有关的各种状态变化和能量转化的规律的科学

0th law: 阐述热平衡特点

1st law: 能量转化在数值上守恒

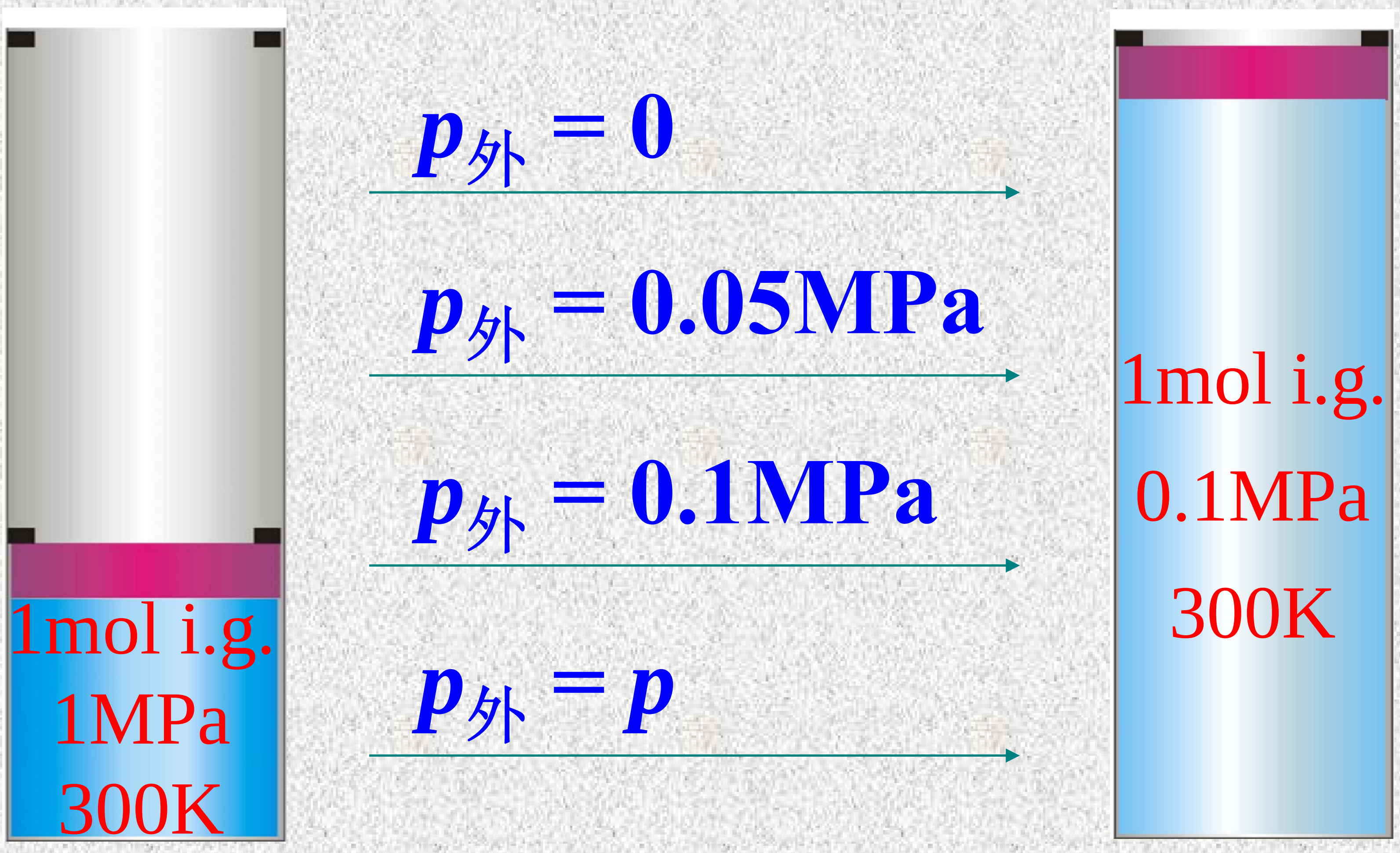
2nd law: 阐述热和功的本质差别

3rd law: 0K时恒温过程的熵变趋于零

应用

★运用1st law， 可以建立热和功之间的定量关系;

★运用1st law、2nd law， 研究过程的方向和限度。



1mol i.g.
1MPa
300K

$p_{外} = 0$

$p_{外} = 0.05\text{MPa}$

$p_{外} = 0.1\text{MPa}$

$p_{外} = p$

1mol i.g.
0.1MPa
300K

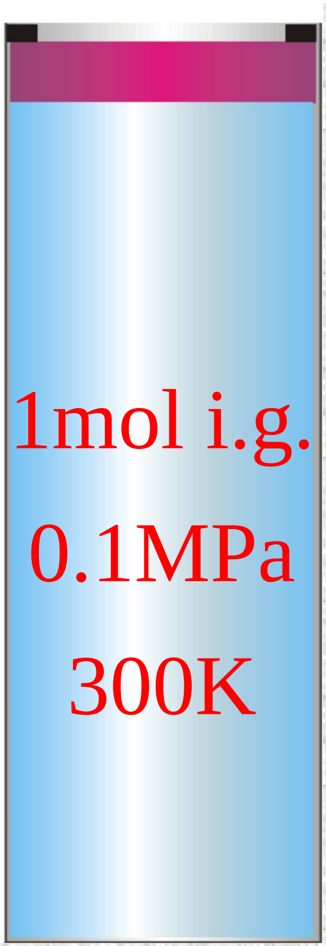
$$p_{外} = 2\mathrm{MPa}$$

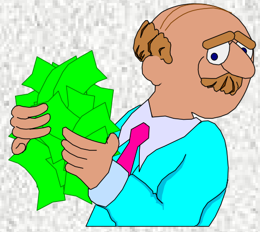
$$W = -\int p_{外}\mathrm{d}V$$

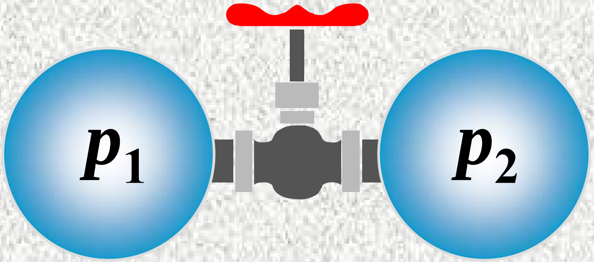
$$= -p_{外}(V_2 - V_1)$$

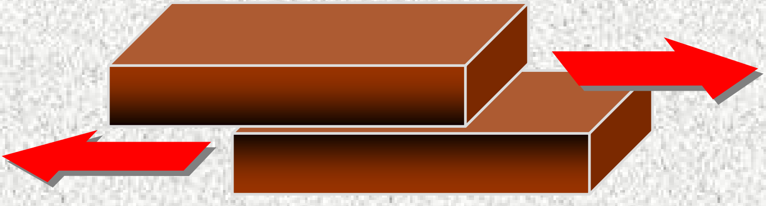
$$= -p_{外}nRT\left(\frac{1}{p_2} - \frac{1}{p_1}\right)$$

$$= -44880\mathrm{J}$$









$$N_2 + 3H_2 \rightarrow 2NH_3$$

过程在一定的条件下
是　可能进行的
或　已经达到极限（平衡）
或　不可能进行

方向
限度

恒温过程： $T_1=T_2=T_{\text{环}}=$常数

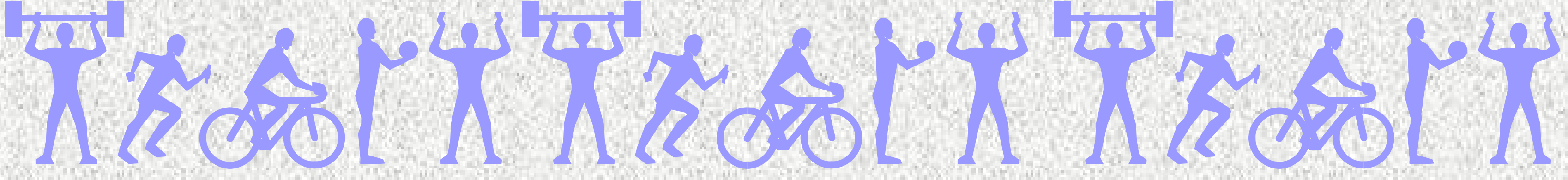
恒压过程： $p_1=p_2=p_{\text{外}}=$常数

恒容过程： $V_1=V_2=$常数

绝热过程： $Q=0$

循环过程： $\oint \mathrm{d}X=0$

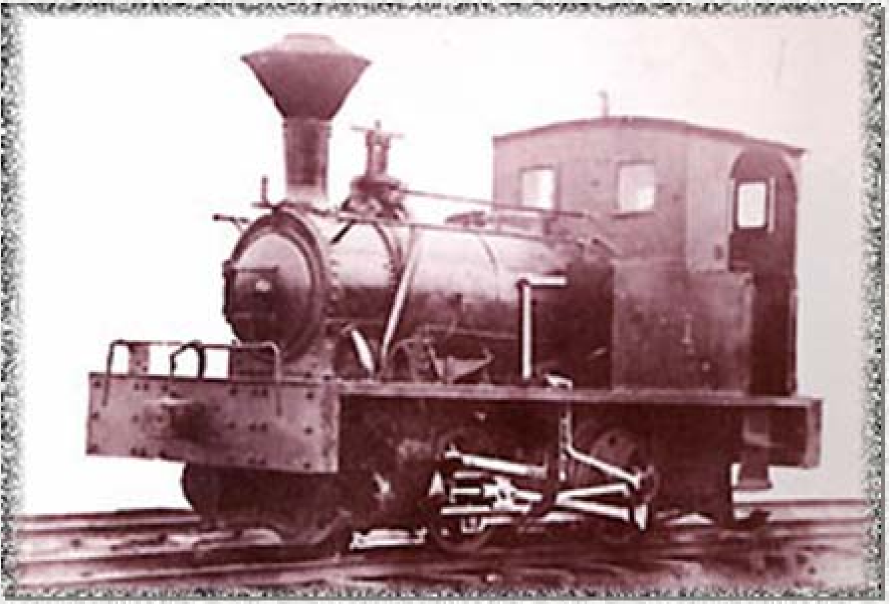
可逆过程： 无限趋近平衡并无摩擦力的条件下进行的过程



2-2

热力学第二定律

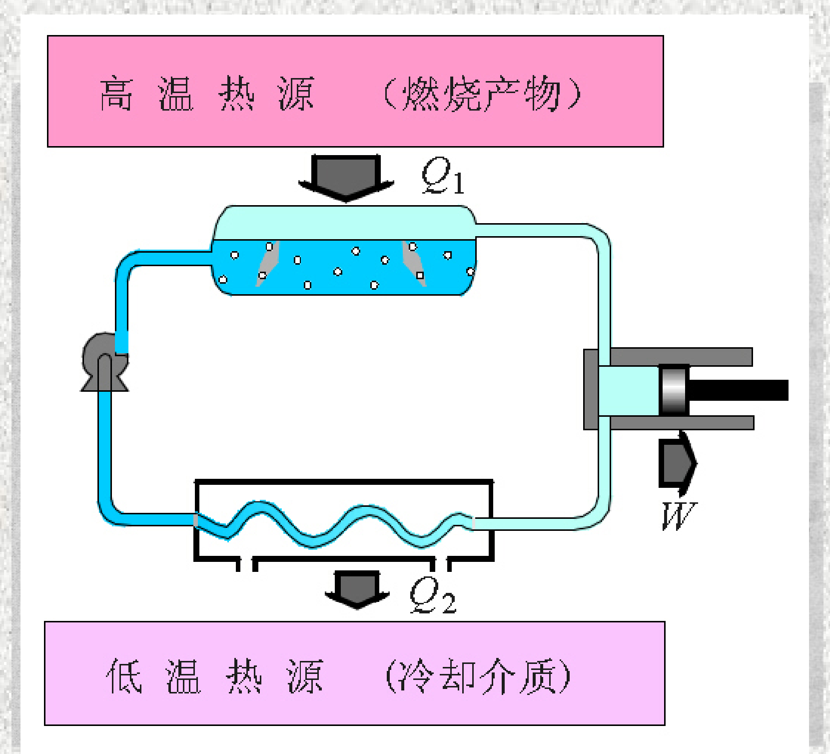
物理化学多媒体课堂教学软件 V1.0版



$$\Delta U = Q_1 + Q_2 + W = 0$$

$$\eta = -\frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1}$$

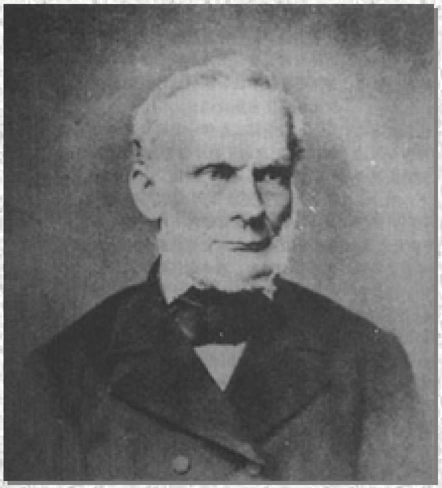
热机效率



高 温 热 源 （燃烧产物）

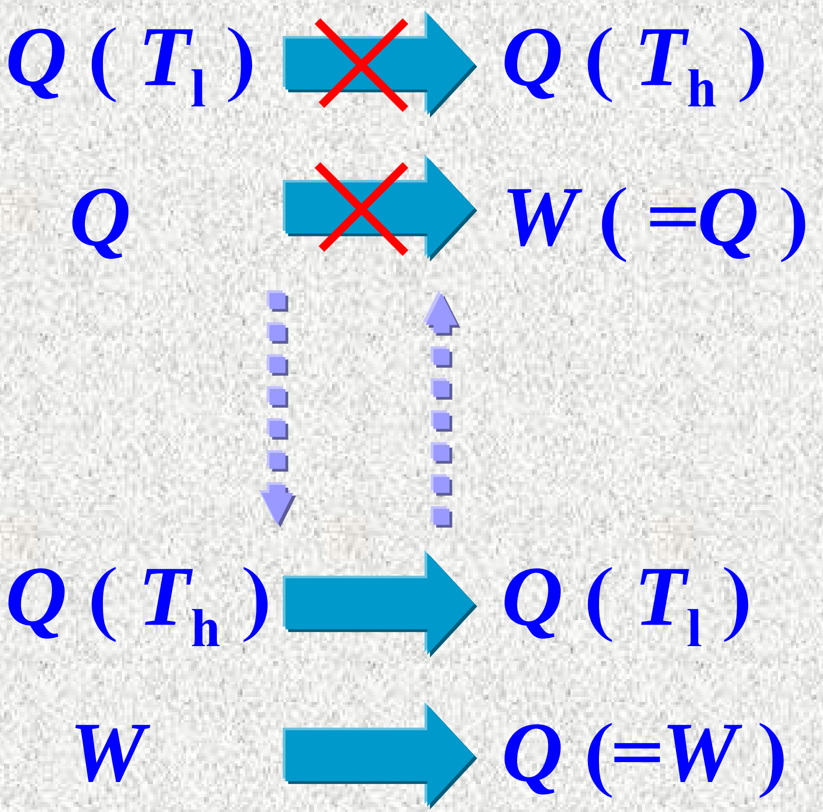
低 温 热 源 （冷却介质）

1. 热力学第二定律的克劳修斯说法和开尔文说法



克劳修斯：热从低温物体传给高温物体而不产生其它变化是不可能的.

开尔文：从一个热源吸热，使之完全转化为功，而不产生其它变化是不可能的。



$Q(T_\mathrm{l}) \not\longrightarrow Q(T_\mathrm{h})$

$Q \not\longrightarrow W(=Q)$

不可能发生

可逆过程

$Q(T_\mathrm{h}) \longrightarrow Q(T_\mathrm{l})$

$W \longrightarrow Q(=W)$

可能发生

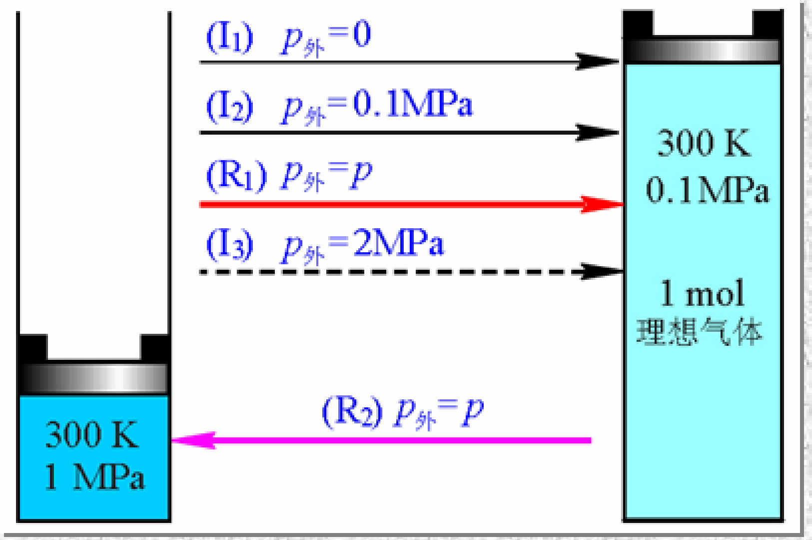
（不可逆过程）

不能简单逆转完全复原的过程

上一页　下一页　节首

2. 可逆过程

无限接近平衡并且没有摩擦力的条件下进行的过程



$$W_{\mathrm{I1}} = 0$$

$$W_{\mathrm{I2}} = -p_{外}(V_2 - V_1) = -p_{外} nRT(1/p_2 - 1/p_1) = -2245\,\mathrm{J}$$

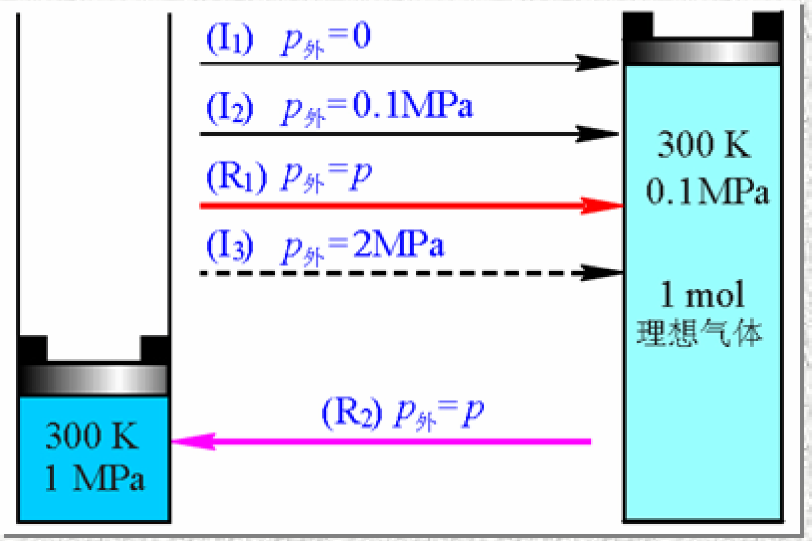
$$W_{\mathrm{R1}} = -\int_{V_1}^{V_2} p\mathrm{d}V = -nRT\int_{V_1}^{V_2}(1/V)\mathrm{d}V = -nRT\ln(V_2/V_1)$$

$$= nRT\ln(p_2/p_1) = -5743\,\mathrm{J}$$

$$W_{\mathrm{I3}} = -44.90\times10^{3}\,\mathrm{J}$$

$$W_{\mathrm{R2}} = nRT\ln(p_1/p_2) = 5743\,\mathrm{J}$$

2. 可逆过程



$W_{I1}=0$ $\qquad W_{I2}=-2245\text{J}$

$W_{R1}=-5743\text{J}$

$W_{I3}=-44.90\times10^{3}\text{J}$

$W_{R2}=5743\text{J}$

I1+R2: $Q=-W=-W_{I1}-W_{R2}=-5743\text{J}$（系统放热，得功）

I2+R2: $Q=-W=-W_{I2}-W_{R2}=-3498\text{J}$（系统放热，得功）

R1+R2: $Q=-W=-W_{R1}-W_{R2}=0$

I3+R2: $Q=-W=-W_{I3}-W_{R2}=39.16\times10^{3}\text{J}$（系统吸热，作功）

不可逆过程： 不能简单逆转完全复原的过程

- 在同样条件下，逆过程不能发生
- 循环后系统复原，环境遗留不可逆变化
- 自然界实际发生的过程都是不可逆过程

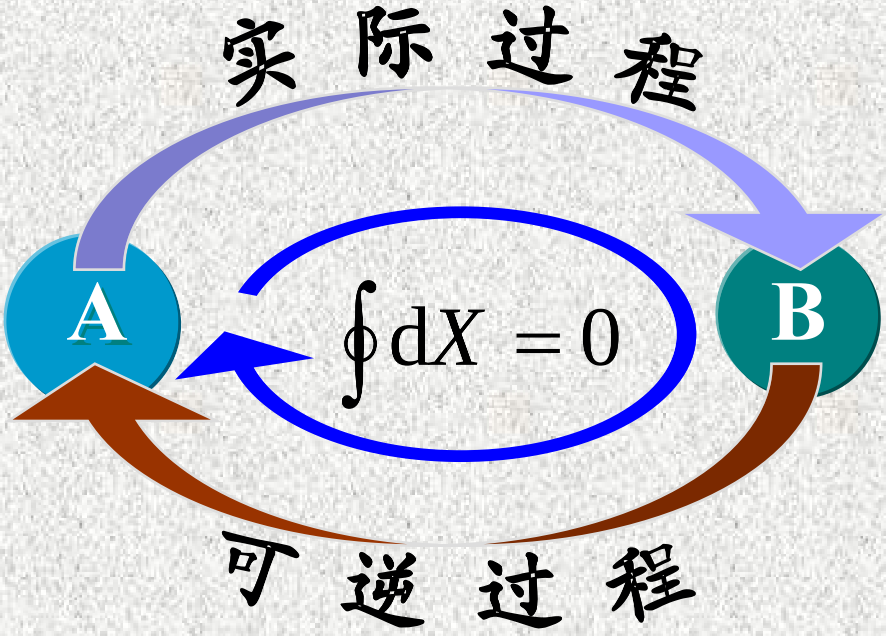
可逆过程： 平衡且没有摩擦力条件下进行的过程

- 在同样条件下，正逆过程都能进行
- 循环后系统复原，环境没有遗留不可逆变化
- 可逆过程是一种抽象的理想过程

实际过程 ⇄ 可逆过程 ⇄ 不可能过程

怎样判断一个过程？

可将该过程与一个以该过程的终态为初态，该过程的初态为终态的可逆过程组成一个循环，然后考察一个循环后环境是否留有任何不可逆变化：



- 没有—可逆过程
- 有　—不可逆过程
- 违反热力学第二定律—不可能过程

2-3 卡诺循环
与卡诺定理

物理化学多媒体课堂教学软件 V1.0版

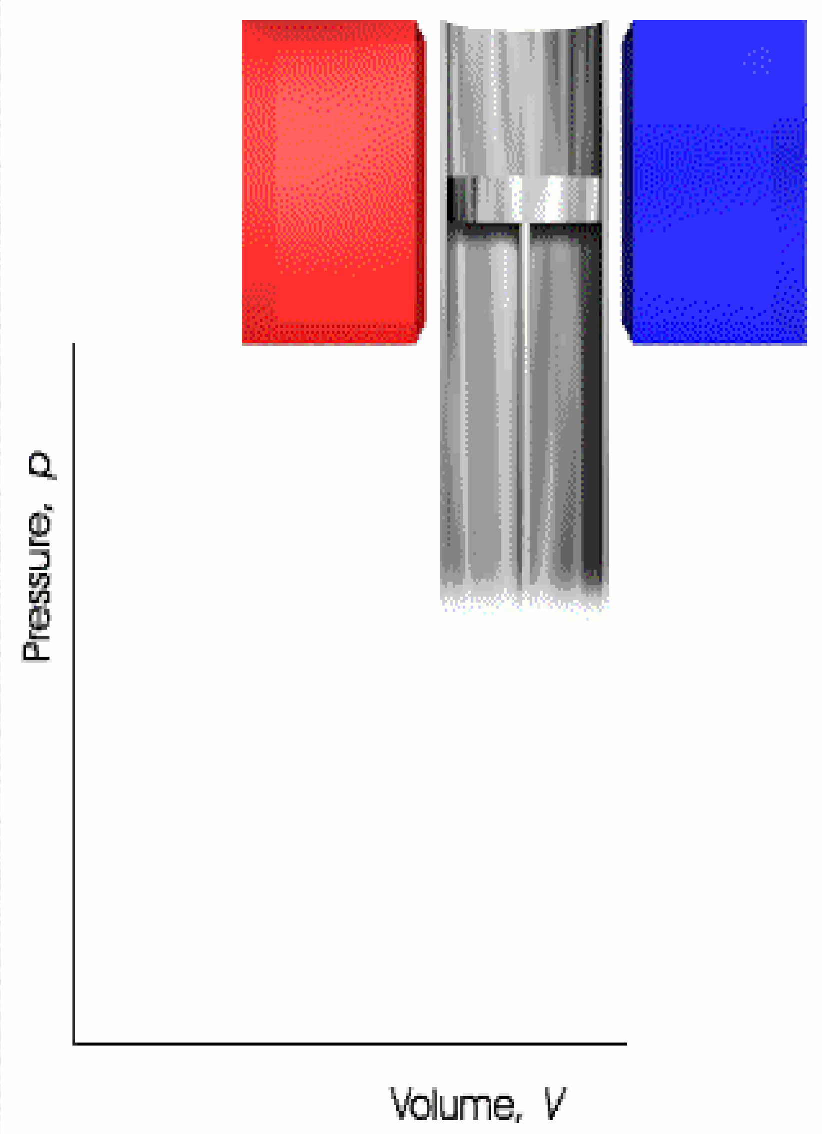
1. 卡诺循环

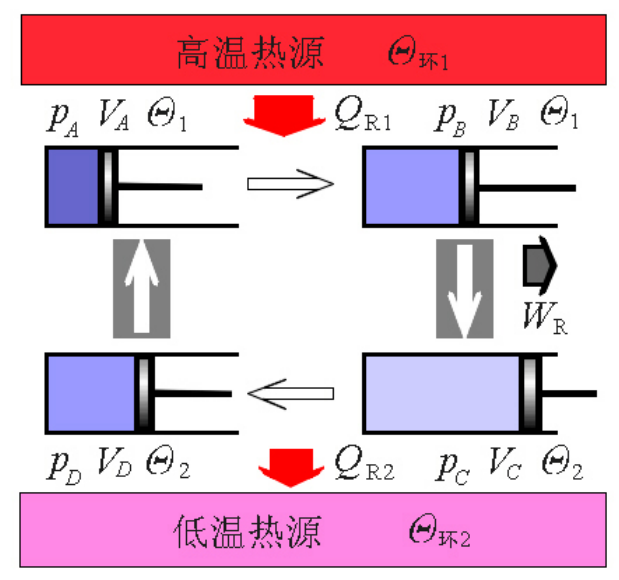
A→*B*：恒温可逆膨胀

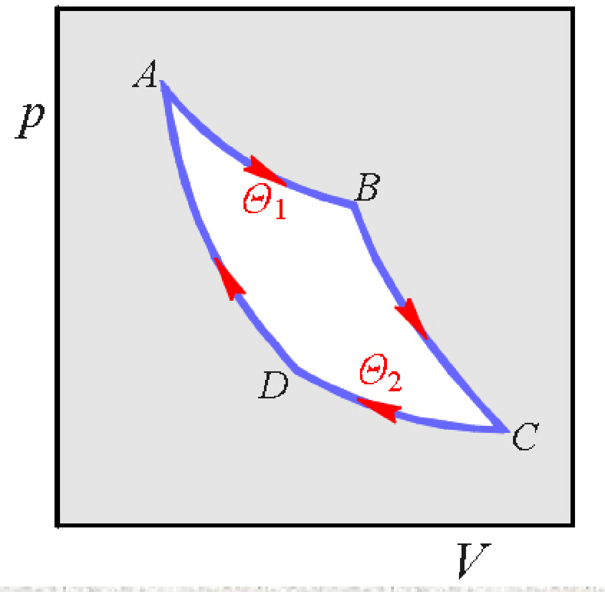
B→*C*：绝热可逆膨胀

C→*D*：恒温可逆压缩

D→*A*：绝热可逆压缩







A→B： 恒温可逆膨胀

B→C： 绝热可逆膨胀

C→D： 恒温可逆压缩

D→A： 绝热可逆压缩

$$W_R + Q_{R1} + Q_{R2} = 0$$

$$\eta_R = -\frac{W_R}{Q_{R1}} = \frac{Q_{R1} + Q_{R2}}{Q_{R1}}$$

2. 卡诺定理

所有工作于两个温度一定的热源之间的热机，以可逆热机的热机效率为最大

$$\eta > \eta_{\mathrm{R}} \quad Q_1 = Q_{\mathrm{R1}}$$

$$-W > -W_{\mathrm{R}}$$

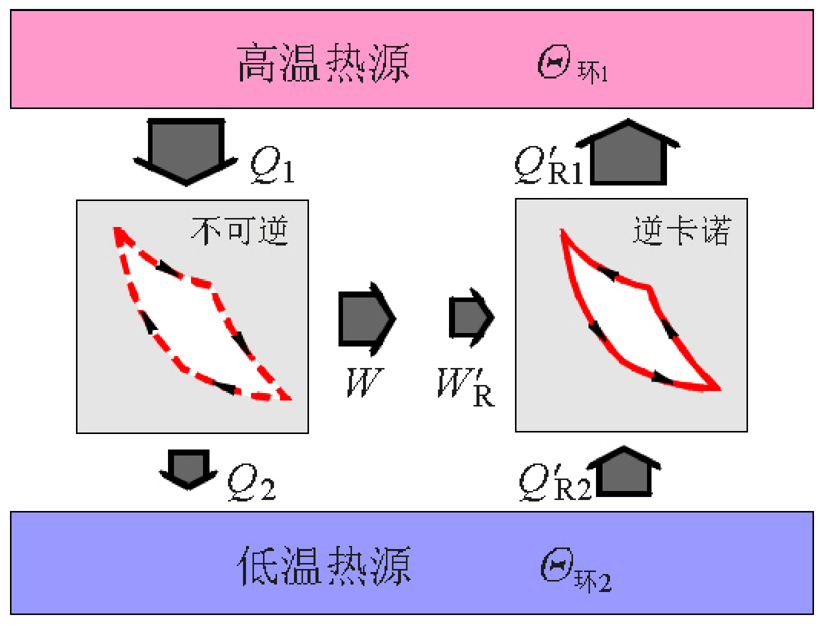
$$W'_{\mathrm{R}} = -W_{\mathrm{R}}$$

$$Q'_{\mathrm{R1}} = -Q_{\mathrm{R1}} \quad Q'_{\mathrm{R2}} = -Q_{\mathrm{R2}}$$

$$-(W + W'_{\mathrm{R}}) > 0$$

$$Q_2 + Q'_{\mathrm{R2}} > 0$$

不可能

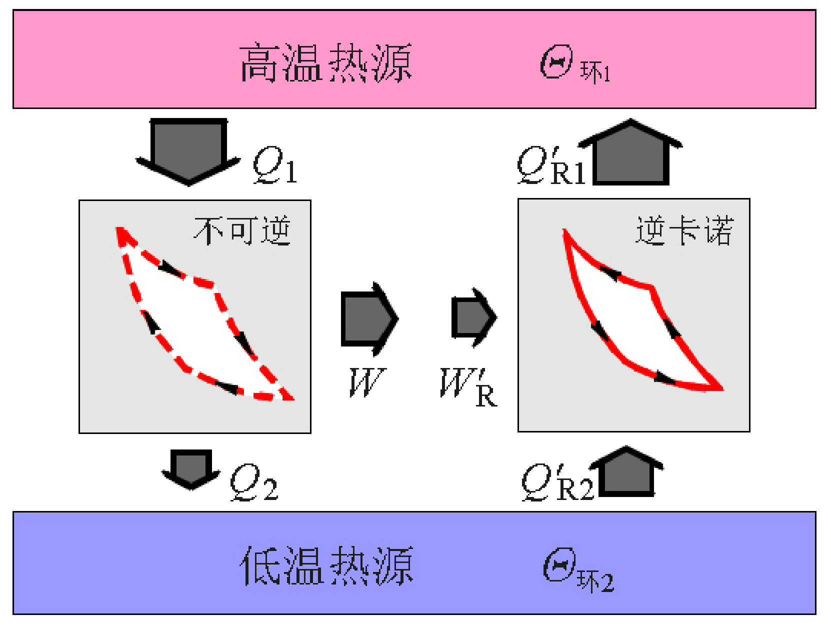


上一页 下一页 节首

2. 卡诺定理

所有工作于两个温度一定的热源之间的热机，以可逆热机的热机效率为最大

- 卡诺热机的效率只决定于两个热源的温度
- 工作于两个温度一定的热源之间的所有可逆热机的效率相等



3. 热力学温标

$$-\frac{Q_{\mathrm{R1}}}{Q_{\mathrm{R2}}}=\frac{1}{1-\eta_{\mathrm{R}}}=F(\Theta_1,\Theta_2)$$

$$-\frac{Q_{\mathrm{R1}}}{Q_{\mathrm{R2}}}=\frac{f(\Theta_1)}{f(\Theta_2)}$$

$$\eta_{\mathrm{R}}=\frac{Q_{\mathrm{R1}}+Q_{\mathrm{R2}}}{Q_{\mathrm{R1}}}=\frac{T_{环1}-T_{环2}}{T_{环1}}$$

第十届国际计量大会决定水的三相点的热力学温度为273.16K

上一页 下一页 节首

2-4 克劳修斯不等式和可逆性判据

物理化学多媒体课堂教学软件 V1.0版

1. 卡诺循环的热温商

$$\eta_{\mathrm{R}} = \frac{Q_{\mathrm{R1}} + Q_{\mathrm{R2}}}{Q_{\mathrm{R1}}} = \frac{T_{\text{环}1} - T_{\text{环}2}}{T_{\text{环}1}}$$

$$1 + \frac{Q_{\mathrm{R2}}}{Q_{\mathrm{R1}}} = 1 - \frac{T_{\text{环}2}}{T_{\text{环}1}} = 1 - \frac{T_2}{T_1}$$

$$\frac{Q_{\mathrm{R1}}}{T_{\text{环}1}} + \frac{Q_{\mathrm{R2}}}{T_{\text{环}2}} = \frac{Q_{\mathrm{R1}}}{T_1} + \frac{Q_{\mathrm{R2}}}{T_2} = 0 \quad \Rightarrow \quad \sum \frac{Q_{\mathrm{R}}}{T} = 0$$

$$\text{热温商} = \frac{\text{系统吸收或放出的热}}{\text{相应的环境温度}}$$

1. 卡诺循环的热温商

$$\eta_{\mathrm{R}} = \frac{Q_{\mathrm{R1}} + Q_{\mathrm{R2}}}{Q_{\mathrm{R1}}} = \frac{T_{\text{环}1} - T_{\text{环}2}}{T_{\text{环}1}}$$

$$1 + \frac{Q_{\mathrm{R2}}}{Q_{\mathrm{R1}}} = 1 - \frac{T_{\text{环}2}}{T_{\text{环}1}} = 1 - \frac{T_2}{T_1}$$

$$\sum \frac{Q_{\mathrm{R}}}{T} = 0$$

循环完成后，环境的变化可通过逆卡诺循环消除，不遗留不可逆变化

2. 两个热源间的不可逆循环

$$\frac{Q_! + Q_2}{Q_1} < \frac{T_{\text{环}1} - T_{\text{环}2}}{T_{\text{环}1}}$$

$$\frac{Q_1}{T_{\text{环}1}} + \frac{Q_2}{T_{\text{环}2}} < 0$$

$$\sum \frac{Q}{T_{\text{环}}} < 0$$

循环完成后，环境遗留不能消除的不可逆变化

上一页 下一页 节首

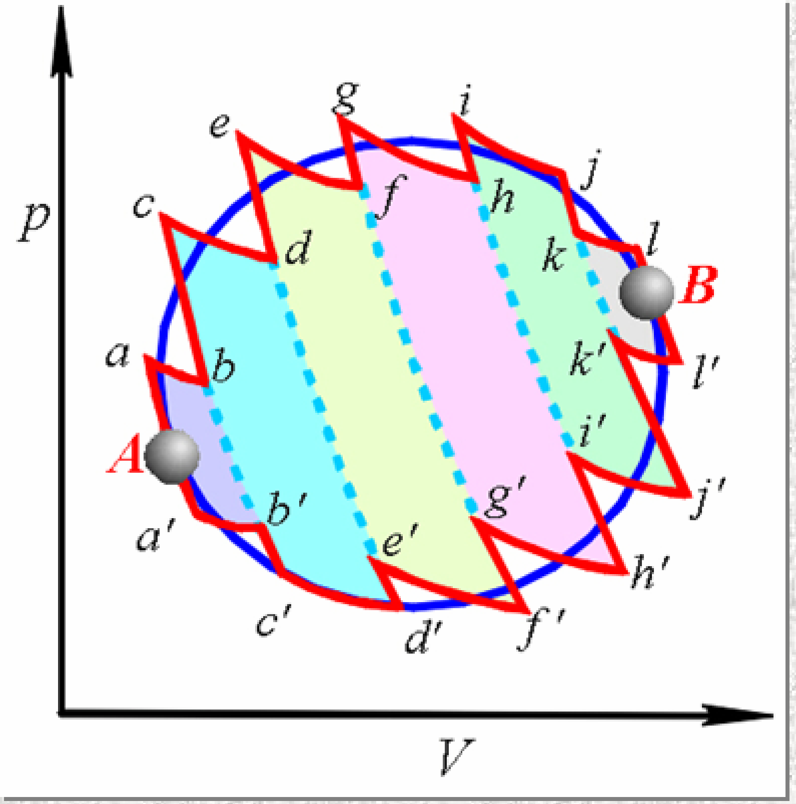
3. 任意可逆循环的热温商

$$\frac{\text{đ}Q_{\mathrm{R}ab}}{T_{ab}}+\frac{\text{đ}Q_{\mathrm{R}\ a'b'}}{T_{a'b'}}=0$$

$$\frac{\text{đ}Q_{\mathrm{R}ab}}{T_{ab}}+\frac{\text{đ}Q_{\mathrm{R}\ a'b'}}{T_{a'b'}}+\frac{\text{đ}Q_{\mathrm{R}cd}}{T_{cd}}$$

$$+\frac{\text{đ}Q_{\mathrm{R}\,c'd'}}{T_{c'd'}}+\cdots=0$$

$$\boxed{\oint\frac{\text{đ}Q_{\mathrm{R}}}{T}=0}$$

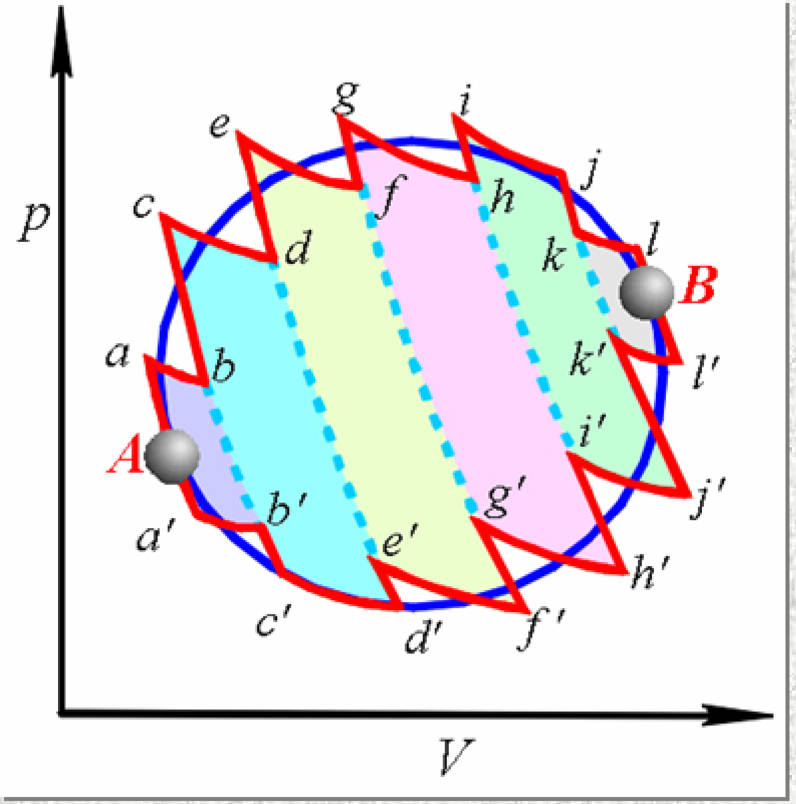


4. 任意不可逆循环的热温商

$$\frac{\text{đ}Q_{ab}}{T_{\text{环}ab}}+\frac{\text{đ}Q_{a'b'}}{T_{\text{环}a'b'}}<0$$

$$\frac{\text{đ}Q_{ab}}{T_{\text{环}ab}}+\frac{\text{đ}Q_{a'b'}}{T_{\text{环}a'b'}}+\frac{\text{đ}Q_{cd}}{T_{\text{环}cd}}$$

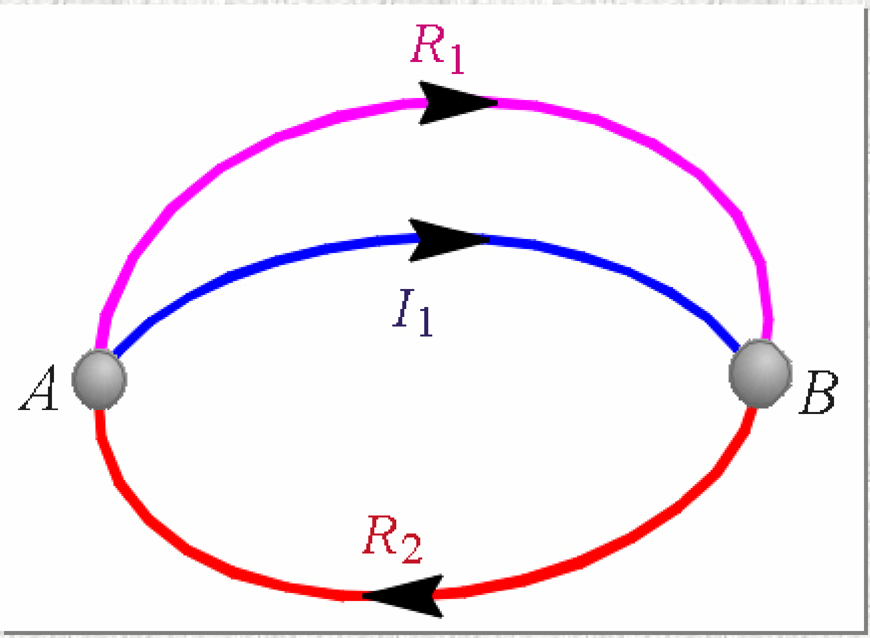
$$+\frac{\text{đ}Q_{c'd'}}{T_{\text{环}c'd'}}+\cdots<0$$



$$\boxed{\oint\frac{\text{đ}Q}{T_{\text{环}}}<0}$$

5. 任意可逆过程的热温商

$$\oint \frac{\text{đ}Q_\text{R}}{T} = \int_{A(\text{沿R1})}^{B} \frac{\text{đ}Q_\text{R}}{T} + \int_{B(\text{沿R2})}^{A} \frac{\text{đ}Q_\text{R}}{T} = 0$$

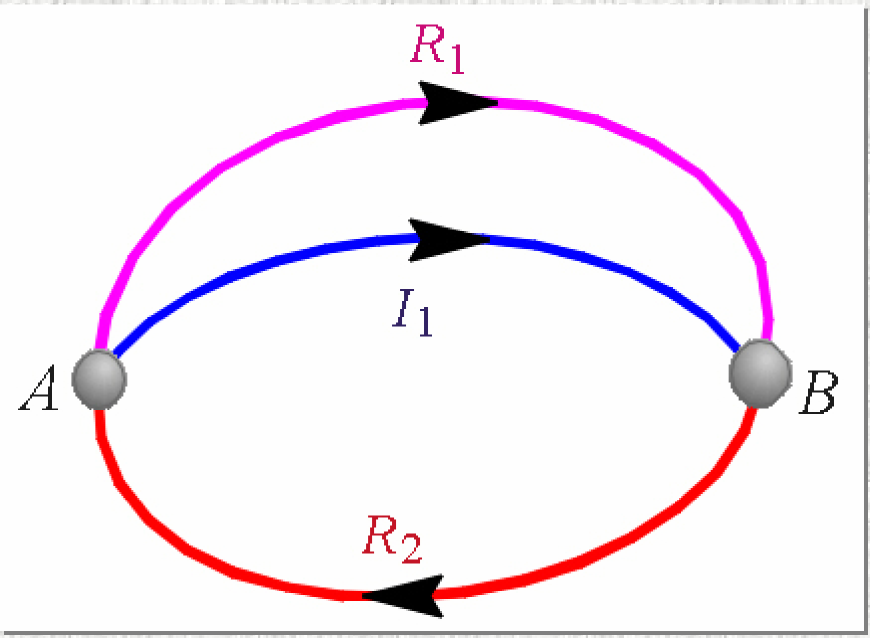


$$\int_{A(\text{沿R1})}^{B} \frac{\text{đ}Q_\text{R}}{T} = \int_{A(\text{沿R2})}^{B} \frac{\text{đ}Q_\text{R}}{T}$$

可逆过程的热温商只决定于初终态，与过程无关

6. 任意不可逆过程的热温商

$$\oint \frac{\text{đ}Q}{T_{\text{环}}} = \int_{A(\text{沿}I1)}^{B} \frac{\text{đ}Q}{T_{\text{环}}} + \int_{B(\text{沿R2})}^{A} \frac{\text{đ}Q_{\mathrm{R}}}{T} < 0$$



$$\boxed{\int_{A}^{B} \frac{\text{đ}Q}{T_{\text{环}}} < \int_{A}^{B} \frac{\text{đ}Q_{\mathrm{R}}}{T}}$$

不可逆过程的热温商恒小于可逆过程的热温商

两个热源间循环的热温商

$$\sum \frac{Q_{\mathrm{R}}}{T} = 0$$

$$\sum \frac{Q}{T_{环}} < 0$$

任意循环的热温商

$$\oint \frac{\text{đ} Q_{\mathrm{R}}}{T} = 0$$

$$\oint \frac{\text{đ} Q}{T_{环}} < 0$$

任意过程的热温商

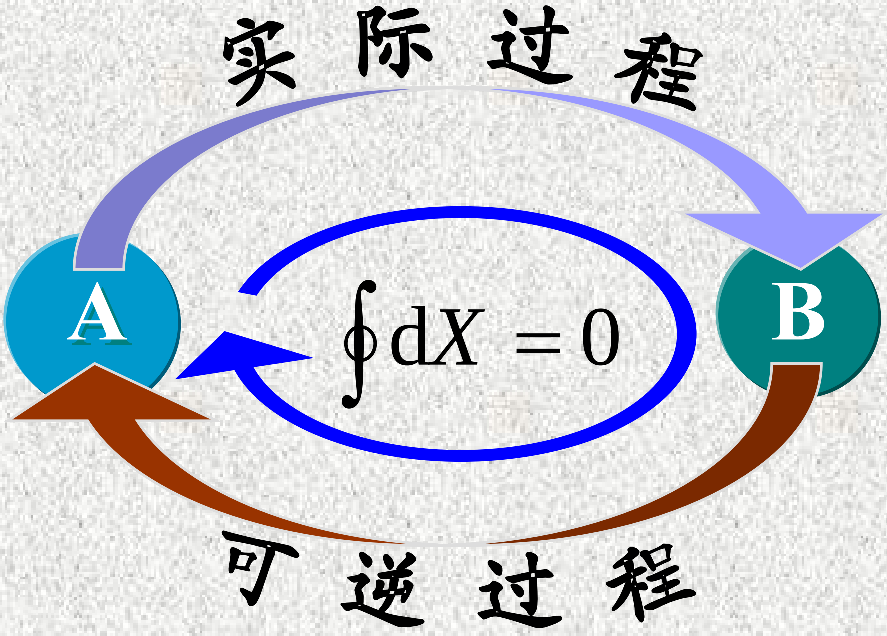
$$\int_{A(沿\mathrm{R1})}^{B} \frac{\text{đ} Q_{\mathrm{R}}}{T} = \int_{A(沿\mathrm{R2})}^{B} \frac{\text{đ} Q_{\mathrm{R}}}{T}$$

$$\int_{A}^{B} \frac{\text{đ} Q}{T_{环}} < \int_{A}^{B} \frac{\text{đ} Q_{\mathrm{R}}}{T}$$

上一页 下一页 节首

判断一个过程是否可逆（1）

可将该过程与一个以该过程的终态为初态，该过程的初态为终态的可逆过程组成一个循环，然后考察一个循环后环境是否留有任何不可逆变化:



◆没有—可逆过程

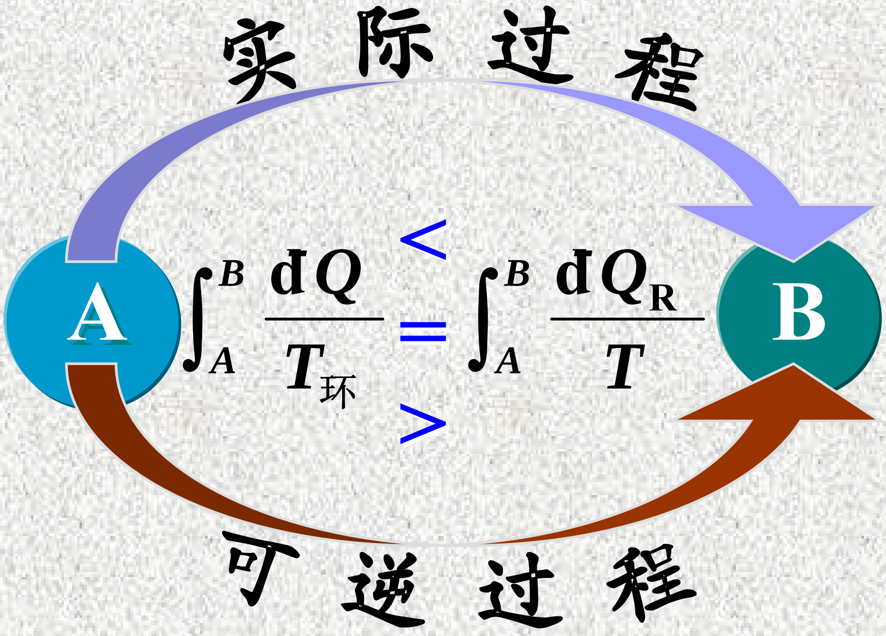
◆有 —不可逆过程

◆违反热力学第二定律

—不可能发生

判断一个过程是否可逆（2）

可将该过程的热温商与一个具有同样初终态的可逆过程的热温商进行比较：



$$\int_A^B \frac{\text{đ}Q}{T_{\text{环}}} \begin{matrix} < \\ = \\ > \end{matrix} \int_A^B \frac{\text{đ}Q_{\text{R}}}{T}$$

- ◆小于　不可逆过程
- ◆等于　可逆过程
- ◆大于　违反热力学第二定律

—不可能发生

7. 克劳修斯不等式和可逆性判据

$$\int_A^B \frac{\text{đ}Q_\mathrm{R}}{T} - \int_A^B \frac{\text{đ}Q}{T_{环}} \geq 0$$

$$\frac{\text{đ}Q_\mathrm{R}}{T} - \frac{\text{đ}Q}{T_{环}} \geq 0$$

>0 不可逆过程

$=0$ 可逆过程

<0 不可能发生

克劳修斯不等式

2-5 熵与熵增原理

物理化学多媒体课堂教学软件 V1.0版

1. 熵的定义

$\int_A^B (đQ_R/T)$ ➡ 与过程无关 ➡ △状态函数 **熵**

$$\Delta S = S_B - S_A \overset{\text{def}}{=\!=} \int_A^B \frac{đQ_R}{T}$$

◆ **熵是一个状态函数，是物质的特性**

◆ **常用单位：J·K^{-1}**

◆ $dS \overset{\text{def}}{=\!=} \dfrac{đQ_R}{T} \qquad \oint dS = \oint \dfrac{đQ_R}{T} = 0$

2. 不可逆程度

$$\Delta S-\int_A^B \frac{\text{đ}Q}{T_{环}}$$

$$\int_A^B T_{环}\,\mathrm{d}S-Q$$

>0 不可逆过程

$=0$ 可逆过程

<0 不可能发生

度量过程的不可逆程度

2. 不可逆程度

$$\mathrm{d}S - \frac{\text{đ}Q}{T_{\text{环}}}$$

$$T_{\text{环}}\mathrm{d}S - \text{đ}Q$$

$\Rightarrow$ >0 不可逆过程

$\Rightarrow$ $=0$ 可逆过程

$\Rightarrow$ <0 不可能发生

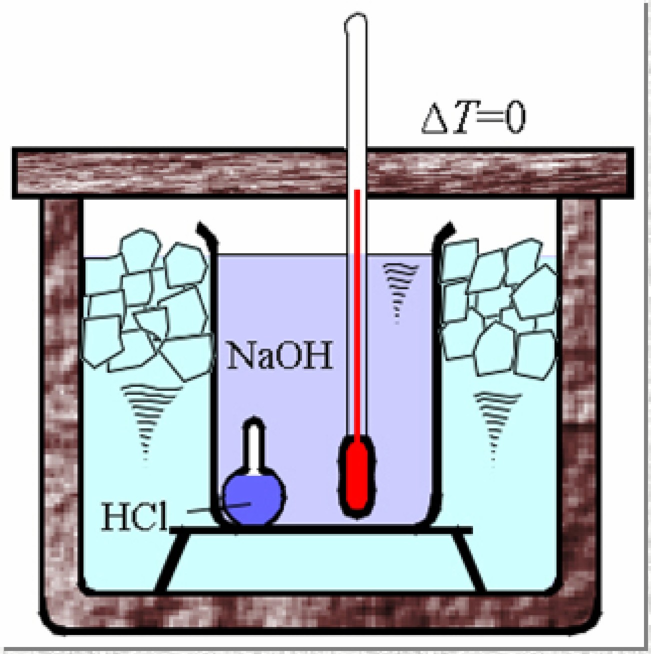
度量过程的不可逆程度

3. 熵增原理　孤立系统的熵有增无减

*孤立系统：

$$\text{đ}Q = 0 \quad \text{đ}W = 0$$

$$\mathrm{d}U = 0 \quad \mathrm{d}V = 0 \quad \text{đ}W' = 0$$



$$\mathrm{d}S - \frac{\text{đ}Q}{T_{环}} \geq 0$$

$$\mathrm{d}S_{孤立} = \mathrm{d}S_{U,V,W'=0} \geq 0$$

>0 不可逆过程

$=0$ 可逆过程

<0 不可能发生

*绝热过程：　$\text{đ}Q = 0$

$$\mathrm{d}S - \frac{\text{đ}Q}{T_{环}} \geq 0 \quad \Longrightarrow \quad \mathrm{d}S_{绝热} = \mathrm{d}S_{Q} \geq 0$$

环境无限大，仅发生微小变化均为可逆过程：

$$\mathrm{d}S_{环} = -\frac{\text{đ}Q}{T_{环}}$$

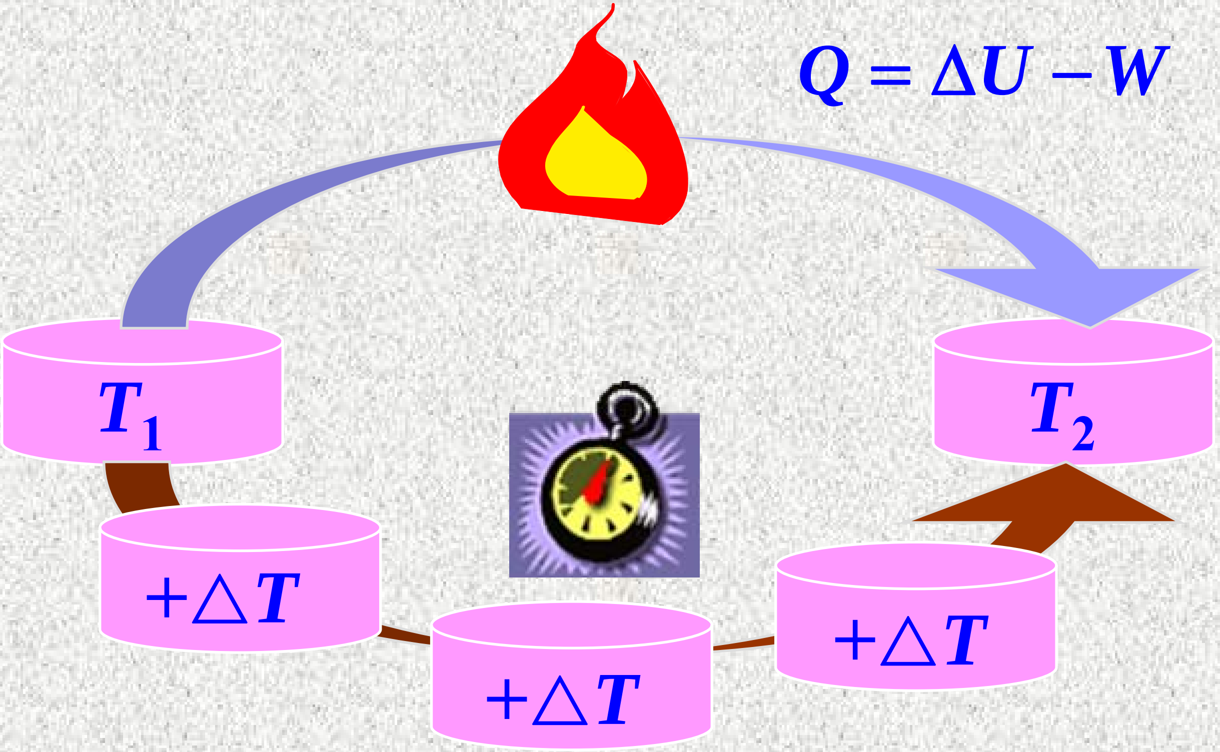
*环境和系统的总和即孤立系统

$$\mathrm{d}S_{系统} + \mathrm{d}S_{环境} = \mathrm{d}S_{孤立} \geq 0$$

上一页　下一页　节首

例1 1molH_2O(l)于0.1MPa下自25℃升温至50℃，求熵变和热温商，并判断可逆性。已知 $C_{p,\mathrm{m}}=75.40\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
(1)热源温度700℃; (2)热源温度100℃。

解:



$$Q=\Delta U-W$$

上一页　下一页　节首

例1 1molH_2O(l)于0.1MPa下自25℃升温至50℃，求熵变和热温商，并判断可逆性。已知 $C_{p,\mathrm{m}}=75.40\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$ (1)热源温度700℃; (2)热源温度100℃。

解:

$$\text{đ}Q_\mathrm{R}=\text{đ}Q_p=nC_{p,\mathrm{m}}\mathrm{d}T$$

$$\Delta S=S_2-S_1=\int_A^B(\text{đ}Q_\mathrm{R}/T)$$

$$=n\int_{T_1}^{T_2}(C_{p,\mathrm{m}}\mathrm{d}T/T)$$

$$\Delta S=S_{50^\circ\mathrm{C}}-S_{25^\circ\mathrm{C}}$$

$$=n\int_{T_1}^{T_2}(C_{p,\mathrm{m}}\mathrm{d}T/T)$$

$$=nC_{p,\mathrm{m}}\ln(T_2/T_1)$$

例1 1molH_2O(l)于0.1MPa下自25℃升温至50℃，求熵变和热温商，并判断可逆性。已知 $C_{p,\mathrm{m}}=75.40\mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1}$ (1)热源温度700℃; (2)热源温度100℃。

解:

$$\Delta S=\left[1\times 75.40\ln\left(\frac{323.3}{298.2}\right)\right]\mathrm{J}\cdot\mathrm{K}^{-1}=6.070\mathrm{J}\cdot\mathrm{K}^{-1}$$

$$\int_A^B(\text{đ}Q/T_{环})=Q/T_{环}=n\int_{T_1}^{T_2}(C_{p,m}\mathrm{d}T)/T_{环}$$

$$=\frac{nC_{p,\mathrm{m}}(T_2-T_1)}{T_{环}}=\left(\frac{1\times 75.40\times 25}{973.2}\right)\mathrm{J}\cdot\mathrm{K}^{-1}=1.937\mathrm{J}\cdot\mathrm{K}^{-1}$$

$$\Delta S-\int_A^B\frac{\text{đ}Q}{T_{环}}=(6.070-1.937)\mathrm{J}\cdot\mathrm{K}^{-1}=4.133\mathrm{J}\cdot\mathrm{K}^{-1}>0$$

例1 1molH_2O(l)于0.1MPa下自25℃升温至50℃，求熵变和热温商，并判断可逆性。已知 $C_{p,\mathrm{m}}=75.40\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ (1)热源温度700℃; (2)热源温度100℃。

解:

$$\Delta S=\left[1\times 75.40\ln\left(\frac{323.3}{298.2}\right)\right]\mathrm{J\cdot K^{-1}}=6.070\mathrm{J\cdot K^{-1}}$$

$$\int_A^B\frac{đQ}{T_{环}}=\frac{Q}{T_{环}}=\left(\frac{1\times 75.40\times 25}{373.2}\right)\mathrm{J\cdot K^{-1}}=5.051\mathrm{J\cdot K^{-1}}$$

$$\Delta S-\int_A^B\frac{đQ}{T_{环}}=(6.070-5.051)\mathrm{J\cdot K^{-1}}=1.019\mathrm{J\cdot K^{-1}}>0$$

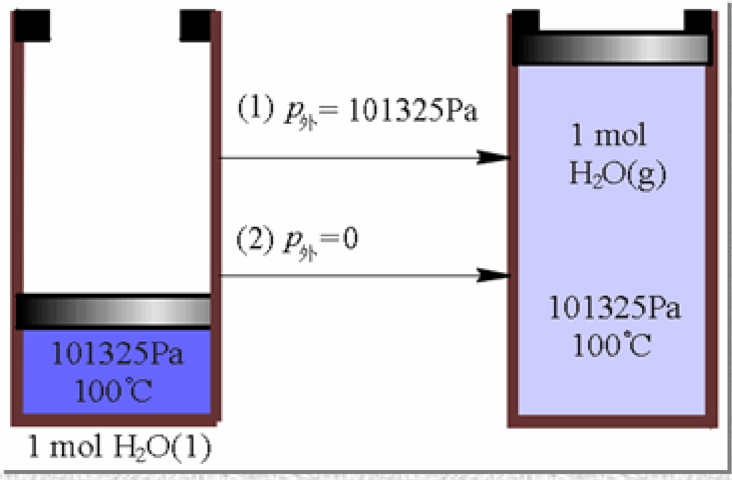
例2 100℃, 101325Pa下1 mol$H_2O(l)$气化为101325Pa的水蒸气，已知此时H_2O (l)的蒸发热为40.66kJmol^{-1}，试计算熵变和热温商，并判断过程可逆性。
(1) $p_{外}$=101325Pa，(2) $p_{外}$=0。

解:

$$\Delta S = S_2 - S_1 = \int_A^B (\text{đ}Q_{\mathrm{R}}/T)$$

$$= \frac{Q_{\mathrm{R}}}{T} = \frac{Q_p}{T} = \frac{\Delta H}{T}$$

$$= 108.9\,\mathrm{J\cdot K^{-1}}$$



$$\int_A^B (\text{đ}Q/T_{环}) = Q_1/T = (40.66\times10^3/373.2)\,\mathrm{J\cdot K^{-1}} = 108.9\,\mathrm{J\cdot K^{-1}}$$

不可逆程度: $$\Delta S - \int_A^B (\text{đ}Q/T_{环}) = 0$$

例2 100℃, 101325Pa下1 mol$H_2O(l)$气化为101325Pa的水蒸气，已知此时H_2O (l)的蒸发热为40.66kJmol^{-1}，试计算熵变和热温商，并判断过程可逆性。
(1) $p_{外}$=101325Pa，(2) $p_{外}$=0。

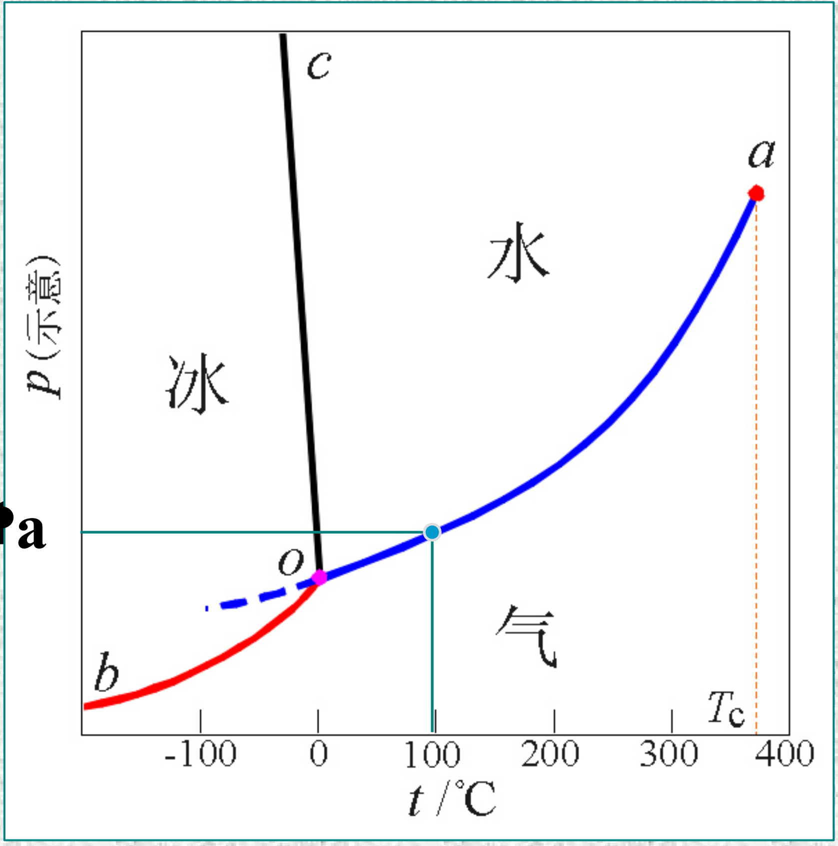
解:

$$\Delta S = 108.9\mathrm{J}\cdot\mathrm{K}^{-1}$$

$$\int_A^B \frac{đQ}{T_{环}} = \frac{Q_2}{T} = \left(\frac{37.61\times10^3}{373.2}\right)\mathrm{J}\cdot\mathrm{K}^{-1} = 100.8\mathrm{J}\cdot\mathrm{K}^{-1}$$

不可逆程度: $\Delta S - \int_A^B \frac{đQ}{T_{环}} = (108.9-100.8)\mathrm{J}\cdot\mathrm{K}^{-1} > 0$

101325Pa



2-6 亥姆霍兹函数和吉布斯函数

物理化学多媒体课堂教学软件 V1.0版

- ◆ **亥姆霍兹函数**

$$A \overset{\text{def}}{=\!=} U - TS$$

- ◆ **吉布斯函数**

$$G \overset{\text{def}}{=\!=} H - TS$$

$$G = H - TS = U + pV - TS = A + pV$$

1. 恒温过程

$$T_{\text{环}} = T$$

$$\text{đ}Q + \text{đ}W = \mathrm{d}U$$

$$\Longrightarrow \quad T\mathrm{d}S - \mathrm{d}U + \text{đ}W \geq 0$$

$$-\mathrm{d}A_T + \text{đ}W \geq 0$$

$$-\mathrm{d}A_T \geq -\text{đ}W \qquad -\Delta A_T \geq -W$$

$$-\mathrm{d}A_T = -\text{đ}W_{\mathrm{R}} \qquad -\Delta A_T = -W_{\mathrm{R}}$$

恒温时系统亥氏函数的减小值等于可逆过程中系统所作的功，大于不可逆过程中所作的功

2. 恒温恒容过程

$$\left.\begin{aligned} \mathrm{d}V &= 0 \\ \text{đ}W &= \text{đ}W' \end{aligned}\right. \quad \Longrightarrow \quad -\mathrm{d}A_{T,V} + \text{đ}W' \geq 0$$

$$-\mathrm{d}A_{T,V} \geq -\text{đ}W' \qquad -\Delta A_{T,V} \geq -W'$$

$$-\mathrm{d}A_{T,V} = -\text{đ}W'_{\mathrm{R}} \qquad -\Delta A_{T,V} = -W'_{\mathrm{R}}$$

$$W' = 0 \quad \Longrightarrow \quad -\mathrm{d}A_{T,V,W'=0} \geq 0$$

$$\mathrm{d}A_{T,V,W'=0} \leq 0 \qquad \Delta A_{T,V,W'=0} \leq 0$$

3. 恒温恒压过程

$$\text{đ}W = \text{đ}W' - p\mathrm{d}V = \text{đ}W' - \mathrm{d}(pV)$$

$$T\mathrm{d}S - \mathrm{d}U - \mathrm{d}(pV) + \text{đ}W' \geq 0$$

$$-\mathrm{d}G_{T,p} + \text{đ}W' \geq 0$$

$$-\mathrm{d}G_{T,p} \geq -\text{đ}W' \qquad -\Delta G_{T,p} \geq -W'$$

$$-\mathrm{d}G_{T,p} = -\text{đ}W'_{\mathrm{R}} \qquad -\Delta G_{T,p} = -W'_{\mathrm{R}}$$

恒温恒压时系统吉氏函数的减小值等于可逆过程中系统所作的非体积功，大于不可逆过程中系统所作非体积功

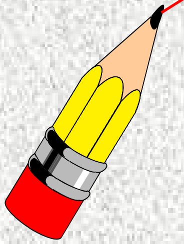
4. 恒温恒压不做非体积功

$$W' = 0$$

$$-\mathrm{d}G_{T,p,W'=0} \geq 0$$

$$\mathrm{d}G_{T,p,W'=0} \leq 0 \quad \Delta G_{T,p,W'=0} \leq 0$$

$$\mathrm{d}G_{T,p,W'=0} = 0 \quad \Delta G_{T,p,W'=0} = 0$$



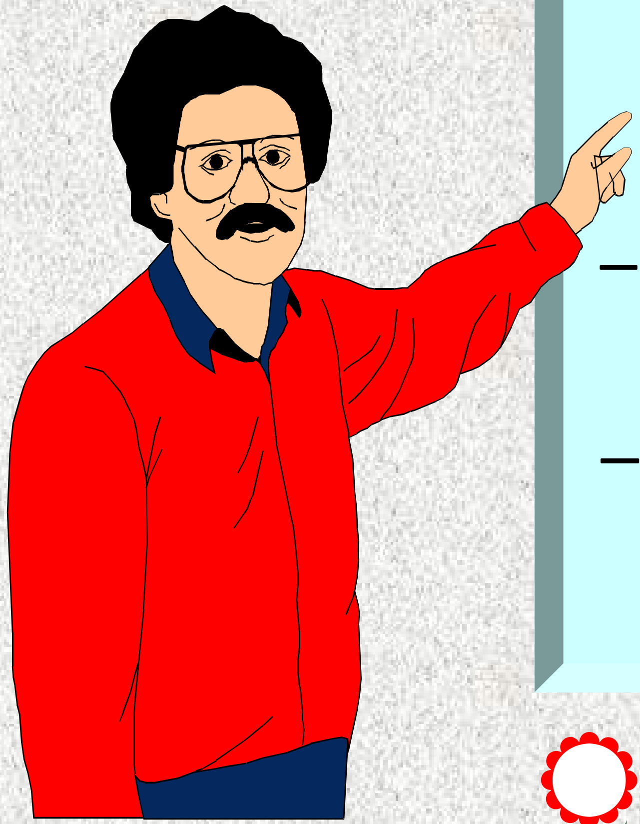
在恒温恒压不做非体积功时，吉氏函数在可逆过程中不变，在不可逆过程中减小，吉氏函数增大则是不可能的。

$$-\mathrm{d}A_T \geq -\text{đ}W$$

$$-\mathrm{d}A_{T,V} \geq -\text{đ}W' \qquad \mathrm{d}A_{T,V,W'=0} \leq 0$$

$$-\mathrm{d}G_{T,p} \geq -\text{đ}W' \qquad \mathrm{d}G_{T,p,W'=0} \leq 0$$

上一页 下一页 节首

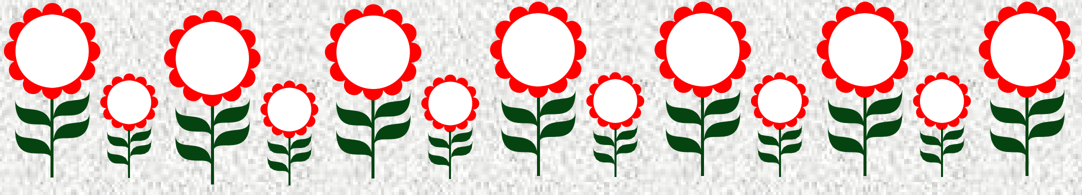


$$\mathrm{d}S \geq \frac{\text{đ}Q}{T_{环}} \qquad \mathrm{d}S_{U,V,W'=0} \geq 0$$

$$-\mathrm{d}A_{T,V} \geq -\text{đ}W' \qquad \mathrm{d}A_{T,V,W'=0} \leq 0$$

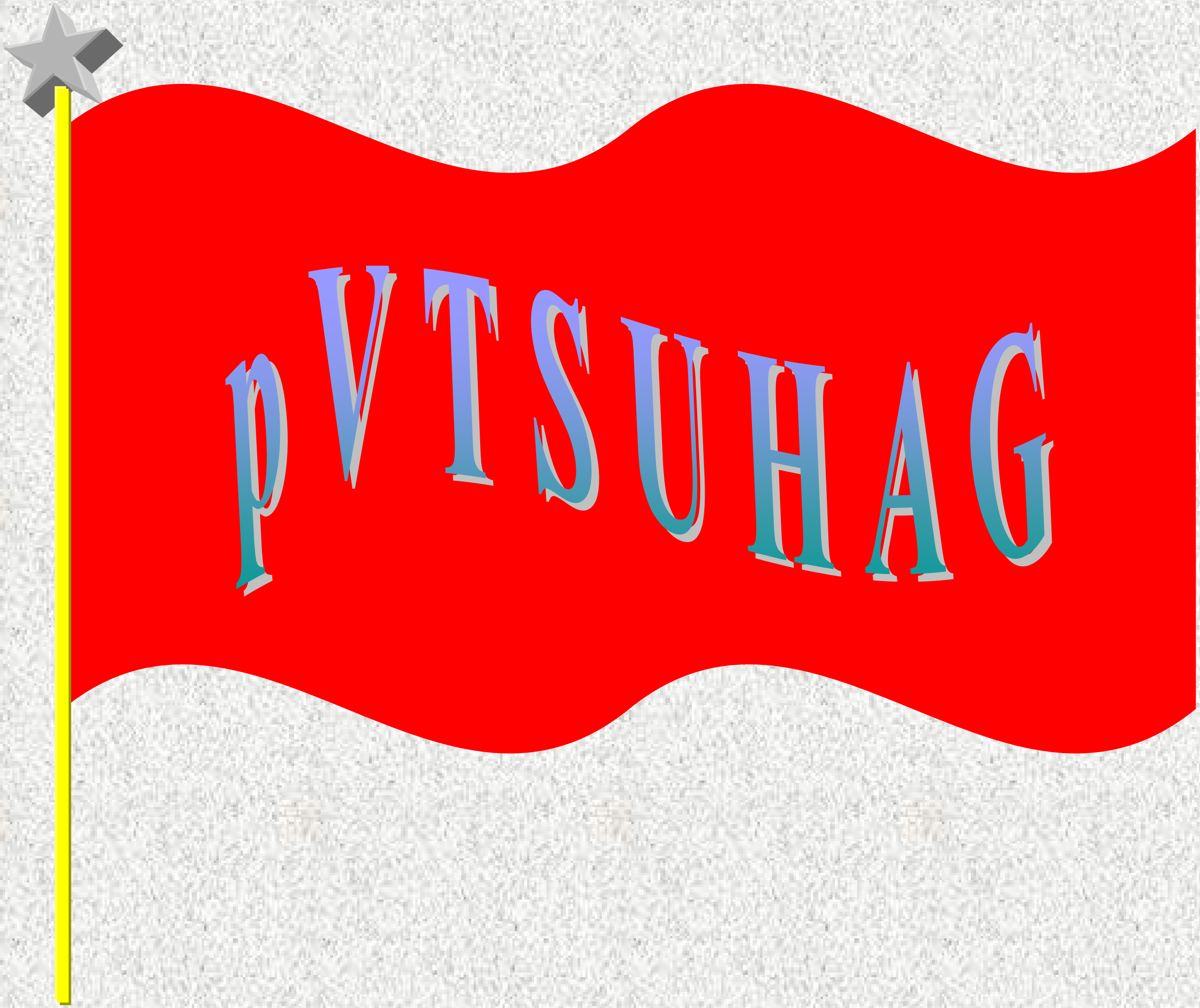
$$-\mathrm{d}G_{T,p} \geq -\text{đ}W' \qquad \mathrm{d}G_{T,p,W'=0} \leq 0$$

$$-\mathrm{d}A_T \geq -\text{đ}W$$



2-7 热力学基本方程

物理化学多媒体课堂教学软件 V1.0版



pVTSUHAG

1. 热力学基本方程

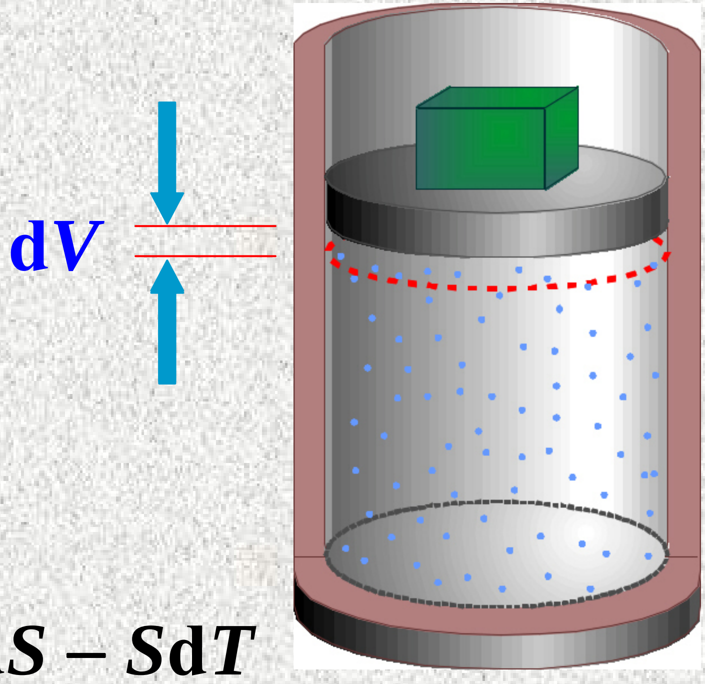
◆ $\mathrm{d}U = \text{đ}Q + \text{đ}W$

◆ $\mathrm{d}S - \text{đ}Q_{\mathrm{R}} / T = 0$

◆ $\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$

◆ $\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T$

◆ $\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T$



$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \qquad \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$$

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V \qquad \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$$

$$U = U(S,V) \qquad A = A(T,V)$$

$$H = H(S,p) \qquad G = G(T,p)$$

$$Z = Z(X,Y) \qquad \mathrm{d}Z = \left(\frac{\partial Z}{\partial X}\right)_Y \mathrm{d}X + \left(\frac{\partial Z}{\partial Y}\right)_X \mathrm{d}Y$$

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

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

$$\Rightarrow$$

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

$$p = -\left(\frac{\partial U}{\partial V}\right)_S$$

上一页 下一页 节首

$$U = U(S,V) \qquad A = A(T,V)$$

$$H = H(S,p) \qquad G = G(T,p)$$

$$Z = Z(X,Y) \qquad \mathrm{d}Z = \left(\frac{\partial Z}{\partial X}\right)_Y \mathrm{d}X + \left(\frac{\partial Z}{\partial Y}\right)_X \mathrm{d}Y$$

$$\left.\begin{array}{l} \mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \\ \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p \end{array}\right\} \rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

$$\left.\begin{array}{l} \mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V \\ \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p \end{array}\right\} \rightarrow S = -\left(\frac{\partial A}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_p$$

上一页 下一页 节首

$$U = U(S,V) \qquad A = A(T,V)$$

$$H = H(S,p) \qquad G = G(T,p)$$

$$Z = Z(X,Y) \qquad \mathrm{d}Z = \left(\frac{\partial Z}{\partial X}\right)_Y \mathrm{d}X + \left(\frac{\partial Z}{\partial Y}\right)_X \mathrm{d}Y$$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial A}{\partial V}\right)_T$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T$$

$$T=\left(\frac{\partial U}{\partial S}\right)_V=\left(\frac{\partial H}{\partial S}\right)_p \quad p=-\left(\frac{\partial U}{\partial V}\right)_S=-\left(\frac{\partial A}{\partial V}\right)_T$$

$$V=\left(\frac{\partial H}{\partial p}\right)_S=\left(\frac{\partial G}{\partial p}\right)_T \quad S=-\left(\frac{\partial A}{\partial T}\right)_V=-\left(\frac{\partial G}{\partial T}\right)_p$$

$$V=\left(\frac{\partial G}{\partial p}\right)_T \longrightarrow \Delta G(T)=\int V\mathrm{d}p$$

$$pV=nRT \longrightarrow \Delta G=nRT\ln\frac{p_2}{p_1}$$

$$T=\left(\frac{\partial U}{\partial S}\right)_V=\left(\frac{\partial H}{\partial S}\right)_p \quad p=-\left(\frac{\partial U}{\partial V}\right)_S=-\left(\frac{\partial A}{\partial V}\right)_T$$

$$V=\left(\frac{\partial H}{\partial p}\right)_S=\left(\frac{\partial G}{\partial p}\right)_T \quad S=-\left(\frac{\partial A}{\partial T}\right)_V=-\left(\frac{\partial G}{\partial T}\right)_p$$

$$p=-\left(\frac{\partial A}{\partial V}\right)_T \longrightarrow \Delta A(T)=-\int p\mathrm{d}V$$

$$pV=nRT \longrightarrow \Delta A=nRT\ln\frac{V_1}{V_2}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \longrightarrow \Delta G(p) = -\int S\mathrm{d}T$$

$$\left[\frac{\partial (G/T)}{\partial T}\right]_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\left[\frac{\partial (1/T)}{\partial T}\right]_p$$

$$= -\frac{S}{T} - \frac{G}{T^2} = -\frac{TS+G}{T^2} = -\frac{H}{T^2}$$

$$\left[\frac{\partial (G/T)}{\partial T}\right]_p = -\frac{H}{T^2}$$

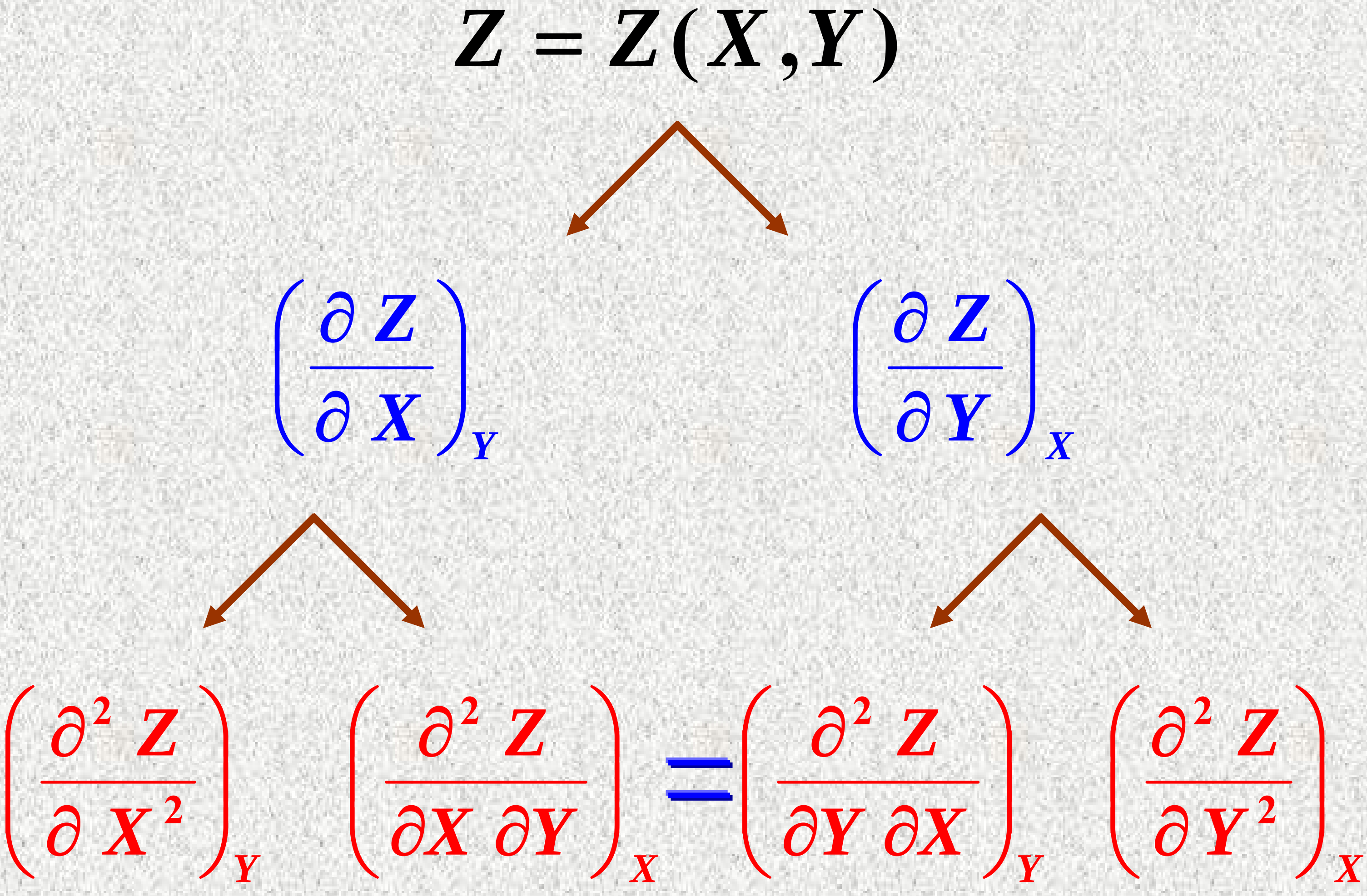
吉布斯–亥姆霍兹方程

2. 吉布斯–亥姆霍兹方程

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2} \Rightarrow \left[\frac{\partial(G/T)}{\partial(1/T)}\right]_p = H$$

$$\left[\frac{\partial(A/T)}{\partial T}\right]_V = -\frac{U}{T^2} \Rightarrow \left[\frac{\partial(A/T)}{\partial(1/T)}\right]_V = U$$

上一页 下一页 节首

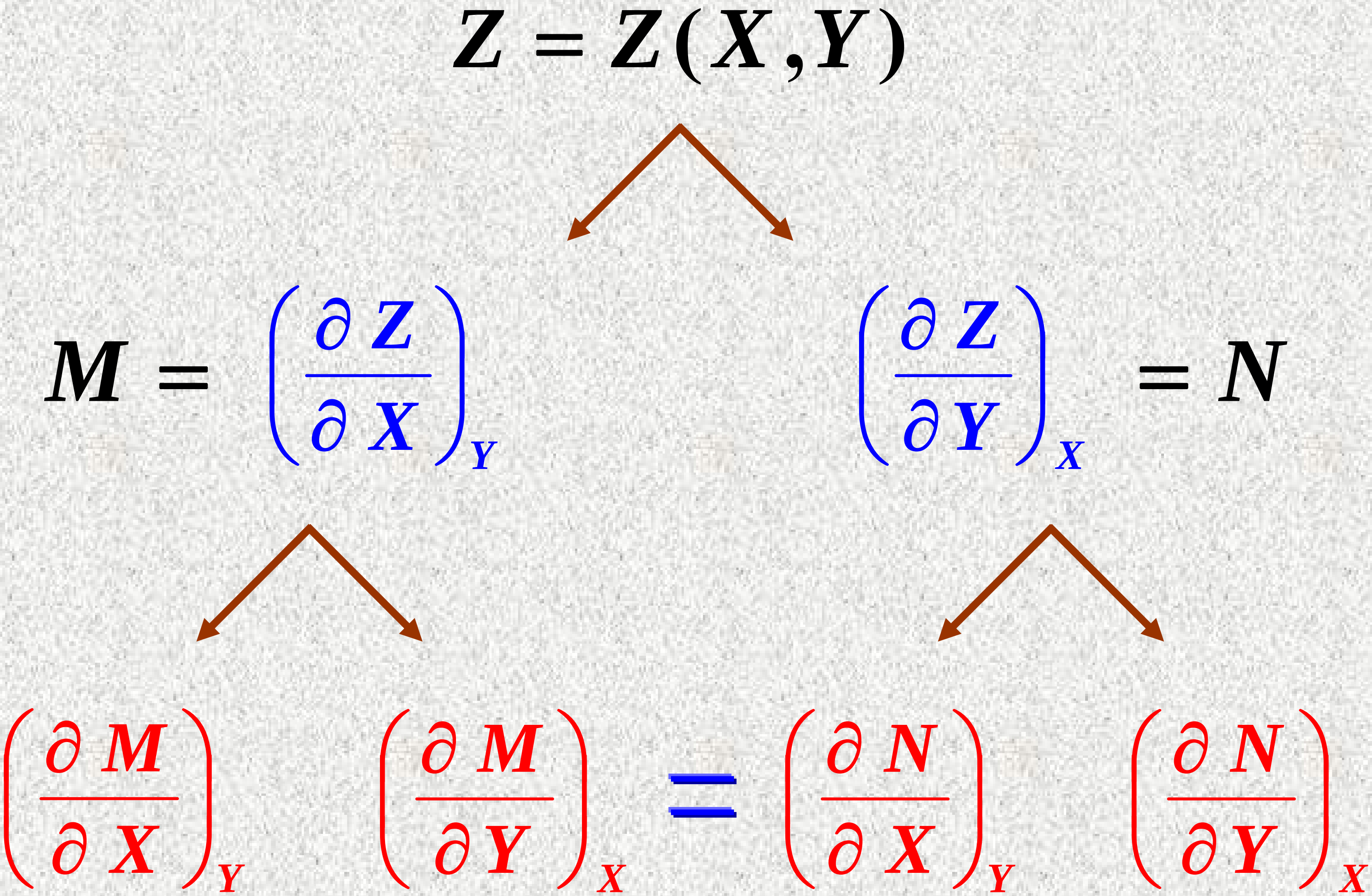


$$Z = Z(X,Y)$$

$$\left(\frac{\partial Z}{\partial X}\right)_Y \qquad \left(\frac{\partial Z}{\partial Y}\right)_X$$

$$\left(\frac{\partial^2 Z}{\partial X^2}\right)_Y \qquad \left(\frac{\partial^2 Z}{\partial X\,\partial Y}\right)_X = \left(\frac{\partial^2 Z}{\partial Y\,\partial X}\right)_Y \qquad \left(\frac{\partial^2 Z}{\partial Y^2}\right)_X$$

上一页 下一页 节首



$$Z = Z(X,Y)$$

$$M = \left(\frac{\partial Z}{\partial X}\right)_Y \qquad \left(\frac{\partial Z}{\partial Y}\right)_X = N$$

$$\left(\frac{\partial M}{\partial X}\right)_Y \qquad \left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y \qquad \left(\frac{\partial N}{\partial Y}\right)_X$$

上一页 下一页 节首

3. 麦克斯韦关系式

$$\mathrm{d}Z = M\mathrm{d}X + N\mathrm{d}Y \qquad (\partial M/\partial Y)_X = (\partial N/\partial X)_Y$$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p \Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p \Rightarrow -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

4.1 热力学能变化

$$U = U(T, V)$$

$$\mathrm{d}U = \underset{\substack{\parallel \\ nC_{V,\mathrm{m}}}}{\left(\frac{\partial U}{\partial T}\right)_V} \mathrm{d}T + \underset{\parallel}{\left(\frac{\partial U}{\partial V}\right)_T} \mathrm{d}V$$

4.1 热力学能变化

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

4.1 热力学能变化

$$U = U(T,V)$$

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

$$nC_{V,m}$$

$$T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\boxed{\mathrm{d}U = nC_{V,m}\mathrm{d}T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\mathrm{d}V}$$

4.2 焓变化

$$H = H(T, p)$$

$$\mathrm{d}H = \underset{\overset{\parallel}{nC_{p,\mathrm{m}}}}{\left(\frac{\partial H}{\partial T}\right)_p} \mathrm{d}T + \underset{\parallel}{\left(\frac{\partial H}{\partial p}\right)_T} \mathrm{d}p$$

4.2 焓变化

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$$

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = -T\left(\frac{\partial V}{\partial T}\right)_p + V$$

4. 2 焓变化

$$H = H(T, p)$$

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p$$

$$nC_{p,\mathrm{m}}$$

$$-T\left(\frac{\partial V}{\partial T}\right)_p + V$$

$$\mathrm{d}H = nC_{p,\mathrm{m}}\mathrm{d}T + \left[-T\left(\frac{\partial V}{\partial T}\right)_p + V\right]\mathrm{d}p$$

上一页 下一页 节首

4.3 熵变化

$$S = S(T,V)$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

$$=$$

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

4.3 熵变化

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \longrightarrow \left(\frac{\partial S}{\partial T}\right)_V = \frac{nC_{V,\mathrm{m}}}{T}$$

4.3 熵变化

$$S = S(T,V)$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$$

$$\frac{nC_{V,\mathrm{m}}}{T} \;=\; \qquad\qquad =\; \left(\frac{\partial p}{\partial T}\right)_V$$

$$\boxed{\mathrm{d}S = \frac{nC_{V,\mathrm{m}}}{T}\mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V}$$

4.3 熵变化

$$S = S(T, p)$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p$$

$$\frac{nC_{p,\mathrm{m}}}{T}$$

$$-\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{\mathrm{d}S = \frac{nC_{p,\mathrm{m}}}{T}\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p}$$

5. 其它重要的的偏导数

$U = U(S, V)$

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V \qquad \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_U + \left(\frac{\partial U}{\partial V}\right)_S = 0$$

$$\left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_S = -1 \qquad \frac{\mathrm{d}U}{\mathrm{d}S} = \left(\frac{\partial U}{\partial S}\right)_V + \left(\frac{\partial U}{\partial V}\right)_S \frac{\mathrm{d}V}{\mathrm{d}S}$$

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

$C_{p,m}$和$C_{V,m}$换算

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \left(\frac{\partial H_{\mathrm{m}}}{\partial T}\right)_p - \left(\frac{\partial U_{\mathrm{m}}}{\partial T}\right)_V$$

$$H = U + PV$$

$$\left(\frac{\partial H_{\mathrm{m}}}{\partial T}\right)_p = \left(\frac{\partial U_{\mathrm{m}}}{\partial T}\right)_p + p\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p$$

$C_{p,m}$和$C_{V,m}$换算

$$C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \left(\frac{\partial H_\mathrm{m}}{\partial T}\right)_p - \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V$$

$$= \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_p + p\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p - \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V$$

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

$C_{p,m}$和$C_{V,m}$换算

$$C_{p,\mathrm{m}}-C_{V,\mathrm{m}}=\left(\frac{\partial H_\mathrm{m}}{\partial T}\right)_p-\left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V$$

$$=\left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_p+p\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p-\left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V$$

$$=\left[\left(\frac{\partial U_\mathrm{m}}{\partial V_\mathrm{m}}\right)_T+p\right]\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p$$

$$\boxed{C_{p,\mathrm{m}}-C_{V,\mathrm{m}}=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V_\mathrm{m}}{\partial T}\right)_p}$$

范德华气体

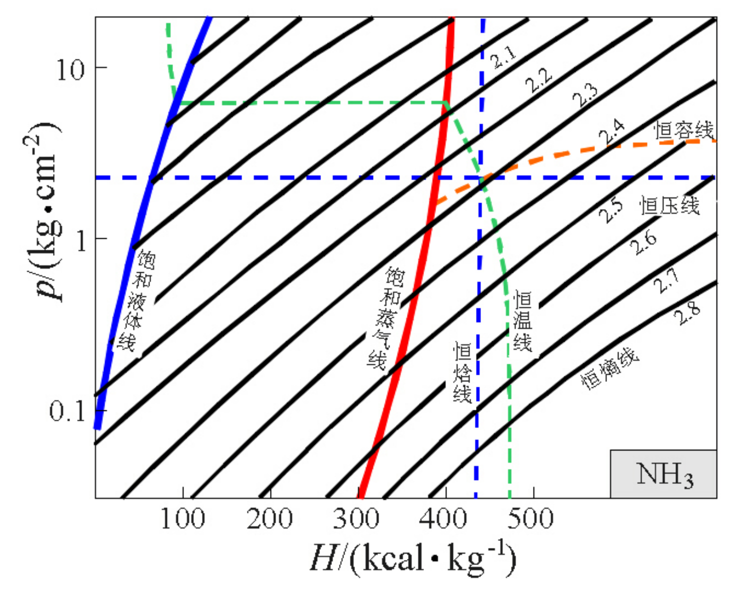
$$p = RT/(V_\mathrm{m} - b) - a/V_\mathrm{m}^2$$

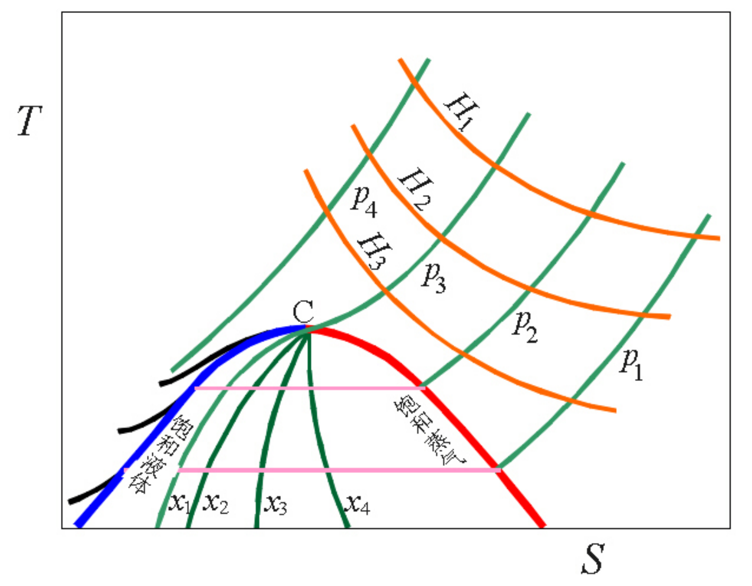
$$(\partial p/\partial T)_V = R/(V_\mathrm{m} - b)$$

$$(\partial U/\partial V)_T = RT/(V_\mathrm{m} - b) - p = a/V_\mathrm{m}^2$$

基本方程的意义在于：可利用能够直接测定的物质特性，即 pVT 关系和热容，来获得那些不能直接测定的U、H、S、A、G的变化。反之，如知道U、H、A、G的变化规律，即那些广义的状态方程，可得到所有的其它热力学信息。

6. 热力学图表

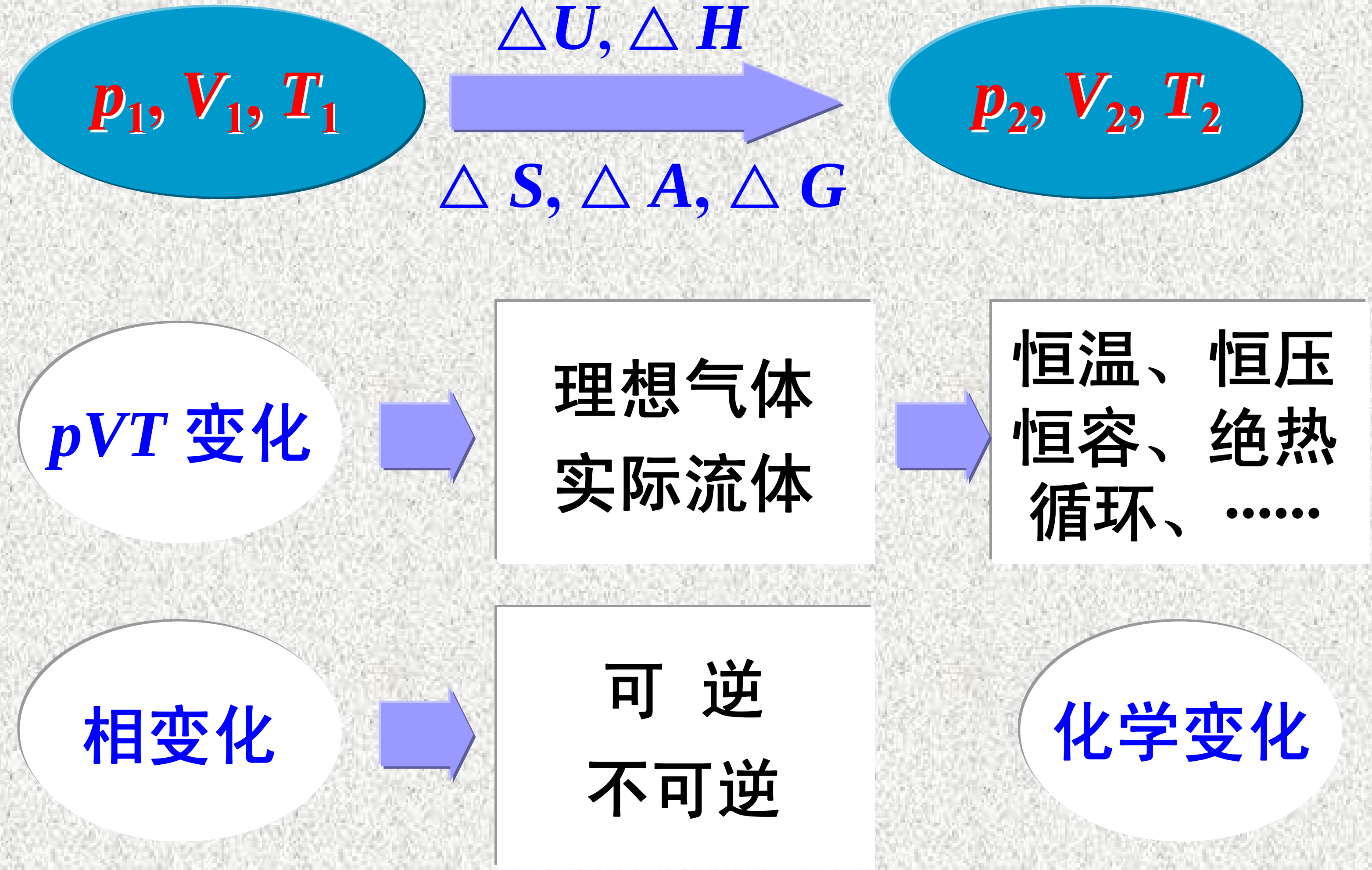




已知： $H=H(S, p)$

$$T=\left(\frac{\partial H}{\partial S}\right)_p \qquad V=\left(\frac{\partial H}{\partial p}\right)_S \qquad \left(\frac{\partial H}{\partial T}\right)_p=nC_{p,\mathrm{m}}$$

热力学计算



p_1, V_1, T_1

$\triangle U, \triangle H$

$\triangle S, \triangle A, \triangle G$

p_2, V_2, T_2

pVT 变化

理想气体
实际流体

恒温、恒压
恒容、绝热
循环、……

相变化

可 逆
不可逆

化学变化

2-8 *pVT* 变化中热力学函数的变化

物理化学多媒体课堂教学软件 V1.0版

上一页 下一页 返回目录

1. 理想气体 *pVT* 变化中热力学函数的变化

$$pV = nRT \qquad (\partial V/\partial T)_p = nR/p$$

$$T(\partial p/\partial T)_V - p = nRT/V - p = p - p = 0$$

$$\mathrm{d}U = nC^{\ominus}_{V,\mathrm{m}}\mathrm{d}T \qquad \mathrm{d}H = nC^{\ominus}_{p,\mathrm{m}}\mathrm{d}T$$

$$\mathrm{d}S = \frac{nC^{\ominus}_{V,\mathrm{m}}}{T}\mathrm{d}T + \frac{nR}{V}\mathrm{d}V = \frac{nC^{\ominus}_{p,\mathrm{m}}}{T}\mathrm{d}T - \frac{nR}{p}\mathrm{d}p$$

$$\mathrm{d}A_T = \mathrm{d}G_T = -\frac{nRT}{V}\mathrm{d}V = \frac{nRT}{p}\mathrm{d}p$$

$$C^{\ominus}_{p,\mathrm{m}} - C^{\ominus}_{V,\mathrm{m}} = R$$

◆理想气体的U、H 只是温度的函数，与p、V无关

$$\left(\frac{\partial U}{\partial V}\right)_T=\left(\frac{\partial U}{\partial p}\right)_T=\left(\frac{\partial H}{\partial V}\right)_T=\left(\frac{\partial H}{\partial p}\right)_T=0$$

$$\mathrm{d}U=nC_{V,\mathrm{m}}^{\ominus}\mathrm{d}T \qquad \Delta U=\int nC_{V,\mathrm{m}}^{\ominus}\mathrm{d}T$$

$$\mathrm{d}H=nC_{p,\mathrm{m}}^{\ominus}\mathrm{d}T \qquad \Delta H=\int nC_{p,\mathrm{m}}^{\ominus}\mathrm{d}T$$

◆理想气体恒温过程

$$\triangle U=0 \qquad \triangle H=0$$

◆理想气体熵变可用统一公式计算

$$\mathrm{d}S=\frac{nC_{V,\mathrm{m}}^{\ominus}}{T}\mathrm{d}T+\frac{nR}{V}\mathrm{d}V=\frac{nC_{p,\mathrm{m}}^{\ominus}}{T}\mathrm{d}T-\frac{nR}{p}\mathrm{d}p$$

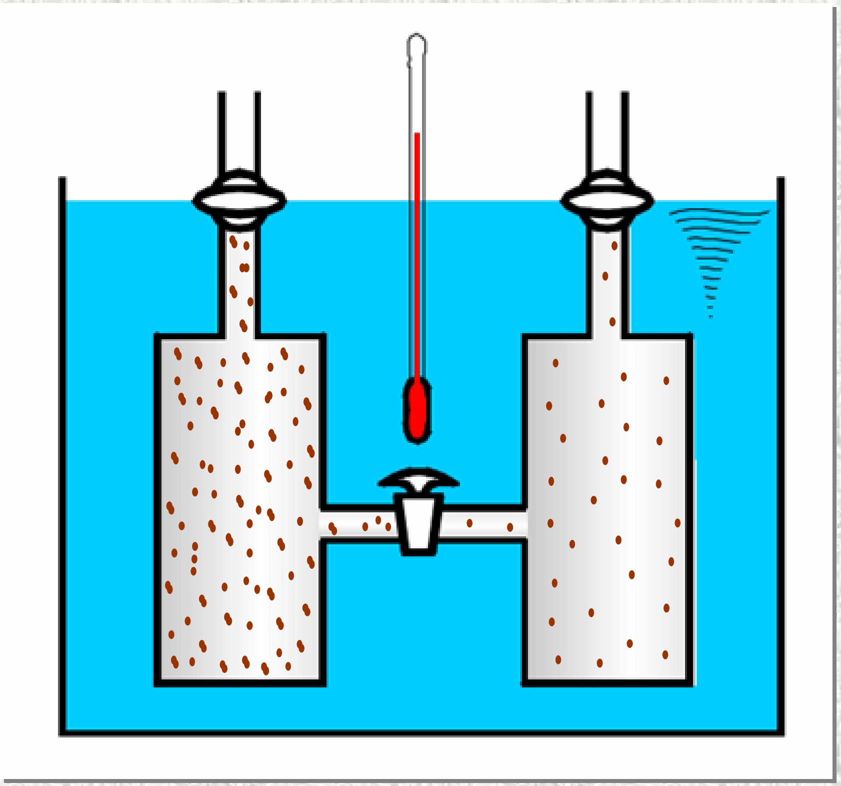
焦耳实验

$W = 0$ $Q = 0$

$\Delta U = 0$

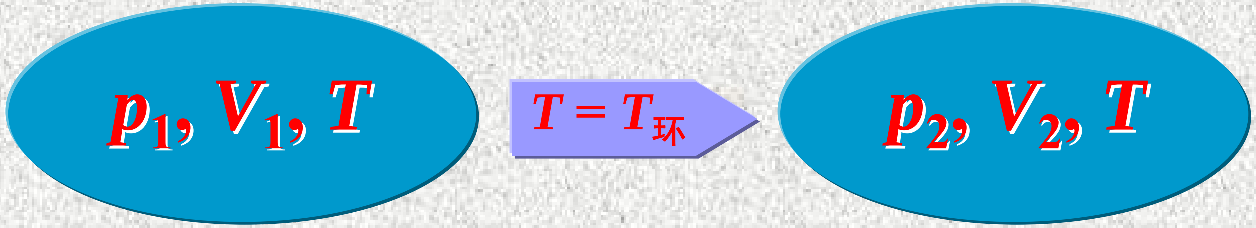
$\mathrm{d}T = 0$ $\mathrm{d}U = 0$

$\mathrm{d}V > 0$ $\mathrm{d}p < 0$



$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T = 0 \qquad \left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T = 0$$

(1) 恒温过程 $T = T_{环} = C$



$$\Delta U = 0 \qquad \Delta H = 0$$

$$\Delta S = -nR\int_{p_1}^{p_2}(\mathrm{d}p/p)$$

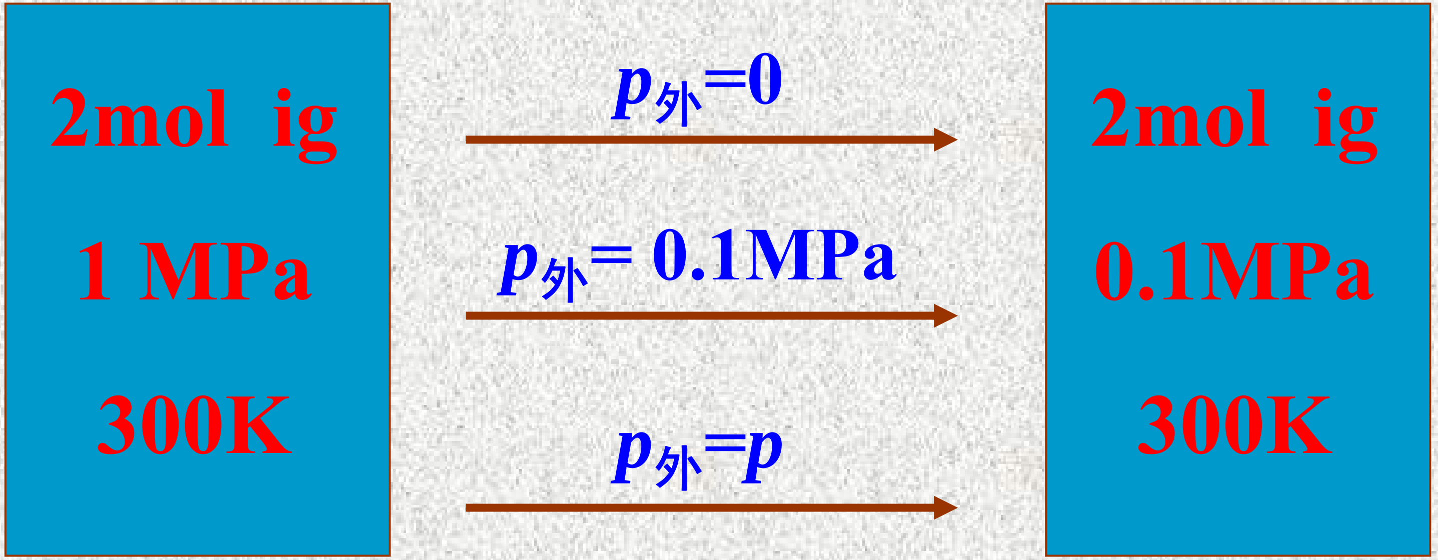
$$= -nR\ln(p_2/p_1) = nR\ln(V_2/V_1)$$

$$\Delta A = \Delta G = nRT\int_{p_1}^{p_2}(\mathrm{d}p/p)$$

$$= nRT\ln(p_2/p_1) = -nRT\ln(V_2/V_1)$$

例1 2mol理想气体在300K时自1MPa恒温膨胀至0.1MPa，计算Q、W、ΔU、ΔH、ΔS、ΔA、ΔG，并判断可逆性。(*a*)$p_{\text{外}}=0$，(*b*) $p_{\text{外}}=0.1\,\text{MPa}$，(*c*) $p_{\text{外}}=p$ 。

解:



2mol ig
1 MPa
300K

$p_{\text{外}}=0$

$p_{\text{外}}=0.1\,\text{MPa}$

$p_{\text{外}}=p$

2mol ig
0.1MPa
300K

状态函数变化与过程无关，三个过程有相同答案。

上一页 下一页 节首

例1 2mol理想气体在300K时自1MPa恒温膨胀至0.1MPa，计算Q、W、ΔU、ΔH、ΔS、ΔA、ΔG，并判断可逆性。(a)$p_{外}$=0，(b) $p_{外}$=0.1MPa，(c) $p_{外}$=p 。

解:

$$\Delta U = 0 \qquad \Delta H = 0$$

$$\Delta S = -nR\int_{p_1}^{p_2}(\mathrm{d}p/p) = -nR\ln(p_2/p_1)$$

$$= [-2\times 8.3145\times \ln(0.1/1)]\mathrm{J\cdot K^{-1}} = 38.29\mathrm{J\cdot K^{-1}}$$

$$\Delta A = \Delta G = nRT\int_{p_1}^{p_2}(\mathrm{d}p/p) = nRT\ln(p_2/p_1)$$

$$= [2\times 8.3145\times 300\times \ln(0.1/1)]\mathrm{J} = -11.49\times 10^3\,\mathrm{J}$$

(a) $Q = -W = 0$

$$\Delta S - Q/T = 38.29\,\mathrm{J\cdot K^{-1}} > 0 \qquad -\Delta A + W = 11.49\times10^{3}\,\mathrm{J} > 0$$

(b) $Q = -W = \int_{V_1}^{V_2} p_{外}\mathrm{d}V = p_{外}(V_2 - V_1) = nRTp_{外}(1/p_2 - 1/p_1)$

$$= [2\times8.3145\times300\times0.1\times(1/0.1 - 1/1)]\mathrm{J} = 4490\mathrm{J}$$

$$\Delta S - Q/T = (38.29 - 4490/300)\mathrm{J\cdot K^{-1}} = 23.32\,\mathrm{J\cdot K^{-1}} > 0$$

$$-\Delta A + W = (11.49\times10^{3} - 4490)\mathrm{J} = 7.00\times10^{3}\,\mathrm{J} > 0$$

(c) $Q = -W = \int_{V_1}^{V_2} p_{外}\mathrm{d}V = \int_{V_1}^{V_2} p\mathrm{d}V = nRT\ln(V_2/V_1) = nRT\ln(p_1/p_2)$

$$= [2\times8.3145\times300\ln(1/0.1)\mathrm{J} = 11.49\times10^{3}\,\mathrm{J}$$

$$\Delta S - Q/T = (38.29 - 11.49\times10^{3}/300)\mathrm{J\cdot K^{-1}} = 0$$

$$-\Delta A + W = 0$$

(2) 绝热过程 $Q = 0$，$\Delta U=W$

$$p_1, V_1, T_1 \xrightarrow{Q = 0} p_2, V_2, T_2$$

绝热可逆过程 $p_{外} = p$ $\mathrm{d}W_{\mathrm{R}} = -p_{外}\mathrm{d}V = -p\mathrm{d}V$

$$\mathrm{d}U = nC_{V,\mathrm{m}}^{\ominus}\mathrm{d}T$$

$$-p\mathrm{d}V = nC_{V,\mathrm{m}}^{\ominus}\mathrm{d}T$$

$$-R\mathrm{d}V/V = C_{V,\mathrm{m}}^{\ominus}\mathrm{d}T/T$$

$$R\ln(V_1/V_2) = C_{V,\mathrm{m}}^{\ominus}\ln(T_2/T_1)$$

$$\gamma = C_{p,\mathrm{m}}^{\ominus}/C_{V,\mathrm{m}}^{\ominus}$$

$$\Rightarrow$$

$$V_1^{\gamma-1}T_1 = V_2^{\gamma-1}T_2 = 常数$$

$$p_1V_1^{\gamma} = p_2V_2^{\gamma} = 常数$$

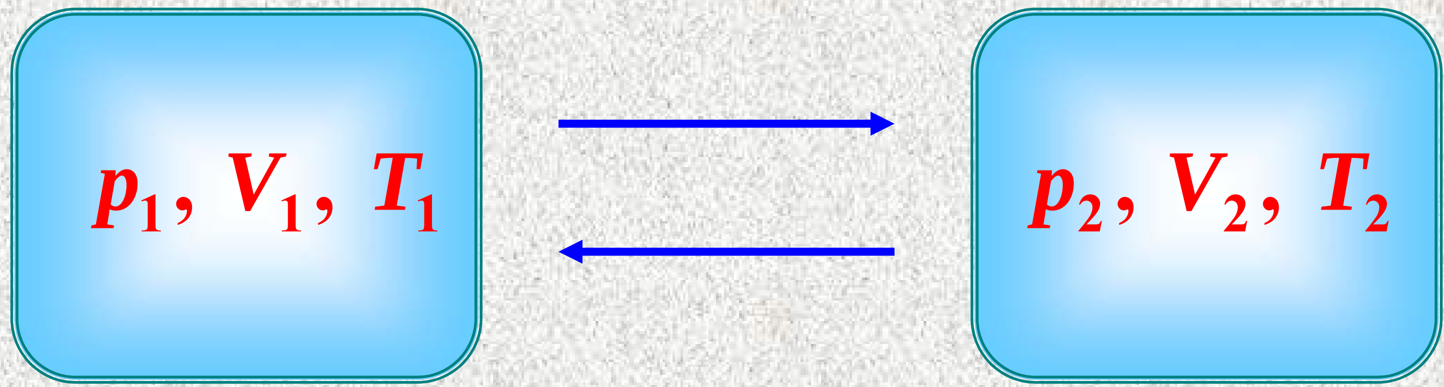
$$p_1^{1-\gamma}T_1^{\gamma} = p_2^{1-\gamma}T_2^{\gamma} = 常数$$

绝热可逆过程方程

$$V_1^{\gamma-1}T_1 = V_2^{\gamma-1}T_2 = C$$

$$p_1V_1^{\gamma} = p_2V_2^{\gamma} = C$$

$$p_1^{1-\gamma}T_1^{\gamma} = p_2^{1-\gamma}T_2^{\gamma} = C$$



p_1, V_1, T_1

p_2, V_2, T_2

$p_1V_1 = nRT_1$ $p_2V_2 = nRT_2$

上一页 下一页 节首

(2) 绝热过程　$Q = 0$，$\triangle U = W$

p_1, V_1, T_1 $\xrightarrow{Q = 0}$ p_2, V_2, T_2

绝热不可逆过程

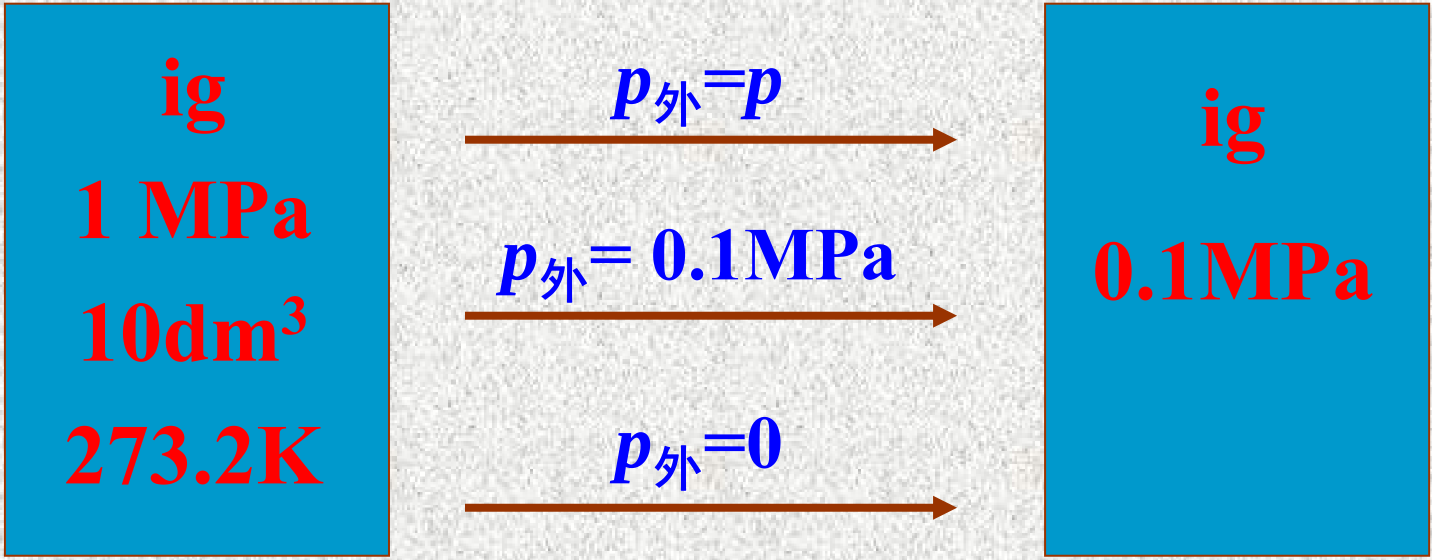
$$\triangle U = W$$

$$\int nC^{\ominus}_{\mathrm{V,m}}\,\mathrm{d}T = -\int p_{外}\,\mathrm{d}V$$

注　**状态方程　≠　过程方程**　意

例2 0℃、1MPa、10dm³的单原子分子理想气体，绝热膨胀至0.1MPa，计算*Q*、*W*、Δ*U*、Δ*H*、Δ*S*，并判断可逆性。(*a*) $p_{外}=p$，(*b*) $p_{外}=0.1\text{MPa}$，(*c*) $p_{外}=0$ 。

解:



ig
1 MPa
10dm³
273.2K

$\xrightarrow{p_{外}=p}$

$\xrightarrow{p_{外}=0.1\text{MPa}}$

$\xrightarrow{p_{外}=0}$

ig
0.1MPa

三个过程终态不同

例2 0℃、1MPa、10dm³的单原子分子理想气体，绝热膨胀至0.1MPa，计算Q、W、ΔU、ΔH、ΔS，并判断可逆性。(*a*) $p_{外}=p$，(*b*) $p_{外}=0.1\mathrm{MPa}$，(*c*) $p_{外}=0$ 。

(*a*) $Q_{\mathrm{R}} = 0 \quad \Delta S = 0$

$$V_2 = (p_1/p_2)^{1/\gamma}V_1 = [(1/0.1)^{3/5}\times 10]\mathrm{dm}^3 = 39.81\mathrm{dm}^3$$

$$n = p_1V_1/(RT_1) = 4.403\mathrm{mol}$$

$$T_2 = p_2V_2/(nR) = 108.7\mathrm{K}$$

$$W_{\mathrm{R}} = \Delta U = nC^{\ominus}_{V,\mathrm{m}}(T_2 - T_1) = -9033\mathrm{J}$$

$$\Delta H = nC^{\ominus}_{p,\mathrm{m}}(T_2 - T_1) = -15.06\times 10^3\mathrm{J} \qquad \Delta S - \int đQ/T_{环} = 0$$

(b) $\Delta U = W \quad nC_{V,\mathrm{m}}^{\ominus}(T_2 - T_1) = -p_{外}(V_2 - V_1)$

$$n(3R/2)(T_2 - T_1) = -p_{外} nR(T_2/p_2 - T_1/p_1)$$

$$3(T_2 - T_1)/2 = -(T_2 - T_1/10), \quad T_1 = 273.2\mathrm{K}$$

$$V_2 = nRT_2/p_2 = 63.99\mathrm{dm}^3$$

$$\boxed{T_2 = 174.8\mathrm{K}}$$

$$W = \Delta U = nC_{V,\mathrm{m}}^{\ominus}(T_2 - T_1) = -5403\mathrm{J}$$

$$\Delta H = nC_{p,\mathrm{m}}^{\ominus}(T_2 - T_1) = -9006\mathrm{J}$$

$$\Delta S = \int_{T_1}^{T_2}(nC_{V,\mathrm{m}}^{\ominus}\mathrm{d}T/T) + \int_{V_1}^{V_2}(nR\mathrm{d}V/V)$$

$$= nC_{V,\mathrm{m}}^{\ominus}\ln(T_2/T_1) + nR\ln(V_2/V_1) = 43.43\mathrm{J}\cdot\mathrm{K}^{-1}$$

$$\Delta S - \int(\text{đ}Q/T_{环}) = 43.43\mathrm{J}\cdot\mathrm{K}^{-1} > 0$$

(c) $Q=0$， $W=0$， $\triangle U=0$，

$T_2=273.2\text{K}$， $V_2=100\text{dm}^3$ （为什么？）

$\triangle H=0$ (为什么?)

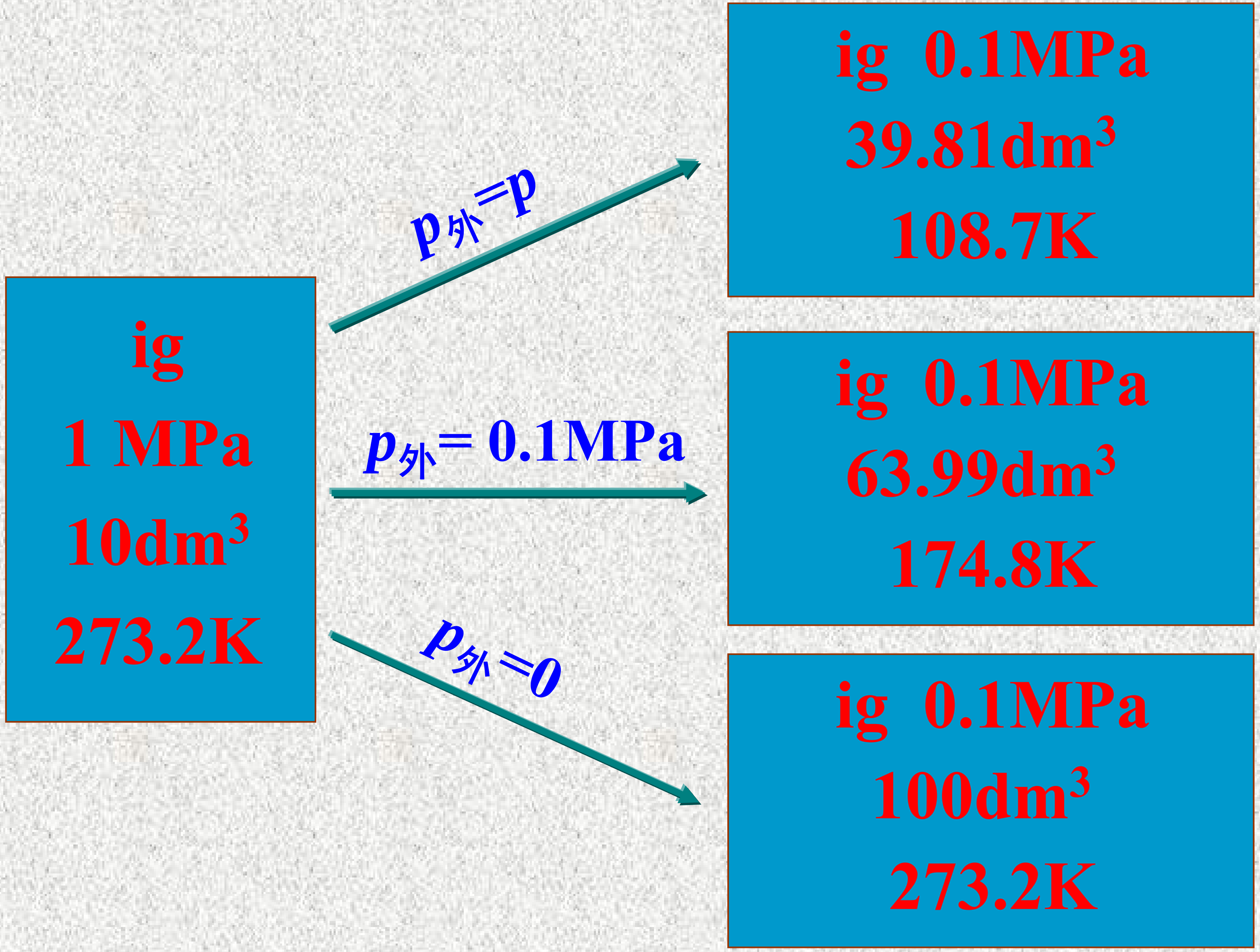
$$\Delta S=-\int_{p_1}^{p_2}(nR\mathrm{d}p/p)=nR\ln(p_1/p_2)$$

$$=84.29\text{J}\cdot\text{K}^{-1}$$

$$\Delta S-\int(\text{đ}Q/T)=84.29\text{J}\cdot\text{K}^{-1}>0$$

(b) $\Delta S-\int(\text{đ}Q/T_{环})=43.43\text{J}\cdot\text{K}^{-1}>0$

(a) $\Delta S-\int\text{đ}Q/T_{环}=0$



ig

1 MPa

10dm^3

273.2K

$p_{外}=p$

ig 0.1MPa

39.81dm^3

108.7K

$p_{外}=0.1\text{MPa}$

ig 0.1MPa

63.99dm^3

174.8K

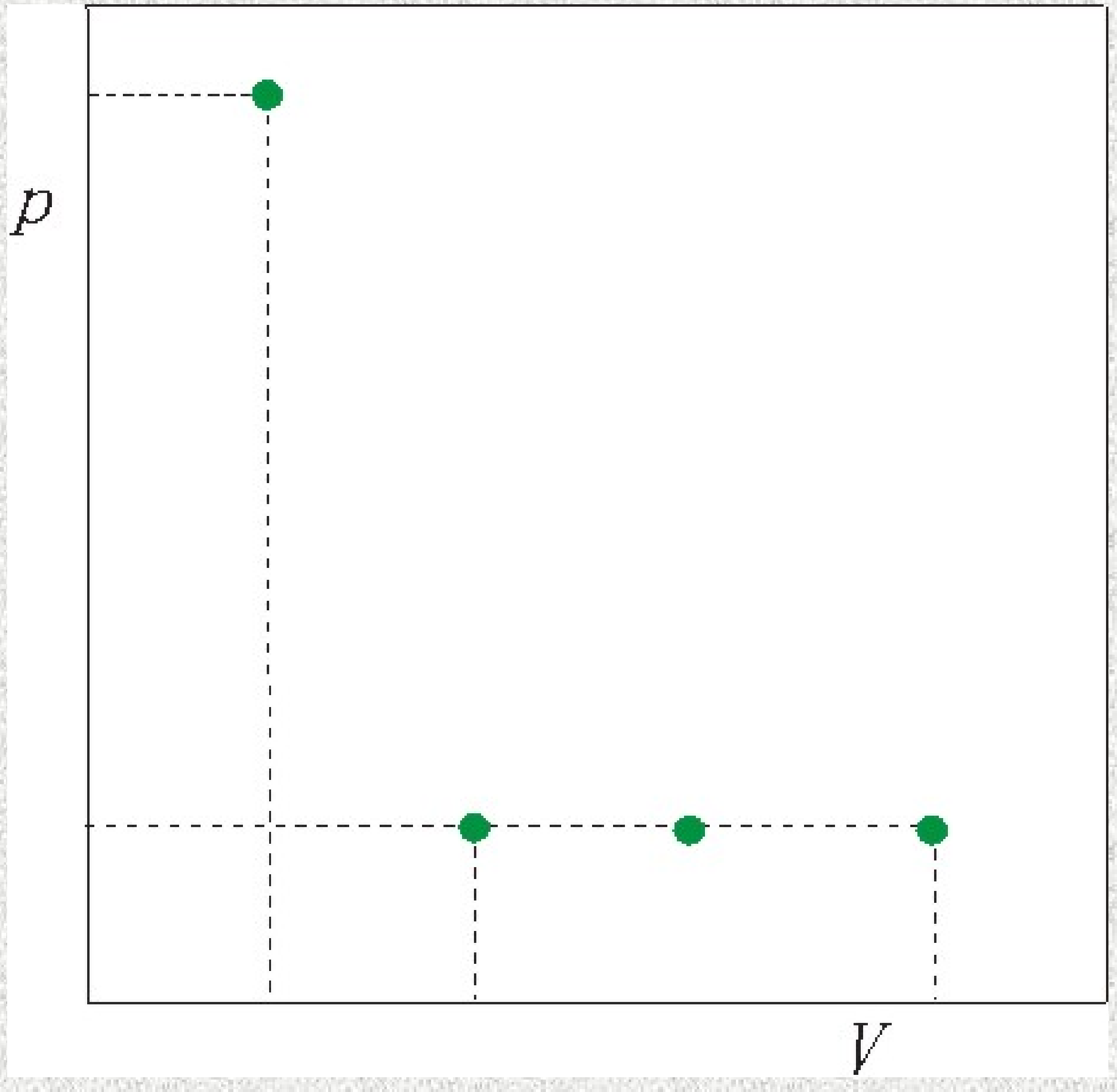
$p_{外}=0$

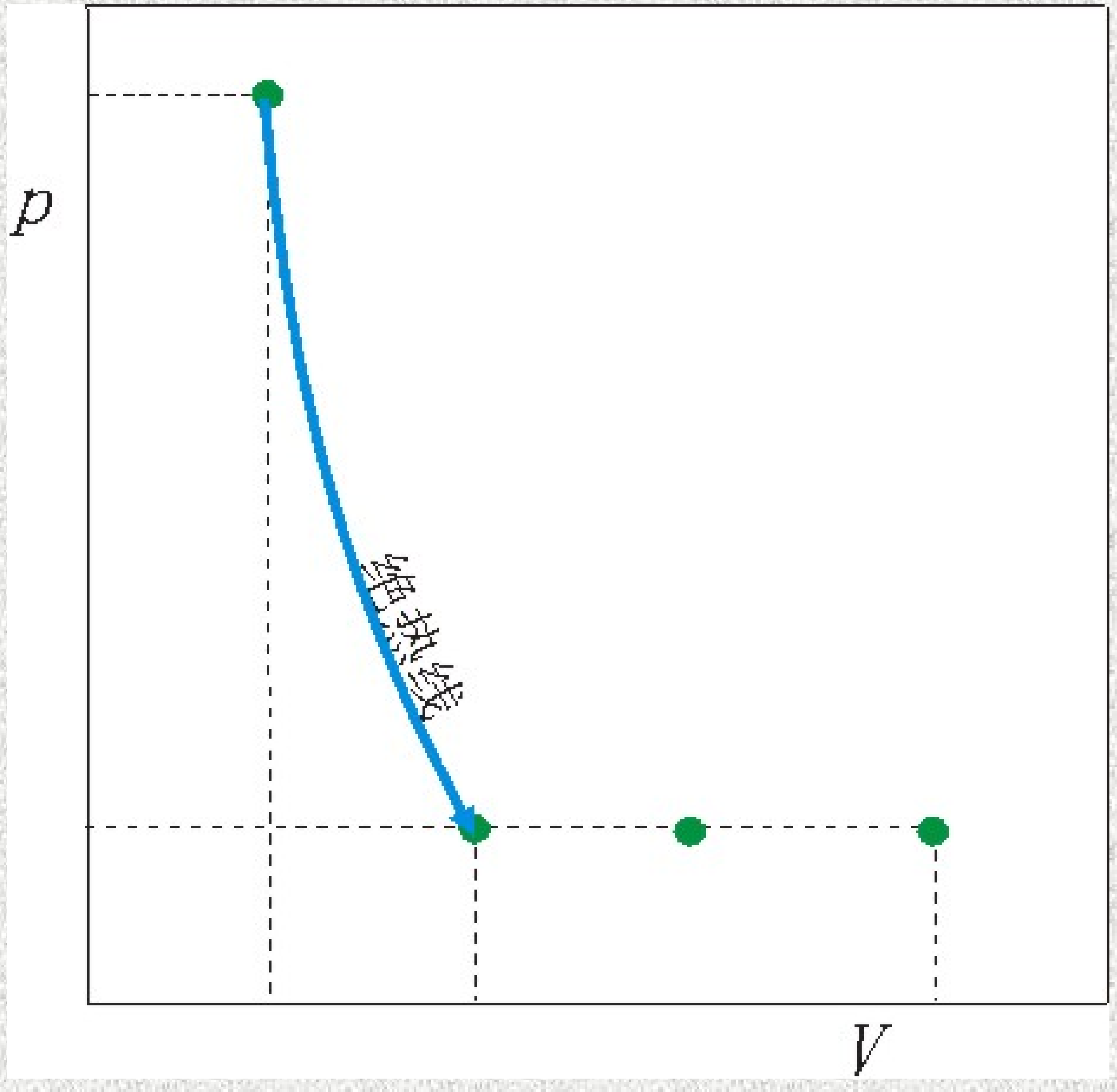
ig 0.1MPa

100dm^3

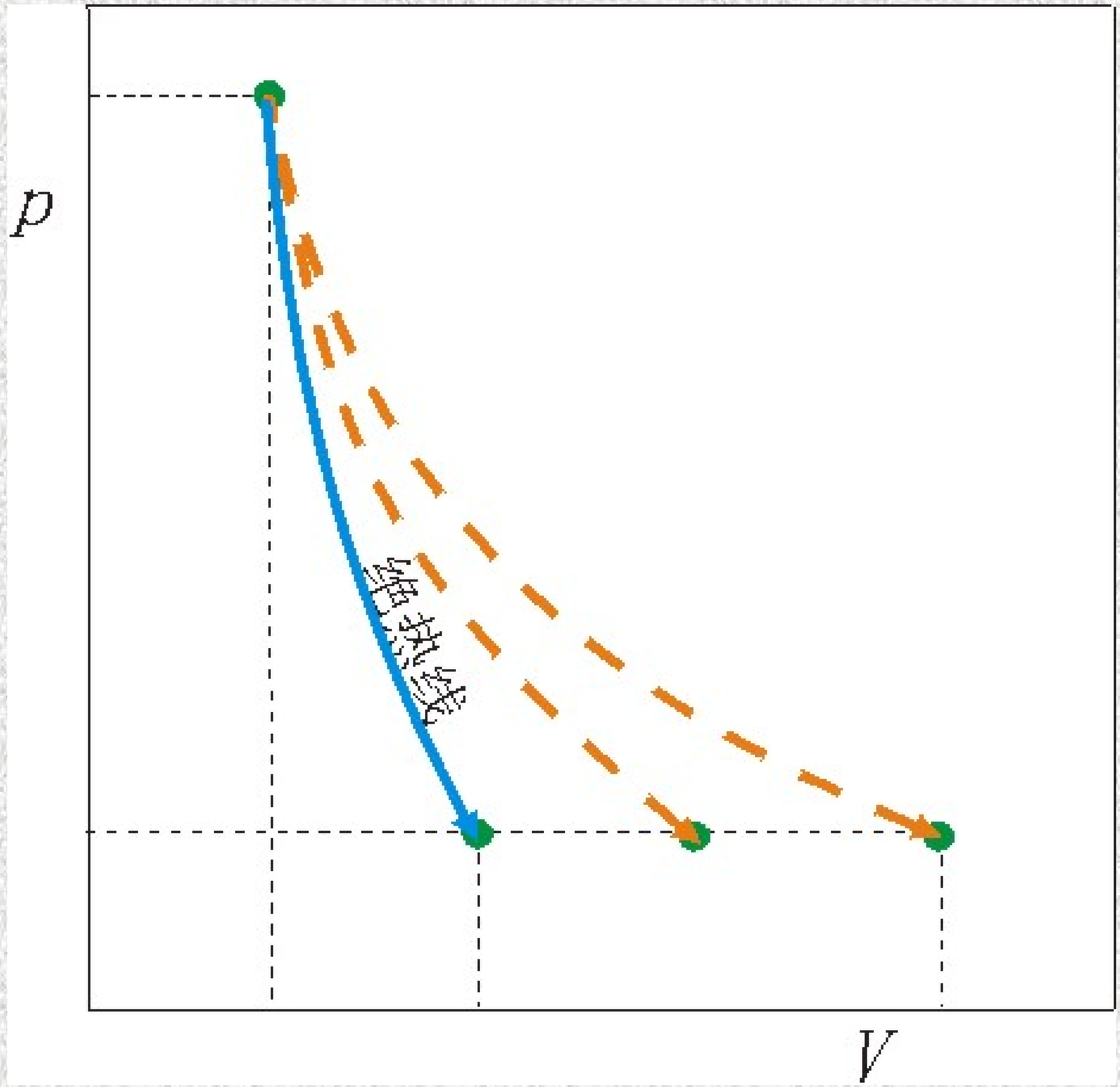
273.2K

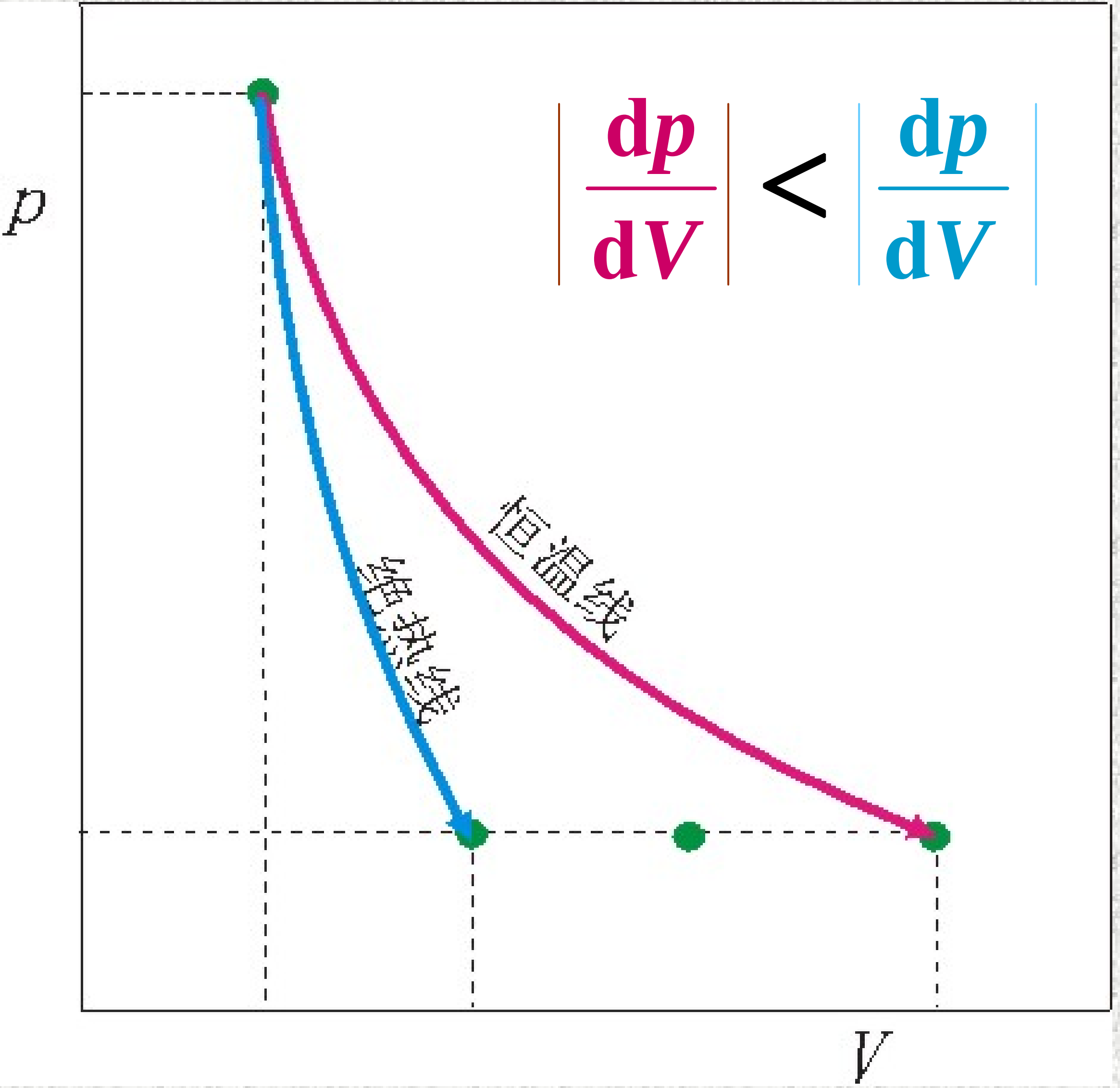
上一页 下一页 节首


p
V



上一页 下一页 节首


p
绝热线
V

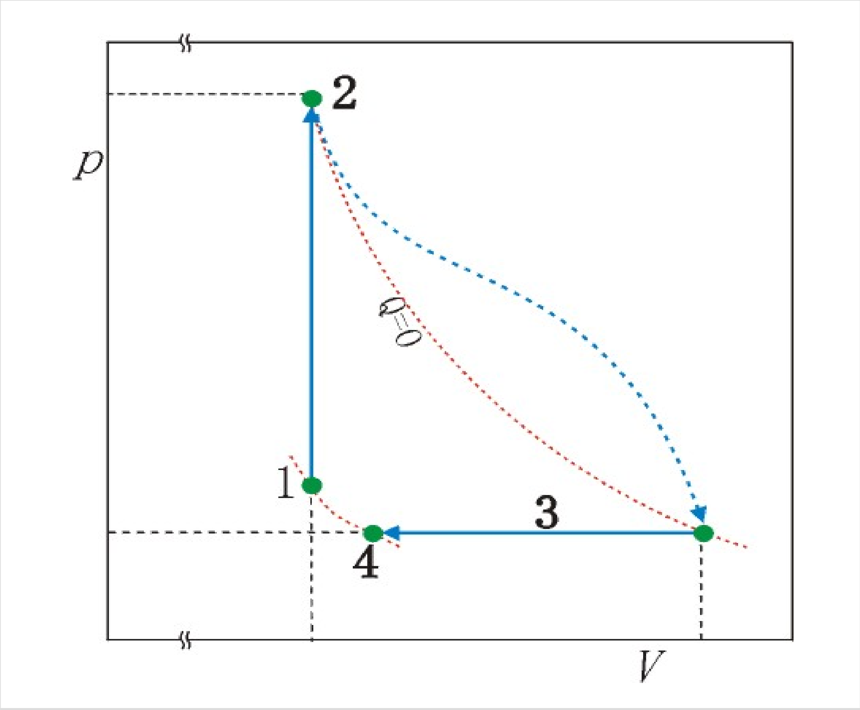


$$\left|\frac{\mathrm{d}p}{\mathrm{d}V}\right| < \left|\frac{\mathrm{d}p}{\mathrm{d}V}\right|$$

(3) 恒容过程与恒压过程

例4 0.1MPa下的1mol双原子分子理想气体连续经历下列几步变化：(*a*)从25℃恒容加热到100℃；(*b*)向真空绝热膨胀至体积增大一倍；(*c*)恒压冷却到25℃；试求总的Q、W、ΔU、ΔH、ΔS。

解：



p_1=0.1MPa
T_1=298K
V_1=24.78dm^3

→

p_3=0.063MPa
T_3=373K
V_3=49.55dm^3

→

p_4=0.063MPa
T_4=298K
V_4=39.6dm^3

$$\Delta U = 0,\quad \Delta H = 0$$

$$\Delta S(a) = \int_{T_1}^{T_2} (nC_{V,\mathrm{m}}^{\ominus} \mathrm{d}T / T) = nC_{V,\mathrm{m}}^{\ominus} \ln(T_2 / T_1) = 4.663\mathrm{J} \cdot \mathrm{K}^{-1}$$

$$\Delta S(b) = \int_{V_2}^{V_3} (nR\mathrm{d}V / V) = nR \ln(V_3 / V_2) = 5.763\mathrm{J} \cdot \mathrm{K}^{-1}$$

$$\Delta S(c) = \int_{T_3}^{T_4} (nC_{p,\mathrm{m}}^{\ominus} \mathrm{d}T / T) = nC_{p,\mathrm{m}}^{\ominus} \ln(T_4 / T_3) = -6.529\mathrm{J} \cdot \mathrm{K}^{-1}$$

$$\Delta S = (4.663 + 5.763 - 6.529)\mathrm{J} \cdot \mathrm{K}^{-1} = 3.897\mathrm{J} \cdot \mathrm{K}^{-1}$$

上一页 下一页 节首

p_1=0.1MPa
T_1=298K
V_1=24.78dm^3

→

p_3=0.063MPa
T_3=393K
V_3=49.55dm^3

→

p_4=0.063MPa
T_4=298K
V_4=39.6dm^3

$$\Delta S = \int_{V_1}^{V_4} (nR\mathrm{d}V/V) = nR\ln(V_4/V_1) = nR\ln(p_1/p_4)$$

$$= 3.895\mathrm{J}\cdot\mathrm{K}^{-1}$$

$$W = -Q = W(a) + W(b) + W(c)$$

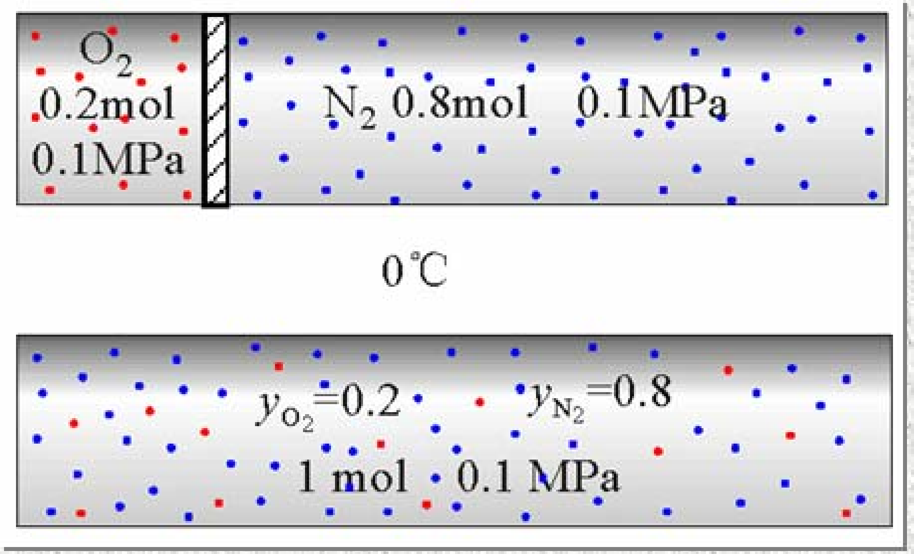
$$= -p\Delta V = \Delta U(c) - Q_p(c)$$

$$= 624\mathrm{J}$$

上一页 下一页 节首

(4) 理想气体恒温混合

例5 如图所示，抽去隔板后，两气体均匀混合。求过程的Q、W、ΔU、ΔH、ΔS、ΔG。并判断可逆性。



解： $\Delta U = 0,\ \ \Delta H = 0,\ \ W = 0,\ \ Q = 0$

$$\Delta S(O_2) = -nR\ln(p_{O_2}/p) = -nR\ln y_{O_2} = 2.676\text{J}\cdot\text{K}^{-1}$$

$$\Delta S(N_2) = -nR\ln(p_{N_2}/p) = -nR\ln y_{N_2} = 1.484\text{J}\cdot\text{K}^{-1}$$

$$\Delta S = \Delta S(O_2) + \Delta S(N_2) = 4.160\text{J}\cdot\text{K}^{-1}$$

$$\Delta A = \Delta G = -T\Delta S = \left(-273.2\times 4.160\right)\text{J} = -1136.7\text{J} < 0$$

2. 非理想气体、液体和固体 *pVT* 变化

- 恒容过程

$$\mathrm{d}U = nC_{V,\mathrm{m}}\mathrm{d}T$$

- 恒压过程

$$\mathrm{d}H = nC_{p,\mathrm{m}}\mathrm{d}T$$

2-9 焦耳-汤姆逊效应

物理化学多媒体课堂教学软件 V1.0版

上一页 下一页 返回目录

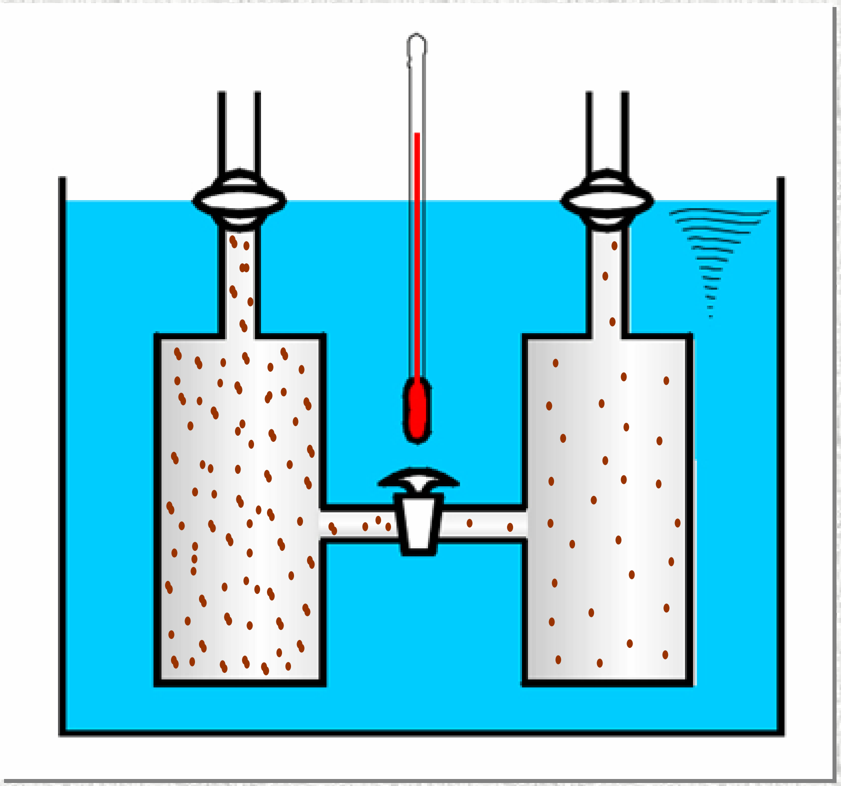
焦耳实验

$W = 0$ $Q = 0$

$\Delta U = 0$

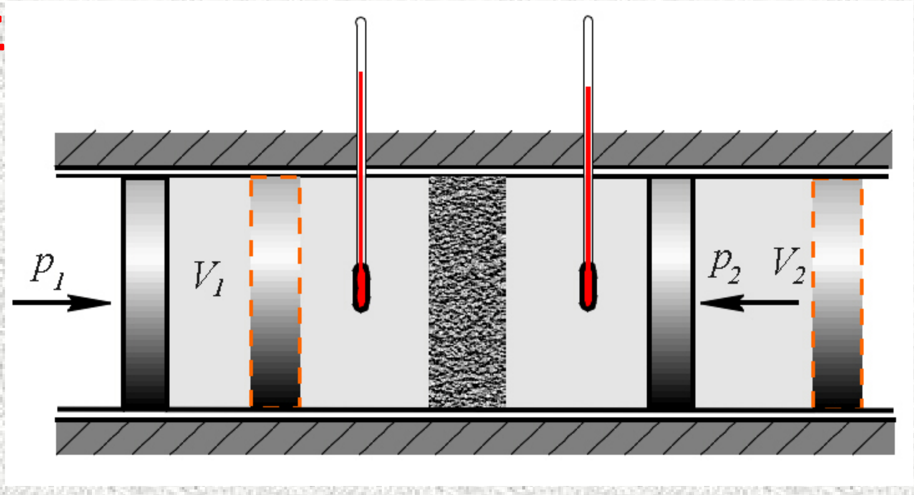
$\mathrm{d}T = 0$ $\mathrm{d}U = 0$

$\mathrm{d}V > 0$ $\mathrm{d}p < 0$



$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T = 0 \qquad \left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T = 0$$

1. 节流过程



$$Q = 0 \quad W = p_1V_1 - p_2V_2$$

$$\Delta U = U_2 - U_1 = p_1V_1 - p_2V_2$$

$$U_2 + p_2V_2 = U_1 + p_1V_1$$

$$H_2 = H_1$$

节流过程是一个恒焓过程

2. 焦耳-汤姆逊系数

$$\mathrm{d}H = nC_{p,\mathrm{m}}\mathrm{d}T + \left[-T\left(\frac{\partial V}{\partial T}\right)_p + V\right]\mathrm{d}p = 0$$

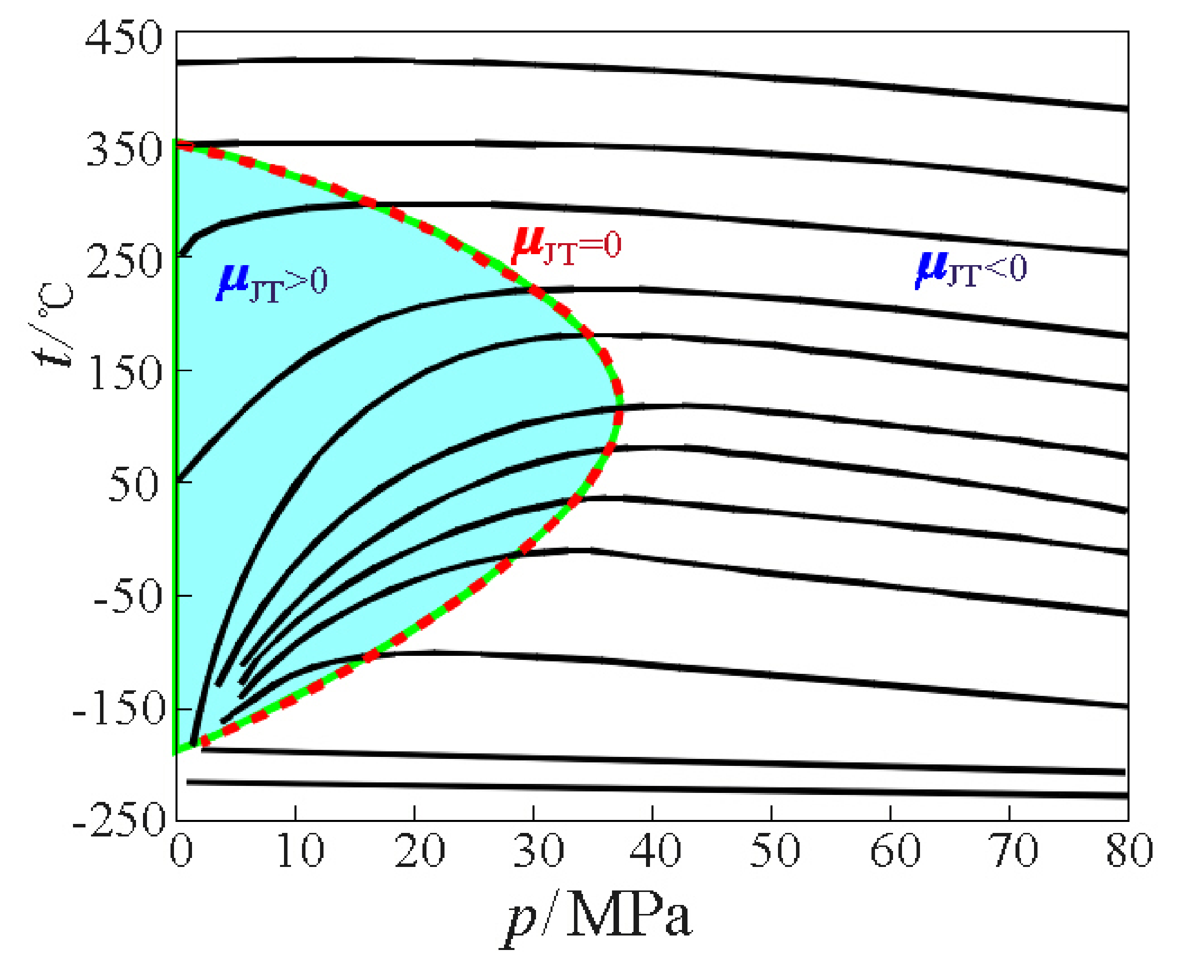
$$\mu_{\mathrm{JT}} \overset{\mathrm{def}}{=\!=} \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_{p,\mathrm{m}}}\left[T\left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p - V_{\mathrm{m}}\right]$$

>0 节流膨胀后，温度降低

<0 节流膨胀后，温度升高

$=0$ 温度不变

3. 转变曲线

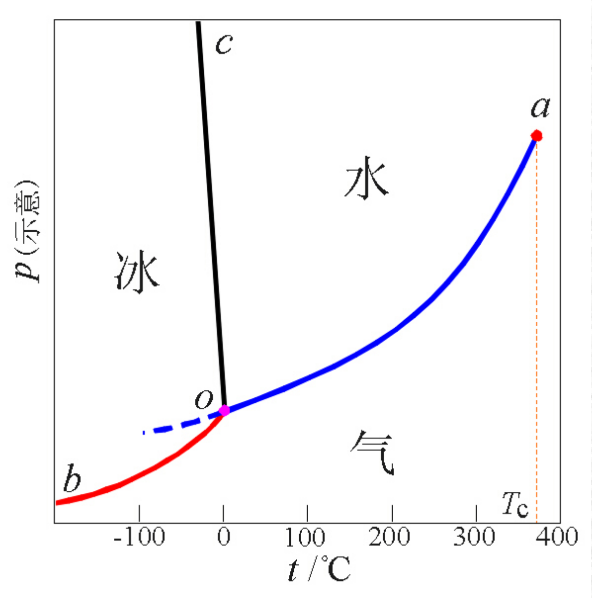

450
350
250
150
50
-50
-150
-250
t/℃
0
10
20
30
40
50
60
70
80
p/MPa
$\mu_{JT}>0$
$\mu_{JT}=0$
$\mu_{JT}<0$

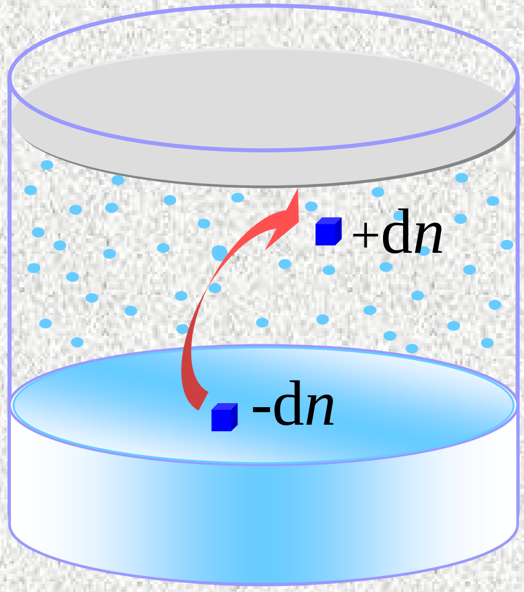
2-10 相变化中热力学函数的变化

物理化学多媒体课堂教学软件 V1.0版

上一页 下一页 返回目录

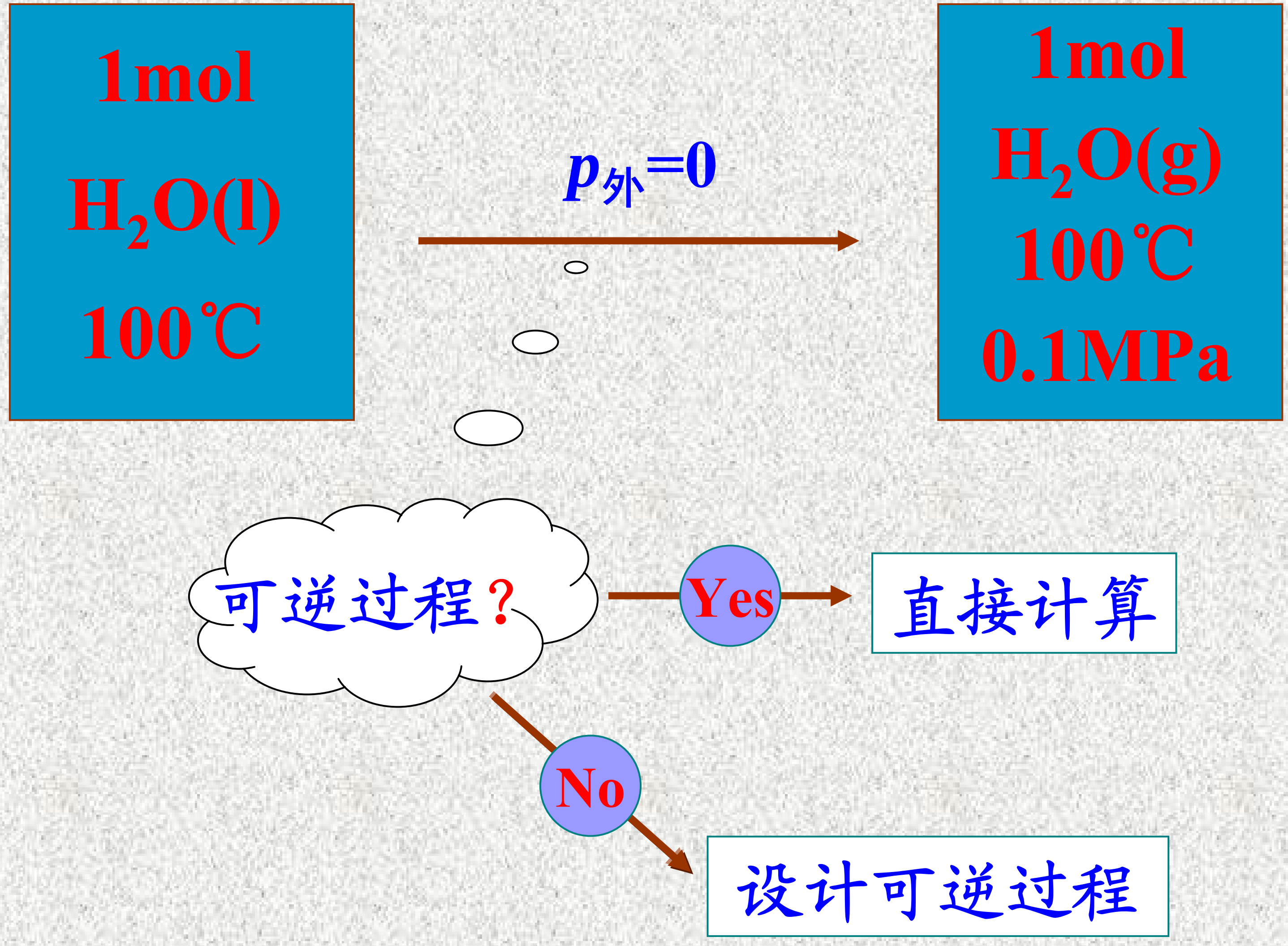
相变化





重要数据:

$$Q_{相变} \overset{?}{=} \Delta_{相变} H$$



1mol

$H_2O(l)$

100℃

$p_{外}=0$

1mol

$H_2O(g)$

100℃

0.1MPa

可逆过程？

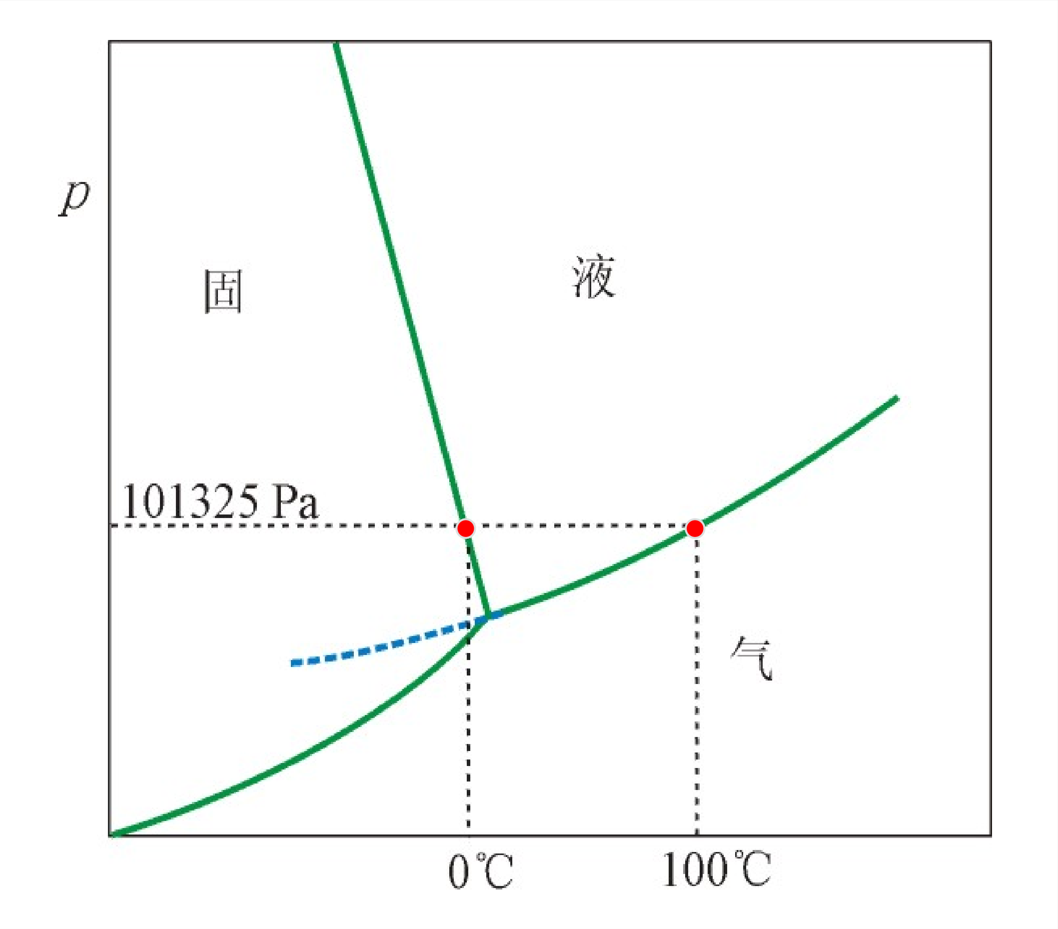
Yes

直接计算

No

设计可逆过程

如何判断过程是否可逆相变化？



初终态是否处于平衡线上？

是否恒温恒压过程？

1. 可逆相变化 $Q_{相变} = \Delta_{相变}H$

$$Q_{相变} = \Delta_{相变}H = H(\beta) - H(\alpha)$$

$$W_{相变} = -p\Delta_{相变}V = -p[V(\beta) - V(\alpha)]$$

$$\Delta_{相变}U = \Delta_{相变}H + W_{相变} = \Delta_{相变}H - p\Delta_{相变}V$$

$$\Delta_{相变}S = Q_{相变}/T = \Delta_{相变}H/T$$

$$\Delta_{相变}A = W_{相变}$$

$$\Delta_{相变}G = 0$$

上一页 下一页 节首

2. 不可逆相变化 $Q_{相变} \neq \Delta_{相变}H$

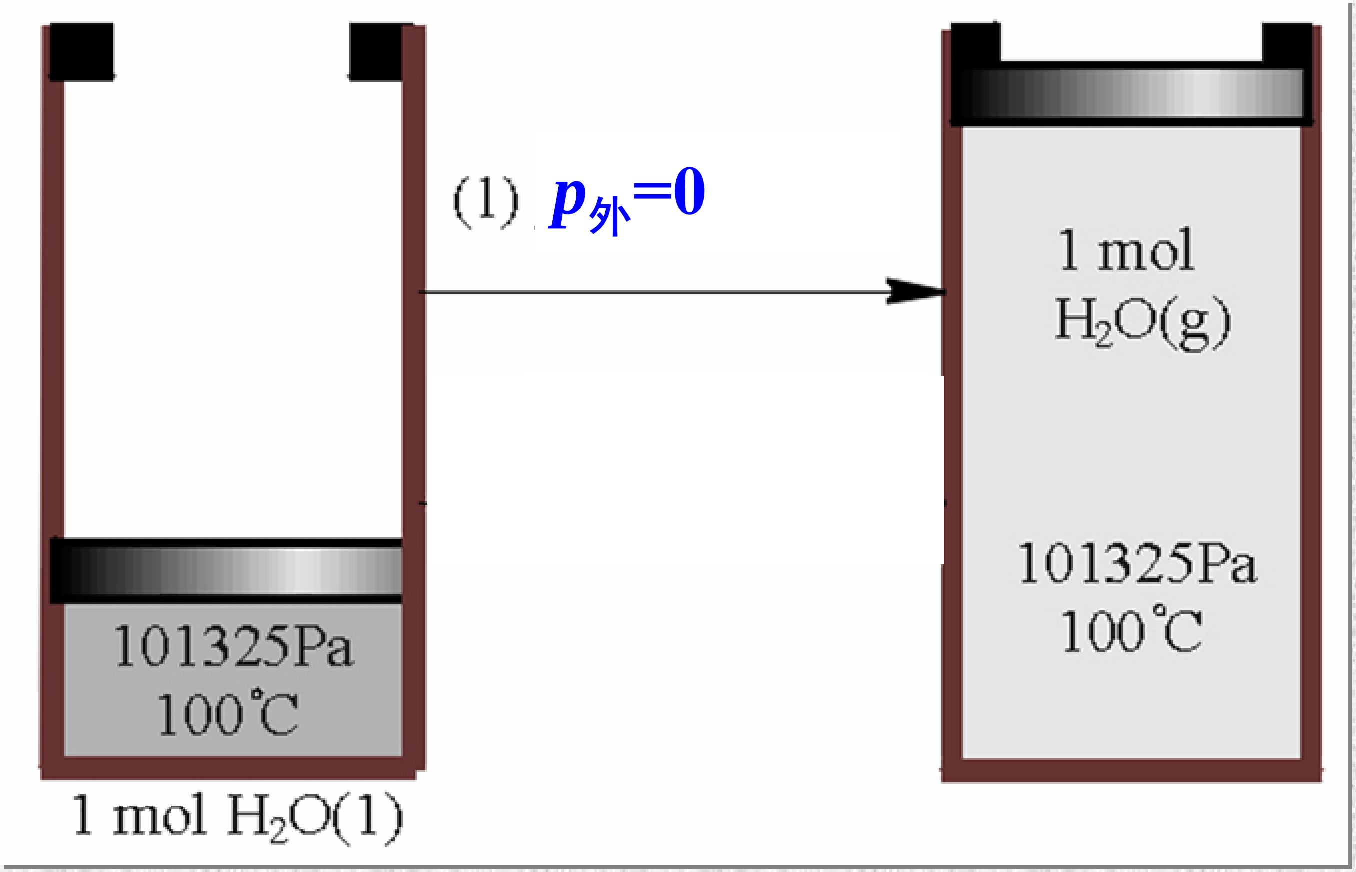
ΔU、ΔH、ΔS、ΔA、ΔG,

按设计的可逆过程计算

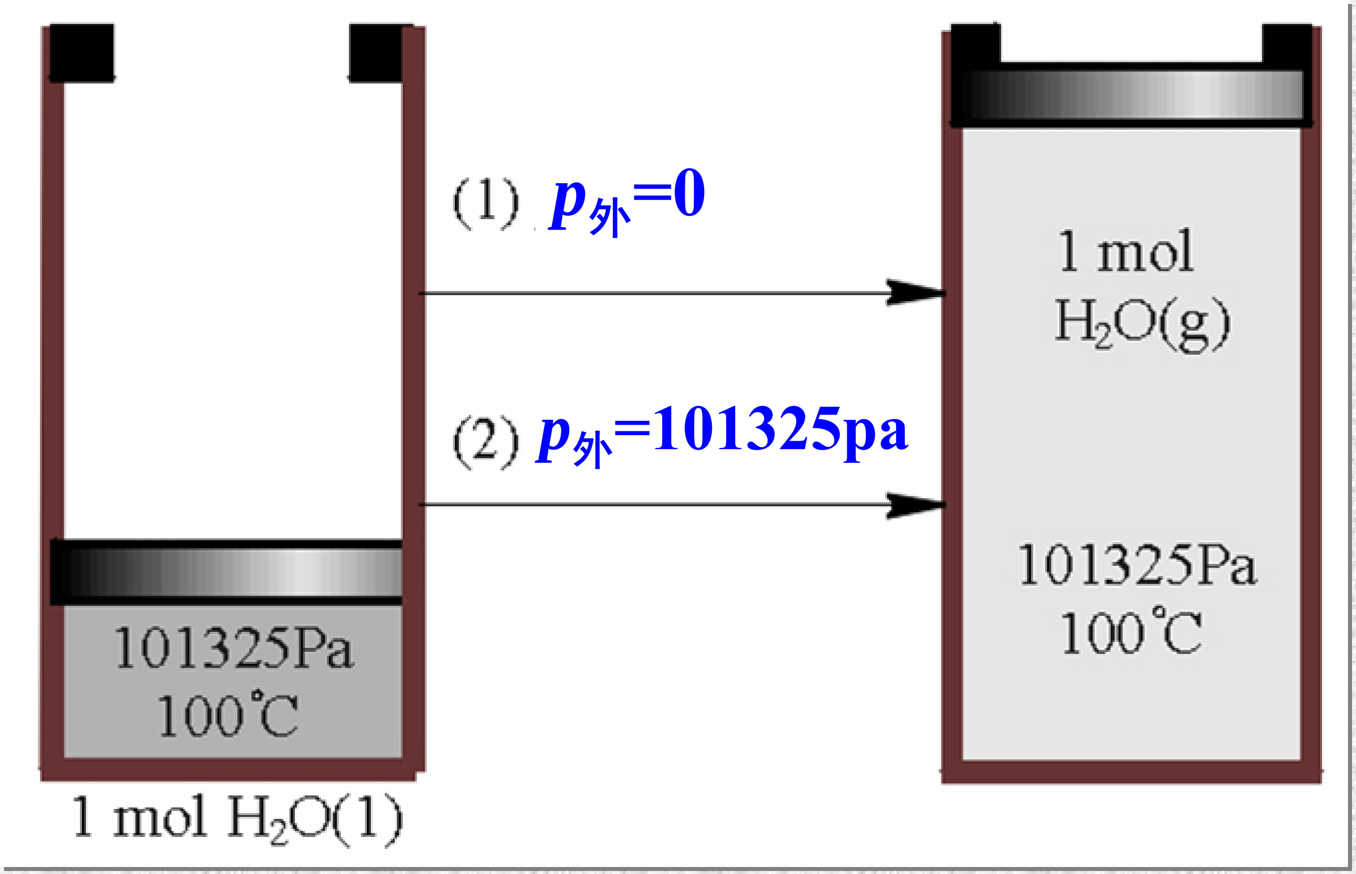
Q、W

按实际过程计算

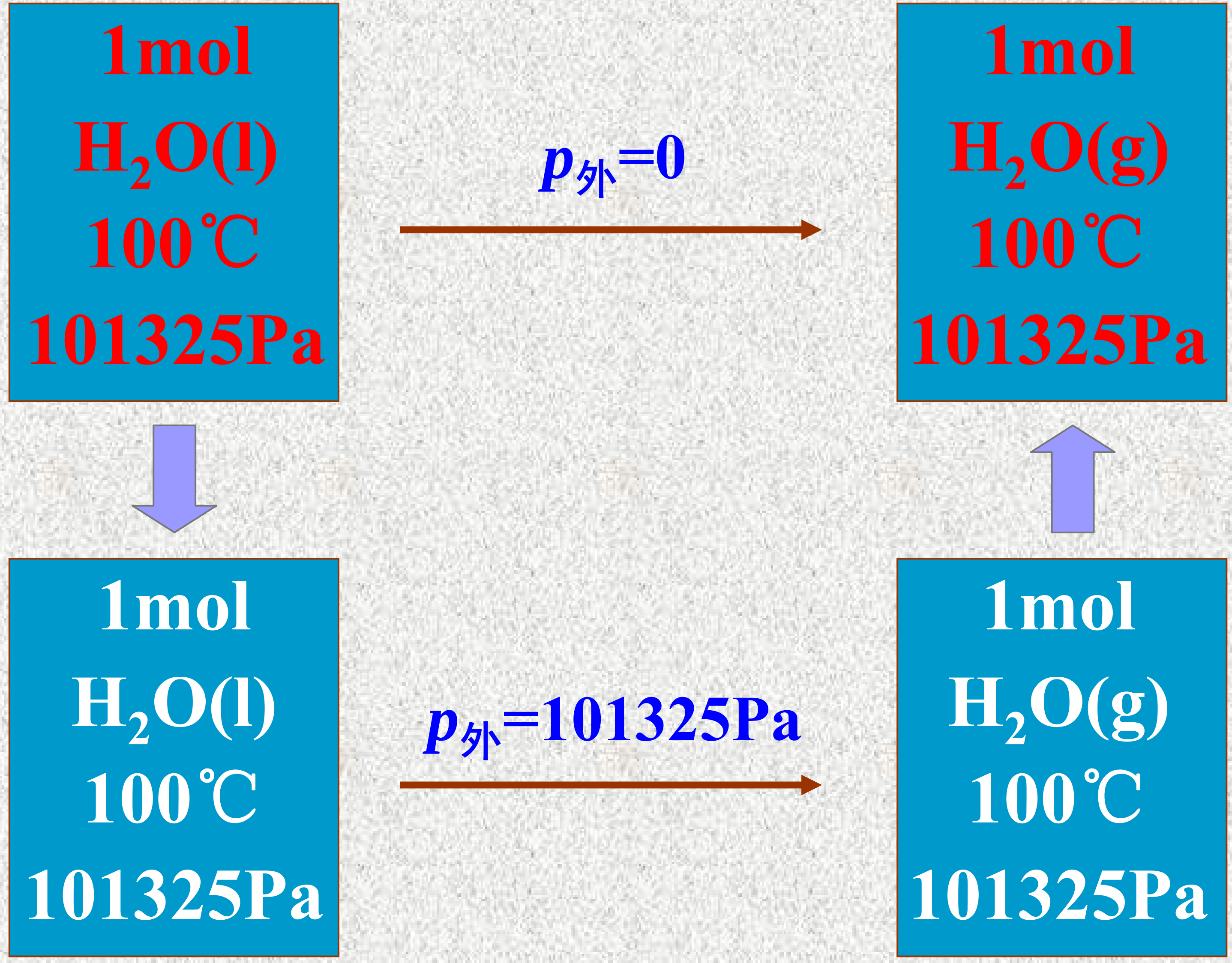
例



例



(1) $p_{外}=0$
(2) $p_{外}=101325pa$
101325Pa
100℃
1 mol $H_2O(1)$
1 mol
$H_2O(g)$
101325Pa
100℃



1mol

$H_2O(l)$

100℃

101325Pa

$p_{外}=0$

1mol

$H_2O(g)$

100℃

101325Pa

1mol

$H_2O(l)$

100℃

101325Pa

$p_{外}=101325Pa$

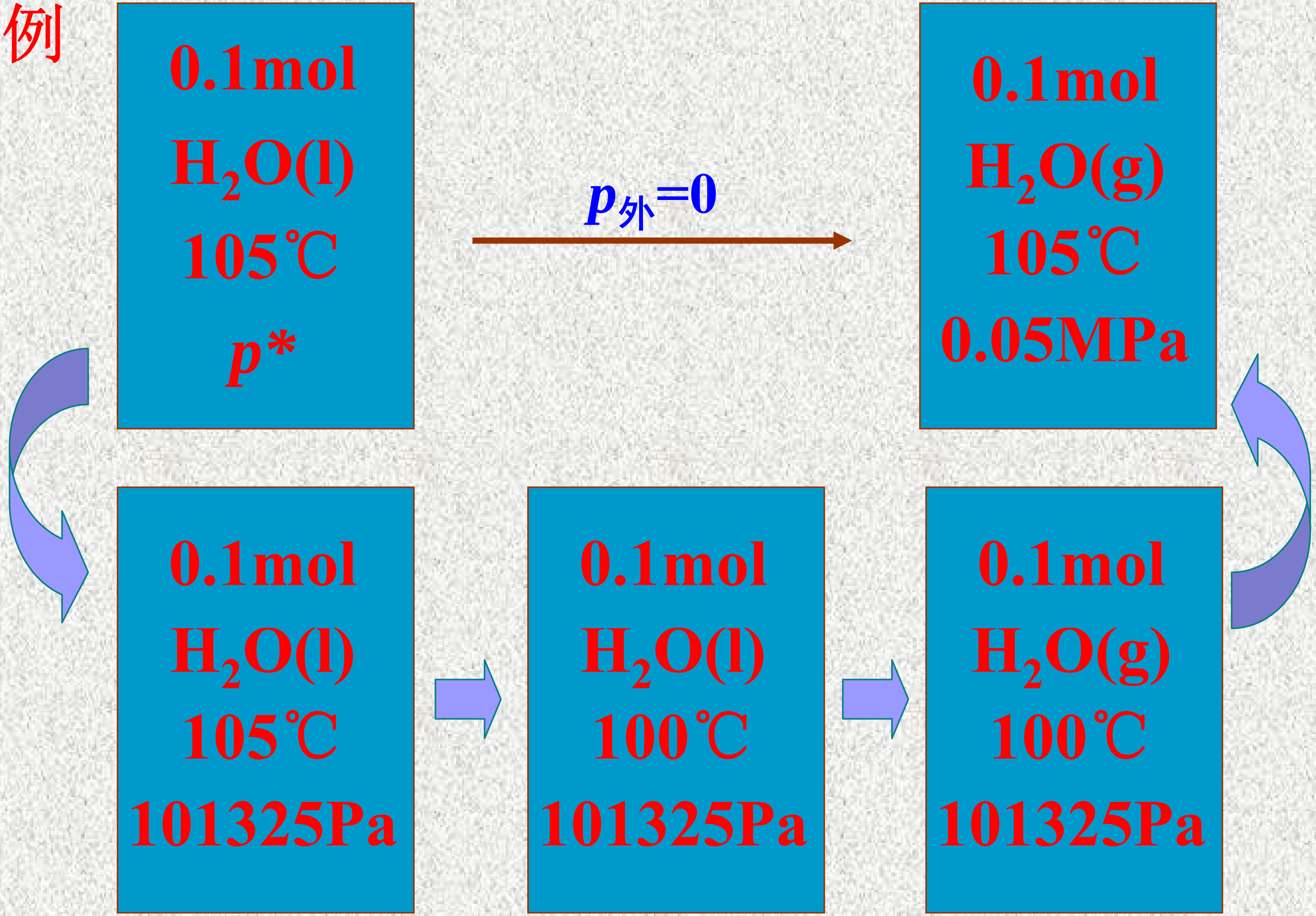
1mol

$H_2O(g)$

100℃

101325Pa

例



0.1mol
$H_2O(l)$
105℃
p^*

$p_{外}=0$

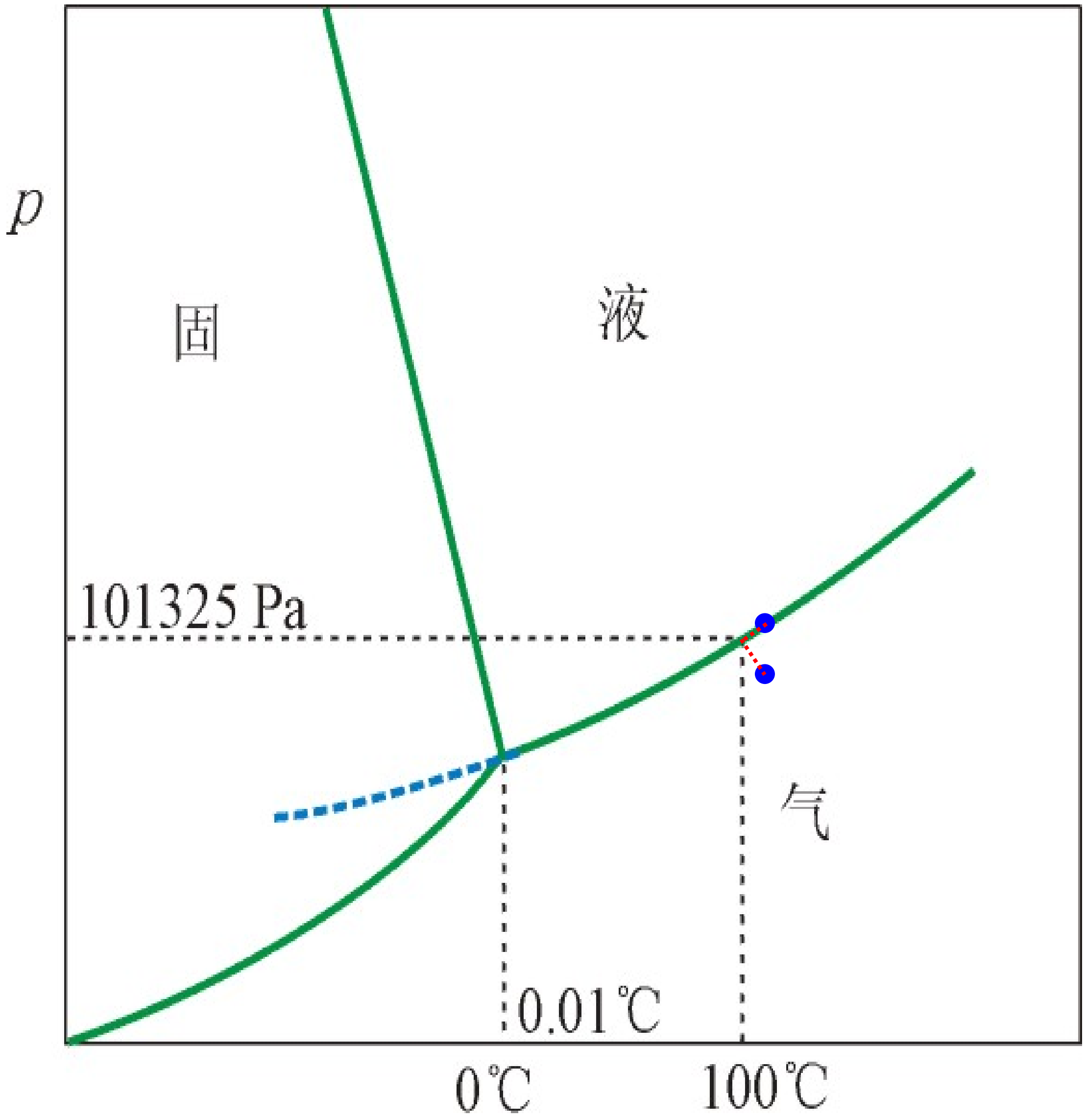
0.1mol
$H_2O(g)$
105℃
0.05MPa

0.1mol
$H_2O(l)$
105℃
101325Pa

0.1mol
$H_2O(l)$
100℃
101325Pa

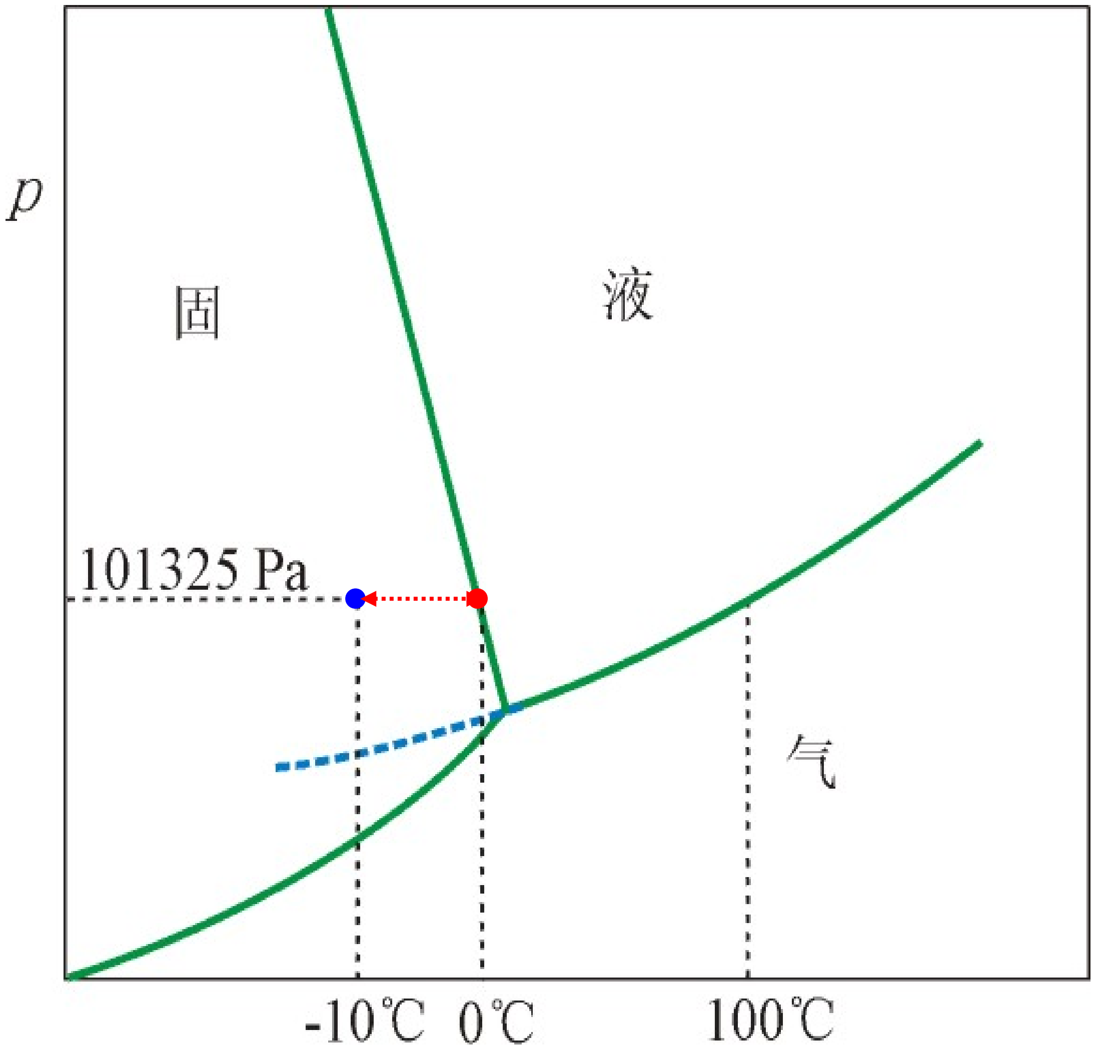
0.1mol
$H_2O(g)$
100℃
101325Pa

上一页 下一页 节首

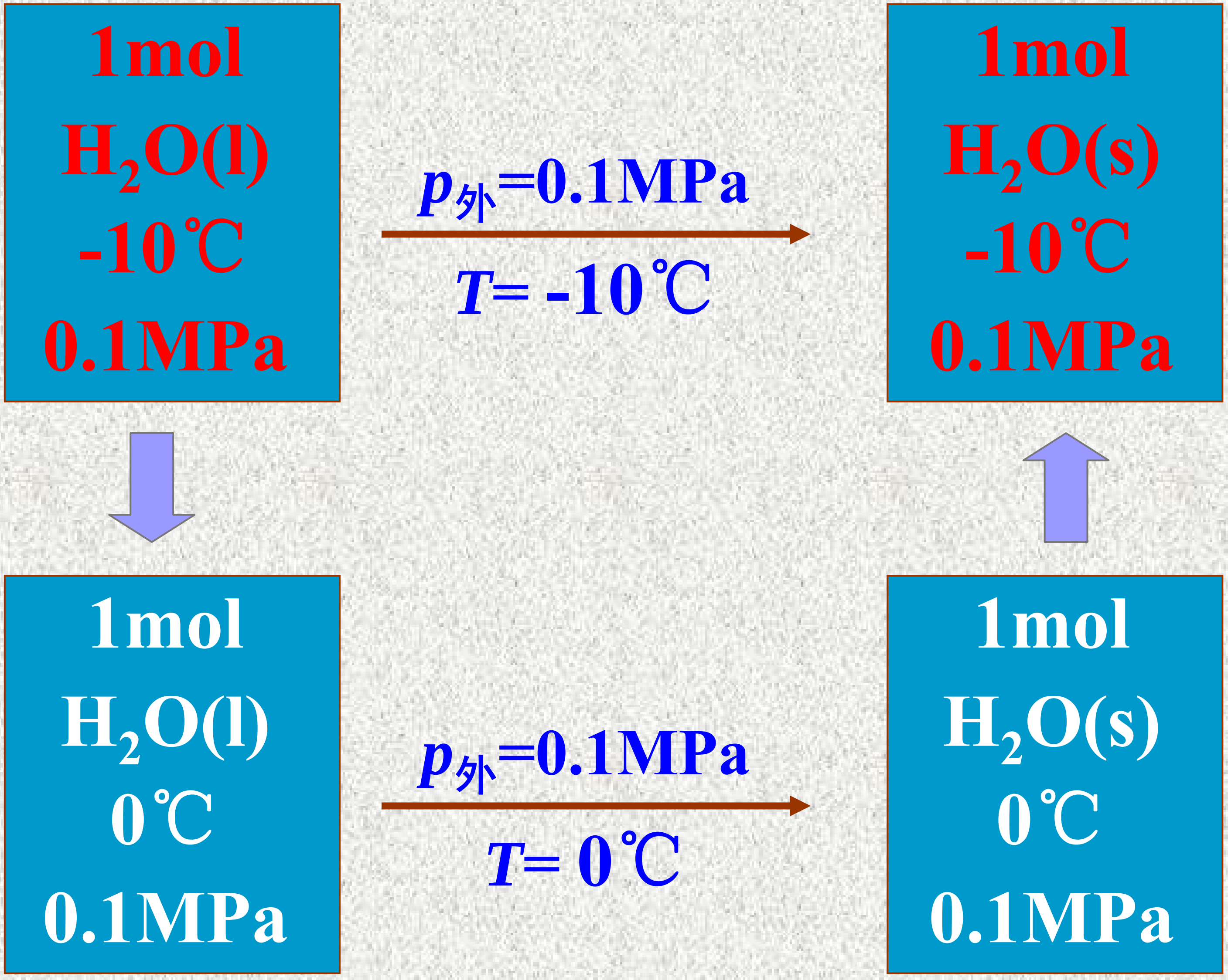

p
固
液
气
101325 Pa
0.01℃
0℃
100℃

例

$$\begin{array}{c}\text{1mol}\\ H_2O(l)\\ -10^{\circ}\text{C}\\ 0.1\text{MPa}\end{array} \xrightarrow[T=-10^{\circ}\text{C}]{p_{外}=0.1\text{MPa}} \begin{array}{c}\text{1mol}\\ H_2O(s)\\ -10^{\circ}\text{C}\\ 0.1\text{MPa}\end{array}$$


p
固
液
气
101325 Pa
-10℃
0℃
100℃

例



1mol
$H_2O(l)$
-10℃
0.1MPa

$p_{外}$=0.1MPa
$\xrightarrow{\hspace{3em}}$
T= -10℃

1mol
$H_2O(s)$
-10℃
0.1MPa

1mol
$H_2O(l)$
0℃
0.1MPa

$p_{外}$=0.1MPa
$\xrightarrow{\hspace{3em}}$
T= 0℃

1mol
$H_2O(s)$
0℃
0.1MPa

上一页 下一页 节首

$$Q_p = (-18.02 \times 312.3 \times 10^{-3})\text{kJ}$$

$$= -5.628\text{kJ}$$

$$W = -p(V_{冰} - V_{水})$$

$$= \left[-101325 \times \left(\frac{1}{0.917} - \frac{1}{1.000} \right) \times 18.02 \times 10^{-9} \right] \text{kJ}$$

$$= -0.165 \times 10^{-3}\text{kJ}$$

$$\Delta H_1 = n \times C_{pm}\big(\mathrm{H_2O(l)}\big) \times \Delta T$$

$$= \big(1 \times 4.184 \times 18.02 \times 10\big)\mathrm{J} = 754.0\mathrm{J}$$

$$\Delta H_2 = -n \times \Delta_{\mathrm{fus}}\big(\mathrm{H_2O}\big)$$

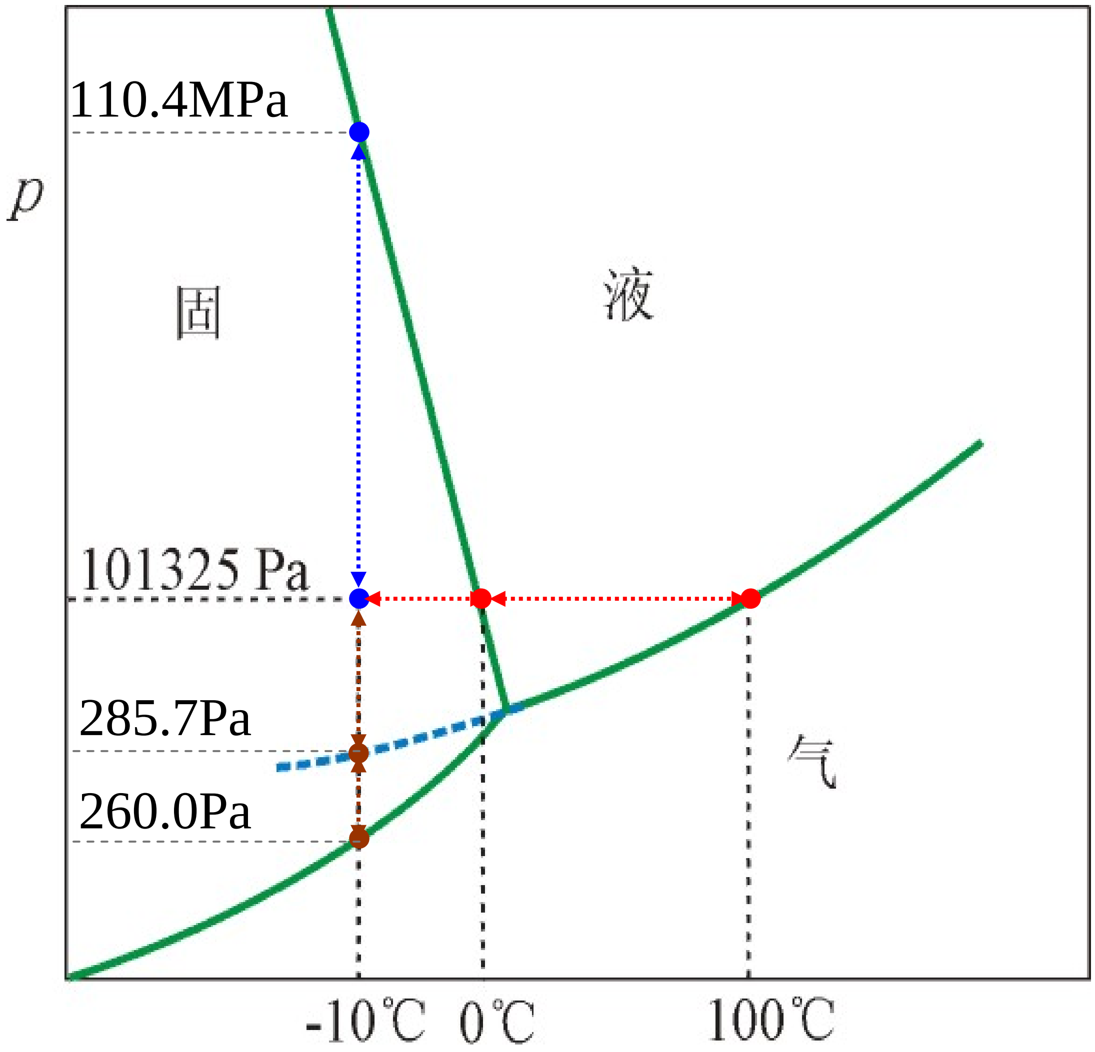
$$= -\big(1 \times 333.4 \times 18.02\big)\mathrm{J} = -6008\mathrm{J}$$

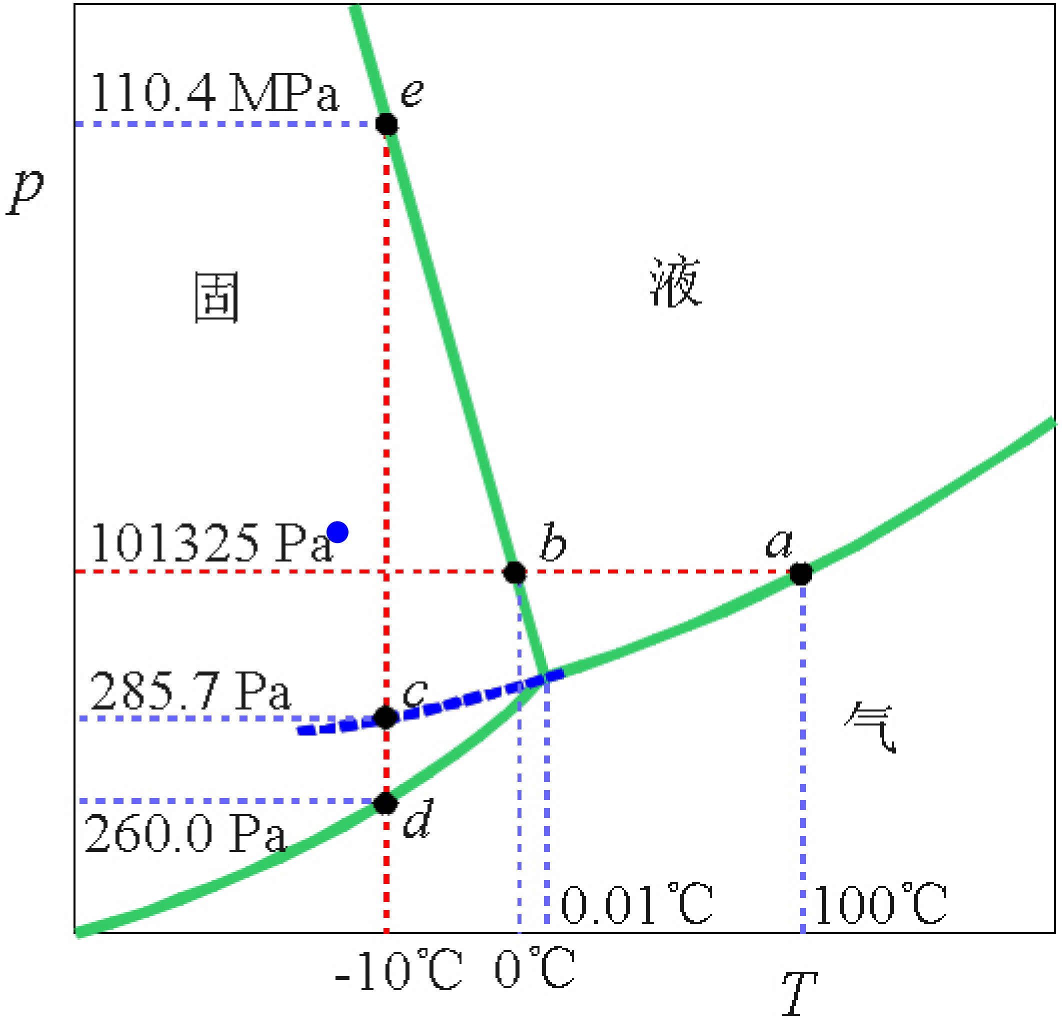
$$\Delta H_3 = n \times C_{pm}\big(\mathrm{H_2O(s)}\big) \times \Delta T$$

$$= \big(1 \times 2.067 \times 18.02 \times -10\big)\mathrm{J} = -372.5\mathrm{J}$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -5.627\mathrm{kJ}$$

上一页 下一页 节首


p
110.4MPa
101325 Pa
285.7Pa
260.0Pa
固
液
气
-10℃
0℃
100℃

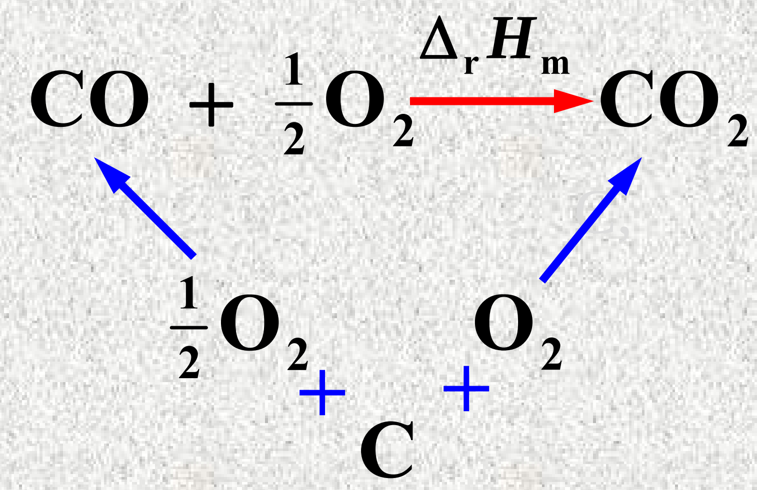

p
110.4 MPa
e
固
液
101325 Pa
b
a
285.7 Pa
c
260.0 Pa
d
气
0.01℃
100℃
-10℃
0℃
T

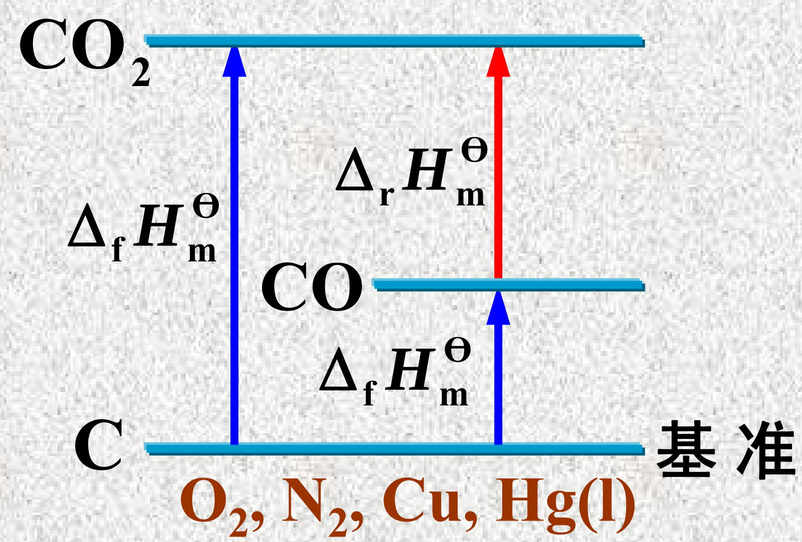
2-11 热力学第三定律

物理化学多媒体课堂教学软件 V1.0版

上一页 下一页 返回目录

△*H* 的计算：





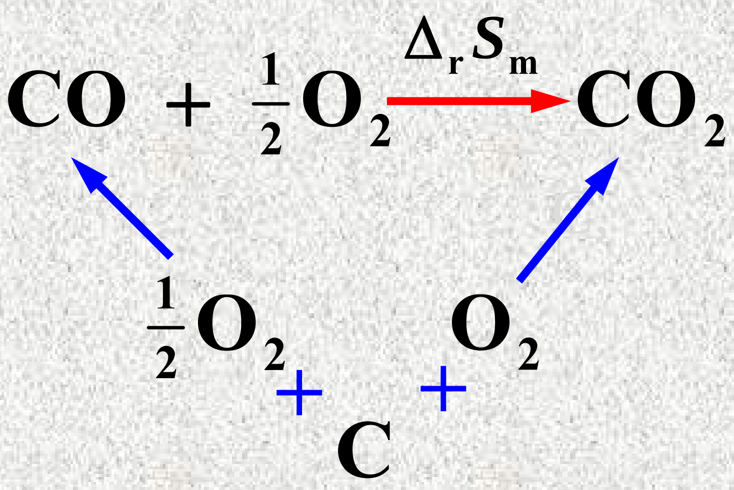
$$\Delta_r H_m = H(CO_2) - H(CO) - \frac{1}{2}H(O_2)$$

$$= \left[H(CO_2) - H(C) - H(O_2)\right] - \left[H(CO) - H(C) - \frac{1}{2}H(O_2)\right]$$

$$= \Delta_f H_m(CO_2) - \Delta_f H_m(CO)$$

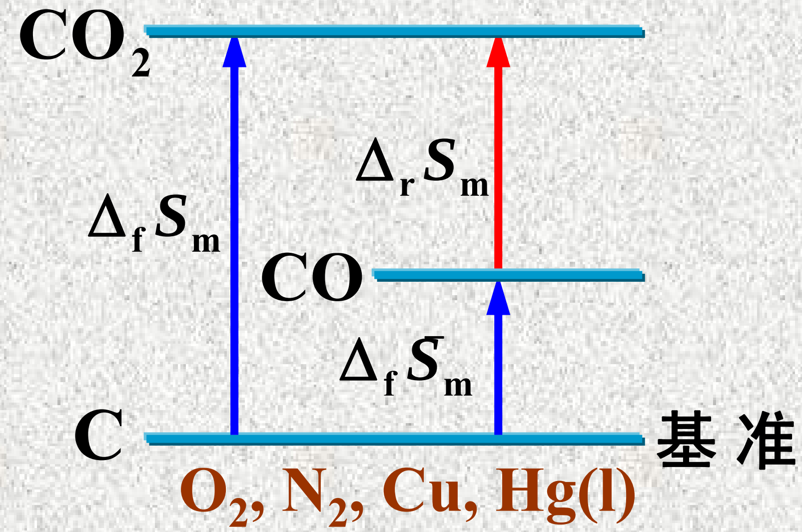
恒压下的量热实验 $\Delta H = Q_p$

△*S* 的计算：



$$CO + \frac{1}{2}O_2 \xrightarrow{\Delta_r S_m} CO_2$$

$$\frac{1}{2}O_2 + C + O_2$$



无法实验测定

$$\Delta_f S_m = \frac{\text{đ}Q_R}{T}$$

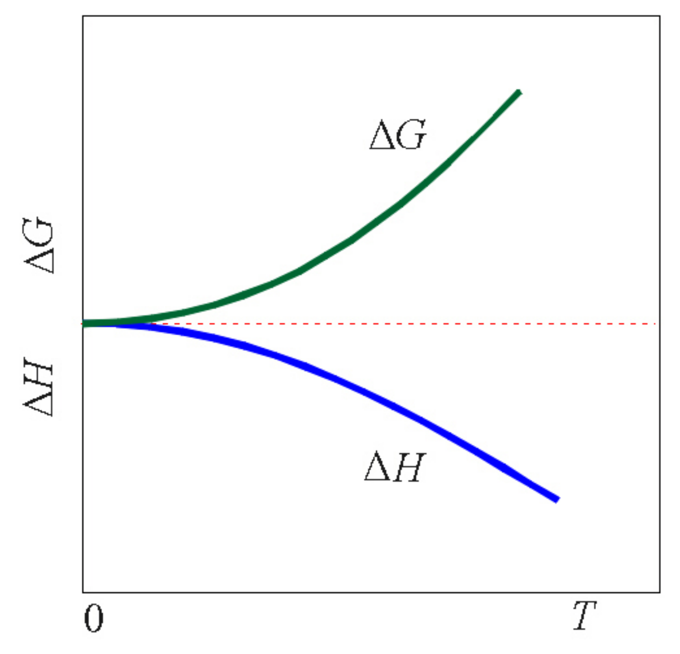
1. 能斯特热定理

理查兹：

$$\lim_{T\to 0}(\Delta H-\Delta G)=0$$

能斯特：

$$\lim_{T\to 0}\left(\frac{\partial\,\Delta H}{\partial\,T}\right)_p=0,\quad \lim_{T\to 0}\left(\frac{\partial\,\Delta G}{\partial\,T}\right)_p=0$$



$$\lim_{T\to 0}\Delta C_p=0$$

$$\lim_{T\to 0}\Delta S=0$$

温度趋于0K时，凝聚系统中恒温过程的熵变趋于零。

2. 普朗克假设

$$\lim_{T\to 0}\Delta S=\sum\nolimits_{\mathrm{B}} v_{\mathrm{B}} S^{*}_{\mathrm{m}}(\mathrm{B},0\mathrm{K})=0$$

$$S^{*}_{\mathrm{m}}(0\mathrm{K})=S^{*}(0\mathrm{K})=0$$

0K时，纯固体和纯液体的熵值等于零。

路易斯、吉布逊

$$S^{*}(0\mathrm{K},\mathrm{eq})=0$$

0K时，纯物质完美晶体的熵值等于零

COCOCOCOCO… → COCOOCCOCO…

3. 热力学第三定律

西蒙， 1927年：

当温度趋于0K，系统中仅涉及处于内部平衡的纯物质时，则恒温过程的熵变趋于零。

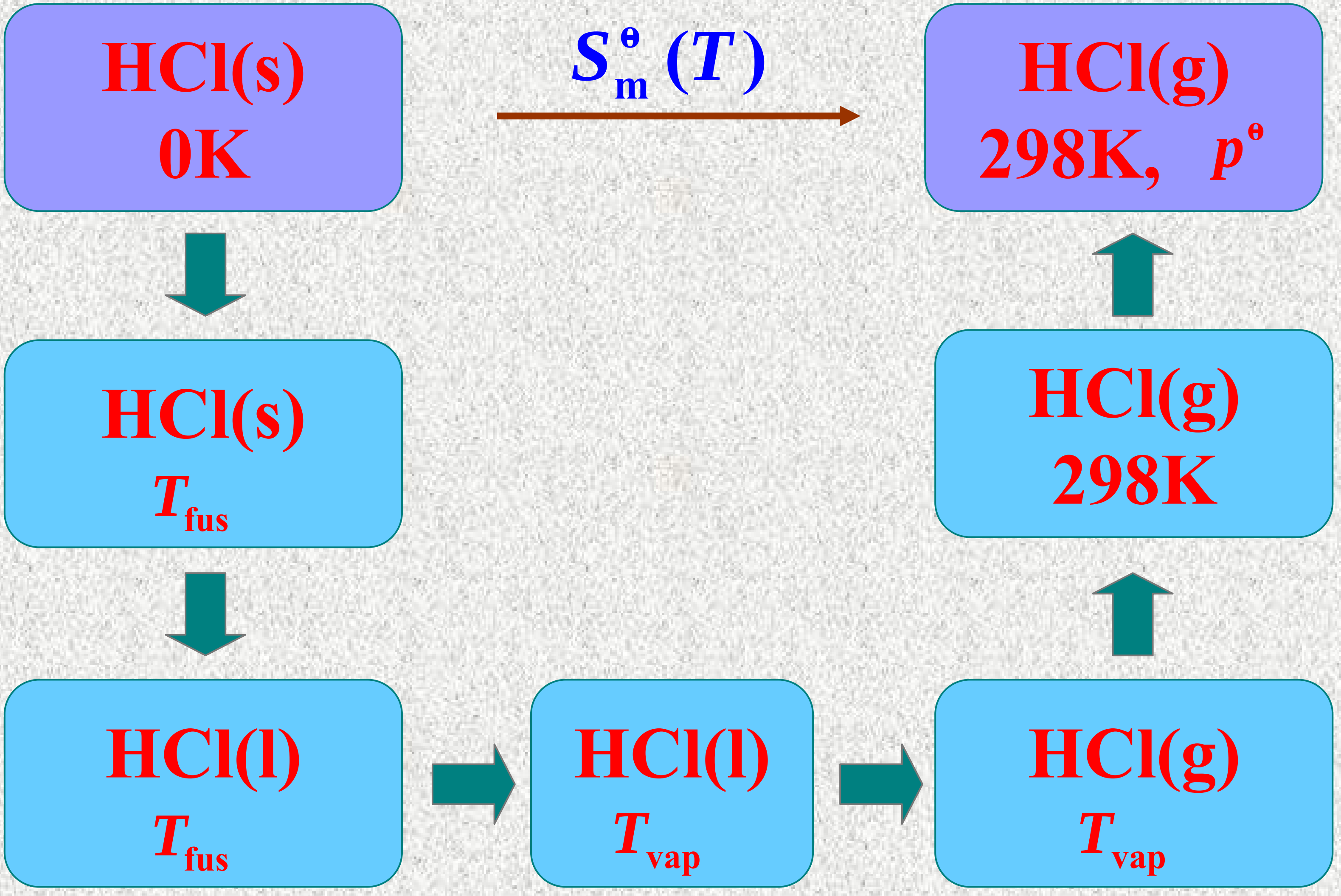
上一页 下一页 节首

$$\begin{tikzcd}
\mathrm{CO}+\frac{1}{2}\mathrm{O}_2 \arrow[r, "\Delta_r S_m^\ominus"] \arrow[d, "-\Delta S_m^\ominus(T)"] & \mathrm{CO}_2 & T\mathrm{K} \\
\mathrm{CO}+\frac{1}{2}\mathrm{O}_2 \arrow[r, "\Delta_r S_m^\ominus = 0"] & \mathrm{CO}_2 \arrow[u, "\Delta S_m^\ominus(T)"'] & 0\mathrm{K}
\end{tikzcd}$$

$$\Delta S_m^\ominus(T) = S_m^\ominus(T) - S_m^\ominus(0\mathrm{K}) = S_m^\ominus(T)$$

$$\boxed{S_m^\ominus(T) \quad \text{标准摩尔规定熵}}$$

$$\Delta_r S_m^\ominus = \sum_B \nu_B S_m^\ominus(\mathrm{B})$$



HCl(s)
0K

$S_m^{\theta}(T)$

HCl(g)
298K, p^{θ}

HCl(s)
T_{fus}

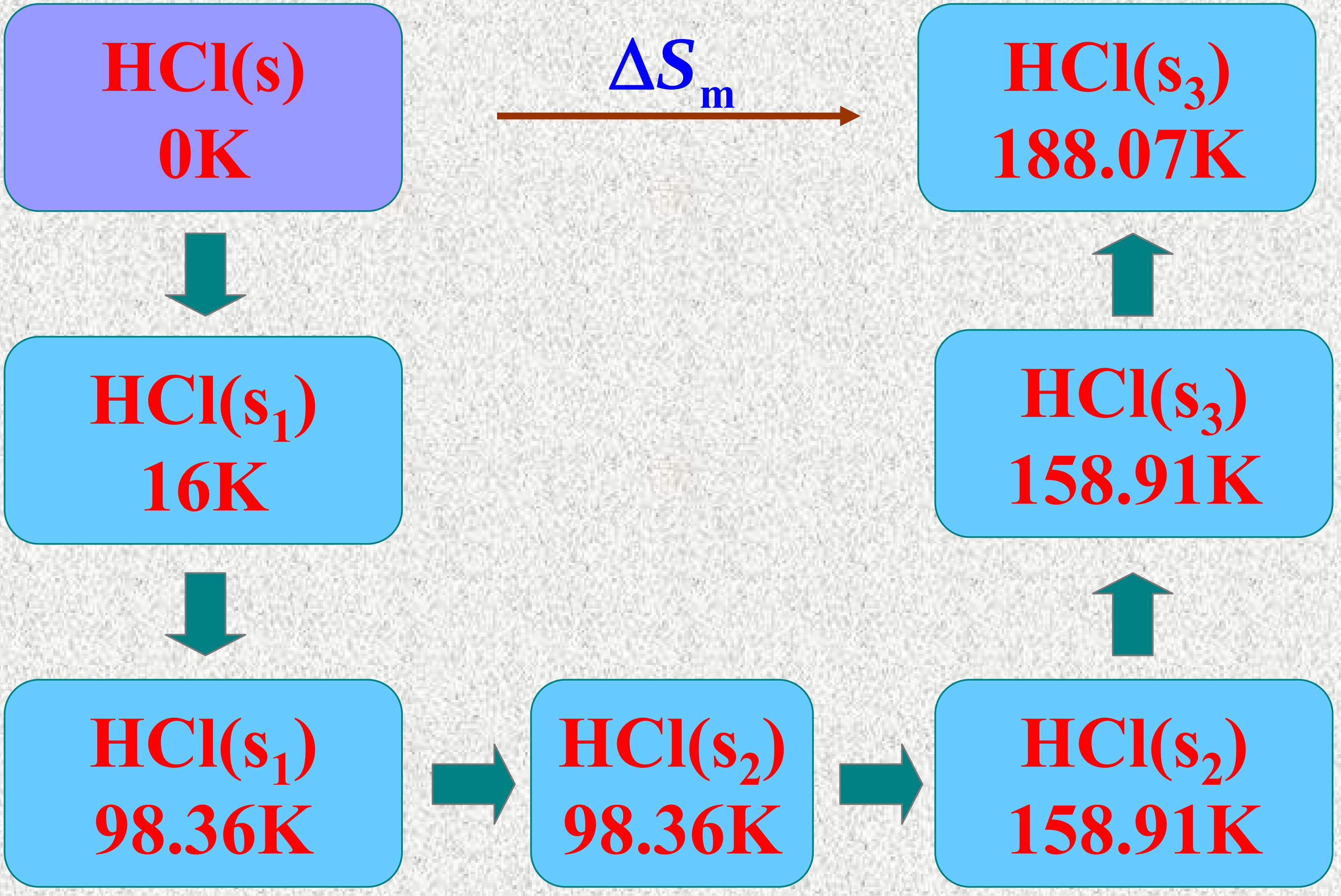
HCl(l)
T_{fus}

HCl(l)
T_{vap}

HCl(g)
T_{vap}

HCl(g)
298K

上一页 下一页 节首



$HCl(s)$ 0K

ΔS_m

$HCl(s_3)$ 188.07K

$HCl(s_1)$ 16K

$HCl(s_3)$ 158.91K

$HCl(s_1)$ 98.36K

$HCl(s_2)$ 98.36K

$HCl(s_2)$ 158.91K

上一页 下一页 节首

$$S_{\mathrm{m}}^{\ominus}(T)=\int_{0}^{16\mathrm{K}}\frac{12}{5}\pi^{4}R\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^{3}\mathrm{d}T+\int_{16\mathrm{K}}^{T_{\mathrm{trs}}}\frac{C_{p,\mathrm{m}}^{\ominus}(\mathrm{crI})}{T}\mathrm{d}T$$

$$+\frac{\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\ominus}}{T_{\mathrm{t}}}+\int_{T_{\mathrm{trs}}}^{T_{\mathrm{f}}}\frac{C_{p,\mathrm{m}}^{\ominus}(\mathrm{crII})}{T}\mathrm{d}T+\frac{\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\ominus}}{T_{\mathrm{f}}}$$

$$+\int_{T_{\mathrm{f}}}^{T_{\mathrm{b}}}\frac{C_{p,\mathrm{m}}^{\ominus}(\mathrm{l})}{T}\mathrm{d}T+\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{T_{\mathrm{b}}}+\int_{T_{\mathrm{b}}}^{T}\frac{C_{p,\mathrm{m}}^{\ominus}(\mathrm{g})}{T}\mathrm{d}T$$

上一页 下一页 节首

$$S_{\mathrm{m}}^{\ominus}(T)=\int_{0}^{16\mathrm{K}}\frac{12}{5}\pi^{4}R\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^{3}\mathrm{d}T+\int_{16\mathrm{K}}^{T_{\mathrm{trs}}}\frac{C_{p,\mathrm{m}}^{\ominus}(\mathrm{crI})}{T}\mathrm{d}T$$

$$+\frac{\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\ominus}}{T_{\mathrm{t}}}+\int_{T_{\mathrm{trs}}}^{T_{\mathrm{f}}}\frac{C_{p,\mathrm{m}}^{\ominus}(\mathrm{crII})}{T}\mathrm{d}T+\frac{\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\ominus}}{T_{\mathrm{f}}}$$

$$+\int_{T_{\mathrm{f}}}^{T_{\mathrm{b}}}\frac{C_{p,\mathrm{m}}^{\ominus}(\mathrm{l})}{T}\mathrm{d}T+\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{T_{\mathrm{b}}}+\int_{T_{\mathrm{b}}}^{T}\frac{C_{p,\mathrm{m}}^{\ominus}(\mathrm{g})}{T}\mathrm{d}T$$

2-12 化学反应中的热力学函数变化

物理化学多媒体课堂教学软件 V1.0版

1. 标准摩尔反应热力学函数

$$0 = \sum_B \nu_B \mathrm{B}$$

恒温：

$$\Delta_r H_m^\ominus = \sum_B \nu_B \Delta_f H_m^\ominus(\mathrm{B})$$

$$= -\sum_B \nu_B \Delta_c H_m^\ominus(\mathrm{B})$$

$$\Delta_r S_m^\ominus = \sum_B \nu_B S_m^\ominus(\mathrm{B})$$

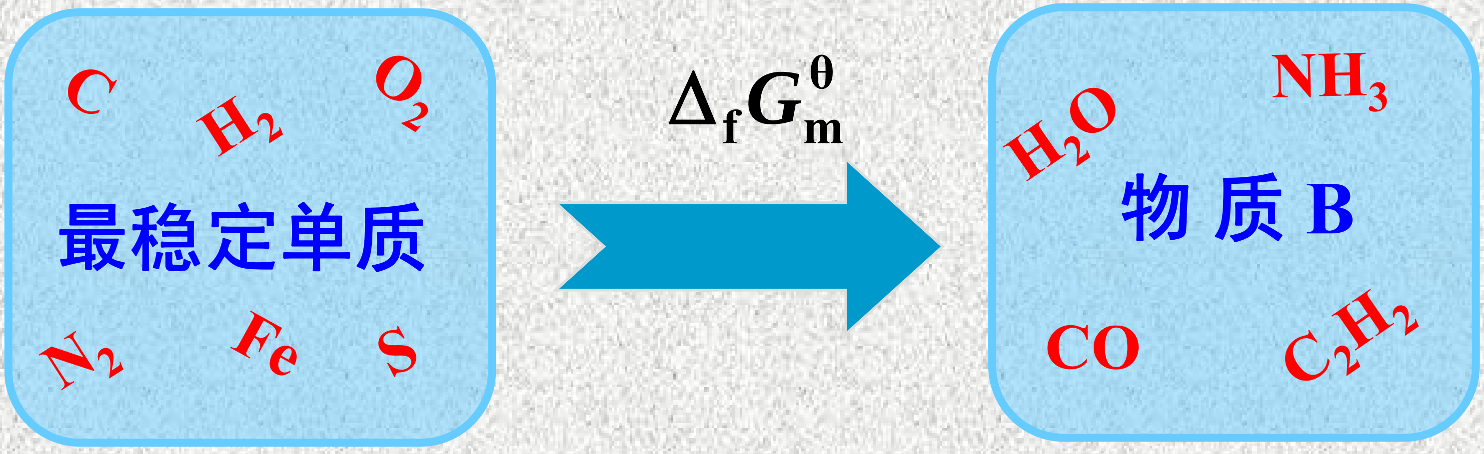
$$\Delta_r U_m^\ominus = \Delta_r H_m^\ominus - p^\ominus \Delta V$$

$$\Delta_r A_m^\ominus = \Delta_r U_m^\ominus - T\Delta_r S_m^\ominus$$

$$\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T\Delta_r S_m^\ominus$$

2. 标准摩尔生成吉氏函数

定义：由最稳定单质生成某物质的标准摩尔反应吉氏函数 $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\theta}$


C H_2 O_2

最稳定单质

N_2 Fe S

$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\theta}$

H_2O NH_3

物 质 B

CO C_2H_2

例：苯的标准摩尔生成吉氏函数

$$6\mathrm{C(s, graphite)} + 3\mathrm{H}_2 \xrightarrow{\Delta_\mathrm{r} G_\mathrm{m}^\theta} \mathrm{C}_6\mathrm{H}_6(\mathrm{l})$$

$$\boxed{\Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{C}_6\mathrm{H}_6) \overset{\mathrm{def}}{=\!=} \Delta_\mathrm{r} G_\mathrm{m}^\theta}$$

$$\Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{H}_2) = \Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{O}_2) = \Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{N}_2) = 0$$

$$\Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{Fe}) = \Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{S}) = \Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{C}, \text{石墨}) = 0$$

上一页 下一页 节首

$$\begin{tikzcd}
\mathrm{CO}+\frac{1}{2}\mathrm{O}_2 \arrow[rr, "\Delta_\mathrm{r} G_1"] \arrow[dr, "\Delta_\mathrm{r} G_2"'] & & \mathrm{CO}_2 \\
& \mathrm{C}+\mathrm{O}_2 \arrow[ur, "\Delta_\mathrm{r} G_3"'] &
\end{tikzcd}$$

$$\Delta_\mathrm{r} G_1 = \Delta_\mathrm{r} G_2 + \Delta_\mathrm{r} G_3$$

$$\Delta_\mathrm{r} G_\mathrm{m}^\theta = -\Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{CO}) + \Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{CO_2})$$

$$= \Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{CO_2}) - \Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{CO})$$

$$= \sum \nu_\mathrm{B} \Delta_\mathrm{f} G_\mathrm{m}^\theta(\mathrm{B})$$

3. 温度的影响和克希霍夫方程

克希霍夫方程

$$\left(\frac{\partial H}{\partial T}\right)_p = nC_{p,\mathrm{m}} \qquad \frac{\mathrm{d}\Delta_\mathrm{r} H_\mathrm{m}^\ominus}{\mathrm{d}T} = \Delta_\mathrm{r} C_{p,\mathrm{m}}^\ominus$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{nC_{p,\mathrm{m}}}{T} \qquad \frac{\mathrm{d}\Delta_\mathrm{r} S_\mathrm{m}^\ominus}{\mathrm{d}T} = \frac{\Delta_\mathrm{r} C_{p,\mathrm{m}}^\ominus}{T}$$

$$\boxed{\Delta_\mathrm{r} C_{p,\mathrm{m}}^\ominus = \sum_\mathrm{B} \nu_\mathrm{B} C_{p,\mathrm{m}}^\ominus(\mathrm{B})}$$

$\Delta_\mathrm{r} C_{p,\mathrm{m}}^\ominus =$ 常数

$$\boxed{\Delta_\mathrm{r} H_\mathrm{m}^\ominus(T) = \Delta H^\ominus(298.2\mathrm{K}) + \Delta_\mathrm{r} C_{p,\mathrm{m}}^\ominus(T/\mathrm{K} - 298.2)}$$

$$C_{p,\mathrm{m}}^{\ominus} = a + bT + cT^2$$

$$\Delta_{\mathrm{r}} C_{p,\mathrm{m}}^{\ominus} = \Delta_{\mathrm{r}} a + \Delta_{\mathrm{r}} bT + \Delta_{\mathrm{r}} cT^2$$

$$\Delta_{\mathrm{r}} a = \sum_{\mathrm{B}} \nu_{\mathrm{B}} a(\mathrm{B})$$

$$\Delta_{\mathrm{r}} b = \sum_{\mathrm{B}} \nu_{\mathrm{B}} b(\mathrm{B})$$

$$\Delta_{\mathrm{r}} c = \sum_{\mathrm{B}} \nu_{\mathrm{B}} c(\mathrm{B})$$

$$\underline{\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus}(T)} = \Delta H_0 + \int \Delta_{\mathrm{r}} C_{p,\mathrm{m}}^{\ominus} \mathrm{d}T$$

$$= \Delta H_0 + \Delta_{\mathrm{r}} aT + \frac{\Delta_{\mathrm{r}} bT^2}{2} + \frac{\Delta_{\mathrm{r}} cT^3}{3}$$

$$\underline{\Delta_{\mathrm{r}} S_{\mathrm{m}}^{\ominus}(T)} = I + \Delta_{\mathrm{r}} a \ln\left(\frac{T}{\mathrm{K}}\right) + \Delta_{\mathrm{r}} bT + \frac{\Delta_{\mathrm{r}} cT^2}{2}$$

$$\underline{\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\ominus}(T)} = \Delta H_0 - IT$$

$$+ \Delta_{\mathrm{r}} aT\left[1 - \ln\left(\frac{T}{\mathrm{K}}\right)\right] - \frac{\Delta_{\mathrm{r}} bT^2}{2} - \frac{\Delta_{\mathrm{r}} cT^3}{6}$$

上一页 下一页 节首

计算类型（△*H*, △*S*, △*G*）

◆ 恒温过程

$T = 298.2\mathrm{K}$

$$\Delta_\mathrm{r} H_\mathrm{m}^\ominus = \sum_\mathrm{B} \nu_\mathrm{B} \Delta_\mathrm{f} H_\mathrm{m}^\ominus(\mathrm{B})$$

$$= -\sum_\mathrm{B} \nu_\mathrm{B} \Delta_\mathrm{c} H_\mathrm{m}^\ominus(\mathrm{B})$$

$$\Delta_\mathrm{r} S_\mathrm{m}^\ominus = \sum_\mathrm{B} \nu_\mathrm{B} S_\mathrm{m}^\ominus(\mathrm{B})$$

$$\Delta_\mathrm{r} G_\mathrm{m}^\ominus = \sum_\mathrm{B} \nu_\mathrm{B} \Delta_\mathrm{f} G_\mathrm{m}^\ominus(\mathrm{B})$$

$$\Delta_\mathrm{r} G_\mathrm{m}^\ominus = \Delta_\mathrm{r} H_\mathrm{m}^\ominus - T\Delta_\mathrm{r} S_\mathrm{m}^\ominus$$

计算类型（△*H*, △*S*, △*G*）

◆ **恒温过程**

$$\Delta H_{\mathrm{m}}^{\ominus}=\Delta H_0+\int \Delta C_{p,\mathrm{m}}^{\ominus}\,\mathrm{d}T$$

$$\Delta S_{\mathrm{m}}^{\ominus}=I+\int \frac{\Delta_{\mathrm{r}} C_{p,\mathrm{m}}^{\ominus}}{T}\,\mathrm{d}T$$

$$\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\ominus}(T)=\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\ominus}(T)-T\Delta_{\mathrm{r}} S_{\mathrm{m}}^{\ominus}(T)$$

$T \neq 298.2\mathrm{K}$

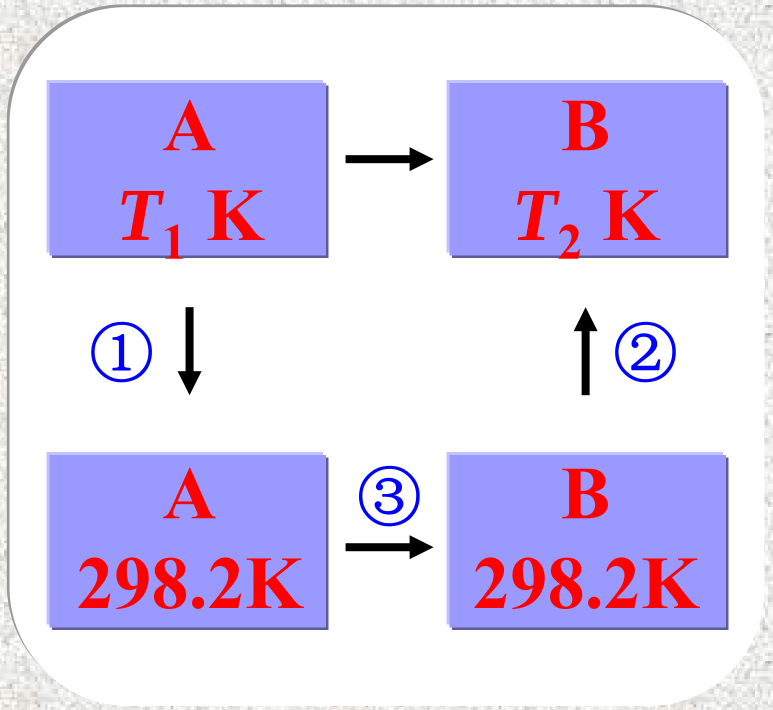
$$\begin{tikzcd}
\begin{matrix}\mathrm{A}\\ T\,\mathrm{K}\end{matrix} \arrow[r] \arrow[d, "①"'] & \begin{matrix}\mathrm{B}\\ T\,\mathrm{K}\end{matrix} \\
\begin{matrix}\mathrm{A}\\ 298.2\mathrm{K}\end{matrix} \arrow[r, "③"] & \begin{matrix}\mathrm{B}\\ 298.2\mathrm{K}\end{matrix} \arrow[u, "②"']
\end{tikzcd}$$

计算类型（△*H*, △*S*, △*G*）

- ◆ 恒温过程
- ◆ 变温过程

求△*H*

求最终温度

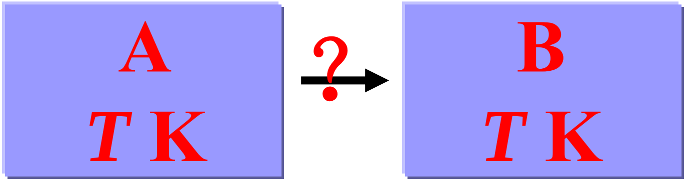


$$\begin{tikzcd}
\text{A} \; T_1\,\text{K} \arrow[r] \arrow[d, "①"'] & \text{B} \; T_2\,\text{K} \\
\text{A} \; 298.2\text{K} \arrow[r, "③"] & \text{B} \; 298.2\text{K} \arrow[u, "②"']
\end{tikzcd}$$

$$\Delta_r G_m^\ominus(T) \xcancel{=} \Delta_r H_m^\ominus(T) - T\Delta_r S_m^\ominus(T)$$

计算类型（$\triangle H$, $\triangle S$, $\triangle G$）

- 恒温过程
- 变温过程
- 判断方向



$$\Delta_r G_m^\ominus(T) \le 0$$

例： 试求反应 $0 = CO_2(g) + H_2(g) - CO(g) - H_2O(g)$ 在 298.15K和1000K时的 $\Delta_r H_m^\ominus$、 $\Delta_r S_m^\ominus$ 和 $\Delta_r G_m^\ominus$。

解： 由附录查得

	$CO(g)$	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
$\Delta_f H_m^\ominus/kJ \cdot mol^{-1}$	-110.525	-241.818	-393.509	0
$S_m^\ominus / J \cdot K^{-1} \cdot mol^{-1}$	197.674	188.825	213.74	130.684
$C_{p,m}^\ominus(300K)/J \cdot K^{-1} \cdot mol^{-1}$	29.16	33.60	37.20	28.85
$C_{p,m}^\ominus(600K)/J \cdot K^{-1} \cdot mol^{-1}$	30.46	36.32	47.32	29.32
$C_{p,m}^\ominus(900K)/J \cdot K^{-1} \cdot mol^{-1}$	32.59	39.96	52.97	29.87
$a/J \cdot K^{-1} \cdot mol^{-1}$	28.70	31.80	22.59	28.45
$b \times 10^3 / J \cdot K^{-2} \cdot mol^{-1}$	0.14	4.47	56.15	1.20
$c \times 10^6 / J \cdot K^{-3} \cdot mol^{-1}$	4.64	5.10	-24.85	0.42

上一页 下一页 节首

298.15K

$$\Delta_r H_m^\ominus(298.15\text{K}) = \Delta_f H_m^\ominus(\text{CO}_2) - \Delta_f H_m^\ominus(\text{CO}) - \Delta_f H_m^\ominus(\text{H}_2\text{O})$$

$$= [-393.509 - (-110.525 - 241.818)]\text{kJ}\cdot\text{mol}^{-1}$$

$$= -41.17\text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r S_m^\ominus(298.15\text{K}) = S_m^\ominus(\text{CO}_2) + S_m^\ominus(\text{H}_2) - S_m^\ominus(\text{CO}) - S_m^\ominus(\text{H}_2\text{O})$$

$$= (213.74 + 130.684 - 197.674 - 188.825)\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$= -42.08\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_r G_m^\ominus(298.15\text{K}) = (-41.17\times10^3 + 298.15\times42.08)\text{J}\cdot\text{mol}^{-1}$$

$$= -28.62\text{kJ}\cdot\text{mol}^{-1}$$

298.15K～1000K

$$\Delta_r a = (22.59 + 28.45 - 28.70 - 31.80)\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$= -9.46\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$\Delta_r b = [(56.15 + 1.20 - 0.14 - 4.47) \times 10^{-3}]\mathrm{J \cdot K^{-2} \cdot mol^{-1}}$$

$$= 52.74 \times 10^{-3}\mathrm{J \cdot K^{-2} \cdot mol^{-1}}$$

$$\Delta_r c = [(-24.85 + 0.42 - 4.64 - 5.10) \times 10^{-6}]\mathrm{J \cdot K^{-3} \cdot mol^{-1}}$$

$$= -34.17 \times 10^{-6}\mathrm{J \cdot K^{-3} \cdot mol^{-1}}$$

1000K

$$\begin{aligned}\Delta_r H_m^\ominus(1000\mathrm{K}) &= \Delta_r H_m^\ominus(298.15\mathrm{K}) + \Delta_r a(T-298.15\mathrm{K}) \\ &+ \frac{\Delta_r b[T^2-(298.15\mathrm{K})^2]}{2} + \frac{\Delta_r c[T^3-(298.15\mathrm{K})^3]}{3} \\ &= \Big[-41.17-9.46(1000-298.15)\times10^{-3} \\ &+ \frac{52.74\times10^{-3}(1000^2-298.15^2)\times10^{-3}}{2} \\ &- \frac{34.16\times10^{-6}(1000^3-298.15^3)\times10^{-3}}{3}\Big]\mathrm{kJ\cdot mol^{-1}} \\ &= (-41.17-6.64+24.03-11.09)\mathrm{kJ\cdot mol^{-1}} \\ &= -34.87\mathrm{kJ\cdot mol^{-1}}\end{aligned}$$

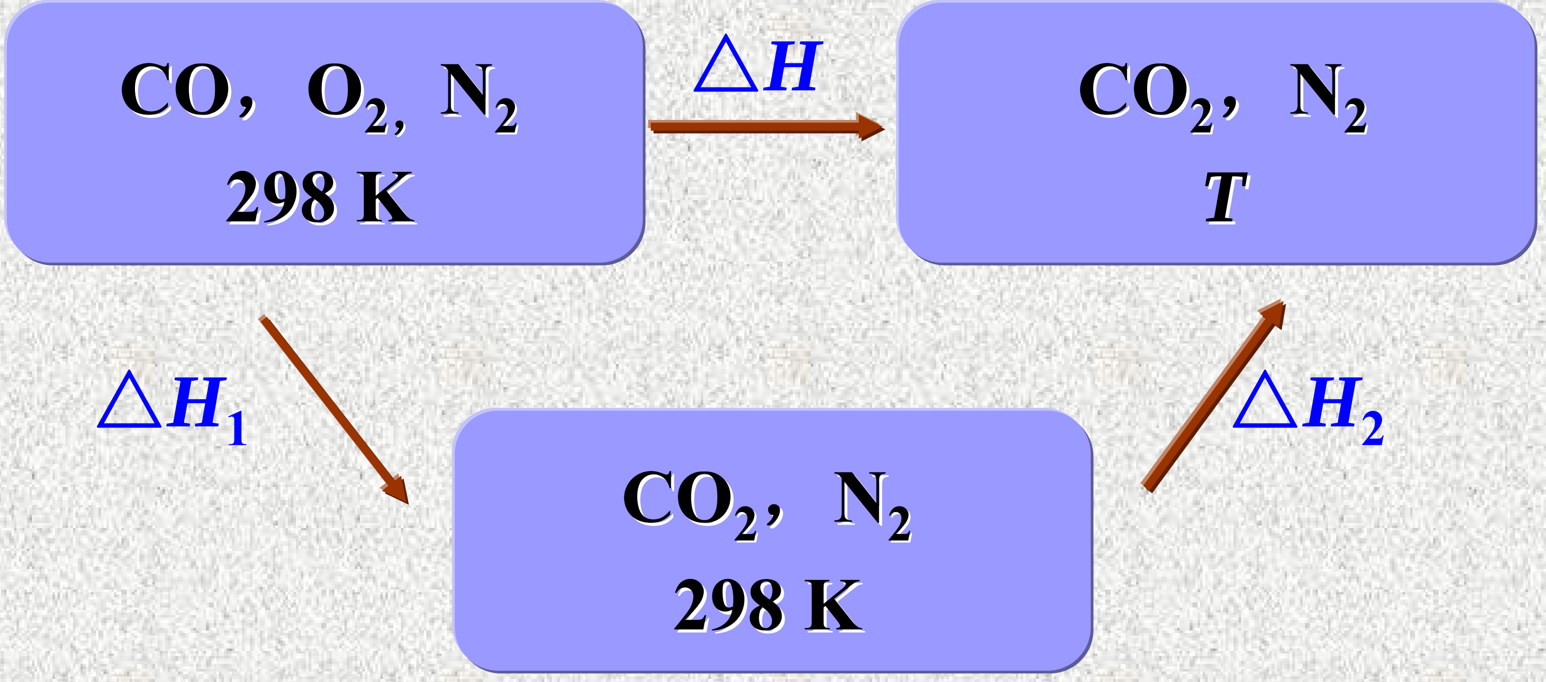
1000K

$$\begin{aligned}\Delta_r S_m^\ominus(1000\mathrm{K}) &= \Delta_r S_m^\ominus(298.15\mathrm{K}) + \Delta_r a\ln(T/298.15\mathrm{K})\\ &\quad + \Delta_r b(T-298.15\mathrm{K}) + \Delta_r c[T^2-(298.15\mathrm{K})^2]/2\\ &= -32.08\mathrm{J\cdot K^{-1}\cdot mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r G_m^\ominus(1000\mathrm{K}) &= (-34.87+1000\times 32.08\times 10^{-3})\mathrm{kJ\cdot mol^{-1}}\\ &= -2.79\mathrm{kJ\cdot mol^{-1}}\end{aligned}$$

$$\begin{tikzcd}
\text{C (石墨）}\ 25℃,\ p' \arrow[r, "\Delta G'"] \arrow[d, "\Delta G_1"'] & \text{C (金刚石）}\ 25℃,\ p' \\
\text{C (石墨）}\ 25℃,\ 101325\text{Pa} \arrow[r, "\Delta G"] & \text{C (金刚石）}\ 25℃,\ 101325\text{Pa} \arrow[u, "\Delta G_2"']
\end{tikzcd}$$

上一页 下一页 节首



CO，O_2，N_2

298 K

ΔH

CO_2，N_2

T

ΔH_1

CO_2，N_2

298 K

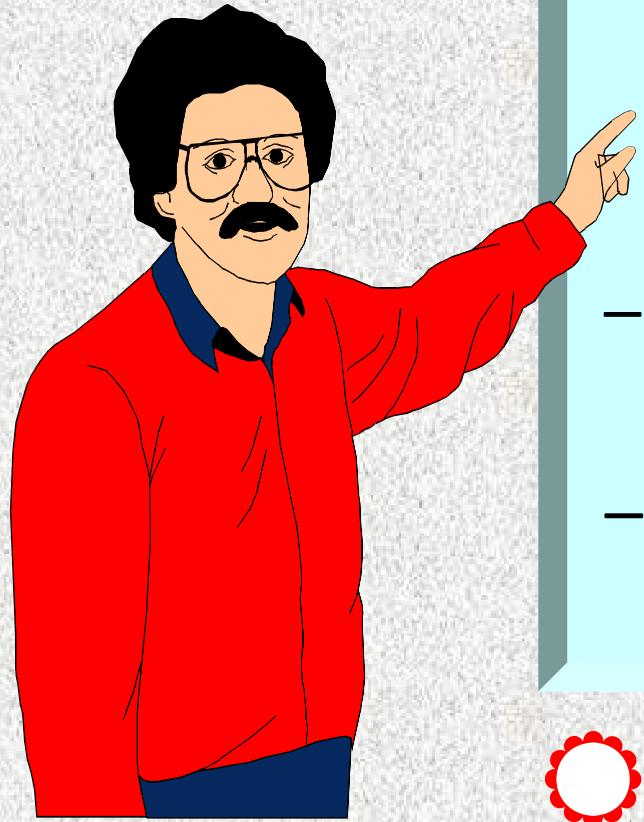
ΔH_2

上一页 下一页 节首

2-13 平衡判据

物理化学多媒体课堂教学软件 V1.0版

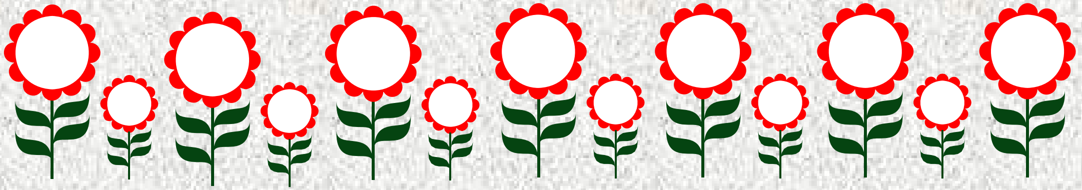
上一页 下一页 返回目录



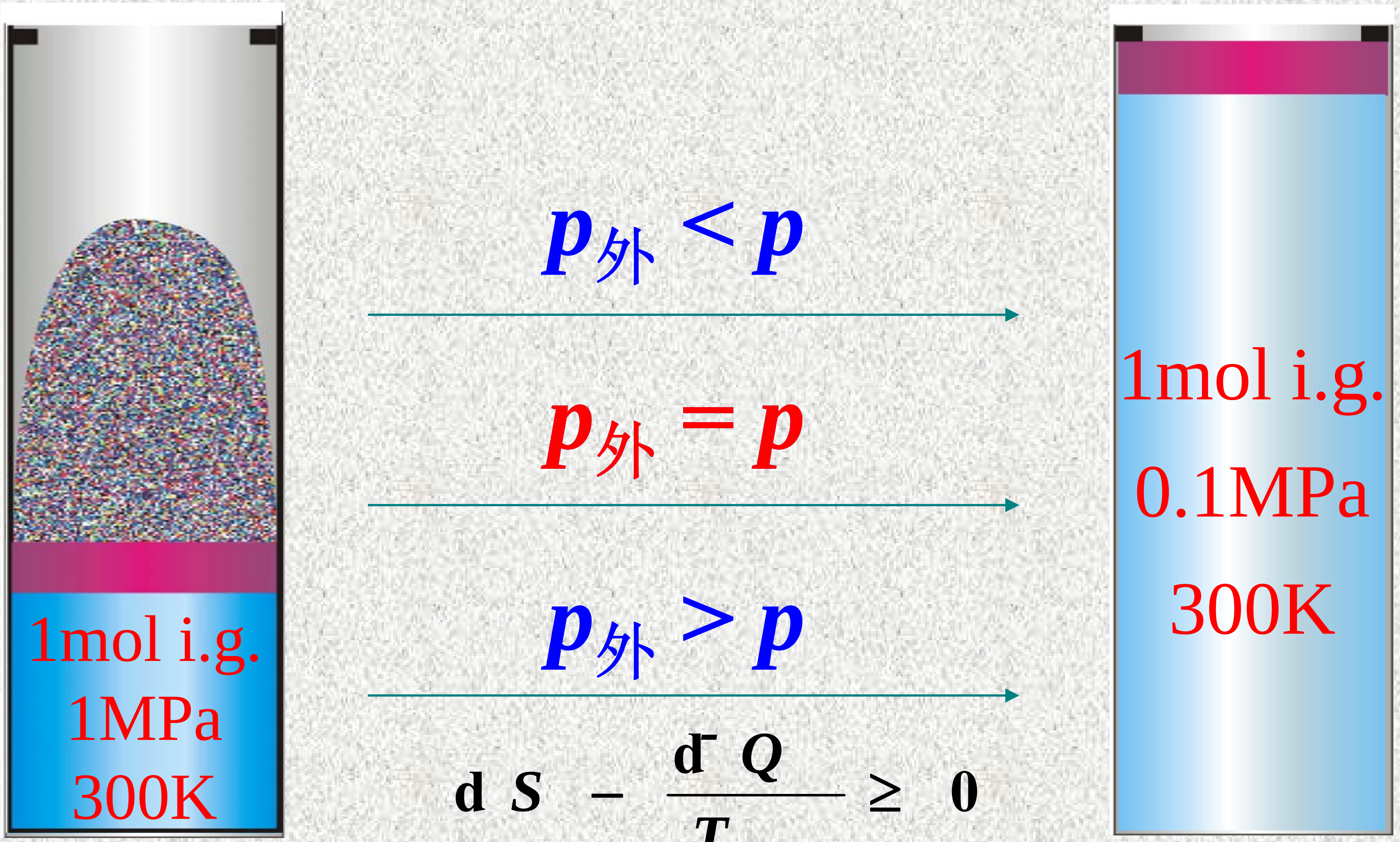
$$\mathrm{d}S \geq \frac{\text{đ}Q}{T_{环}} \qquad \mathrm{d}S_{U,V,W'=0} \geq 0$$

$$-\mathrm{d}A_{T,V} \geq -\text{đ}W' \qquad \mathrm{d}A_{T,V,W'=0} \leq 0$$

$$-\mathrm{d}G_{T,p} \geq -\text{đ}W' \qquad \mathrm{d}G_{T,p,W'=0} \leq 0$$



上一页 下一页 节首

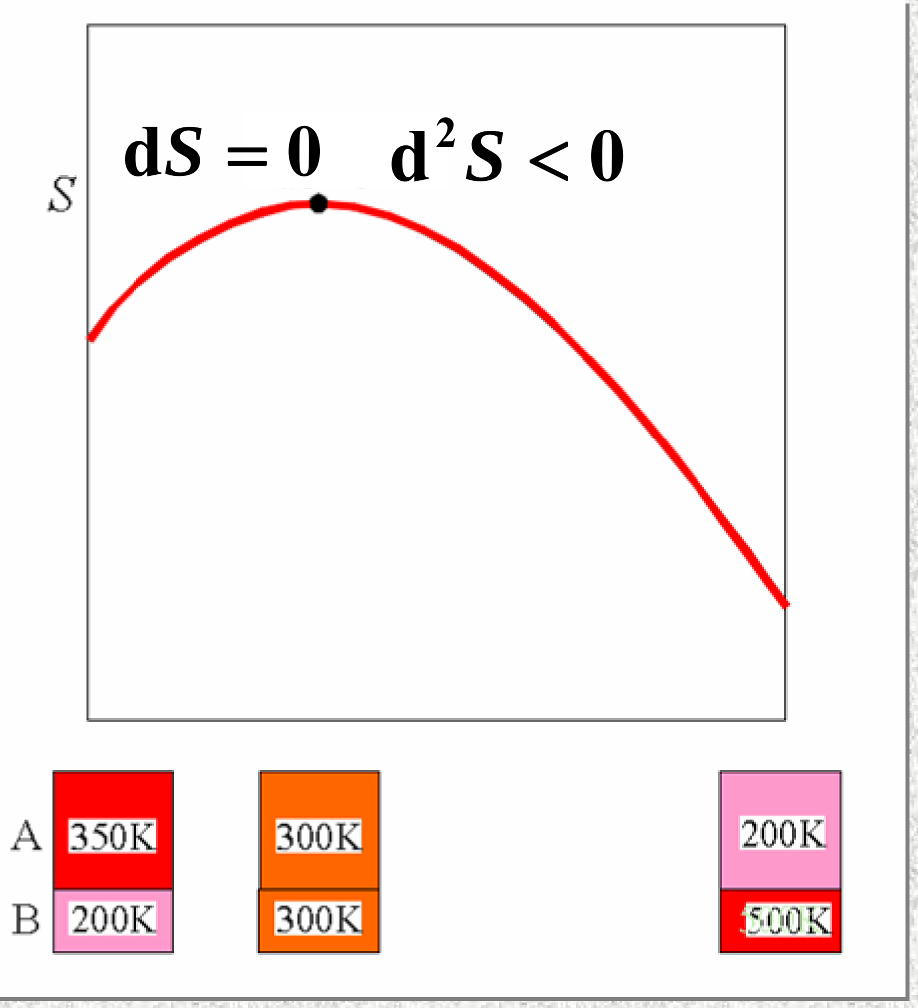


$p_{外} < p$

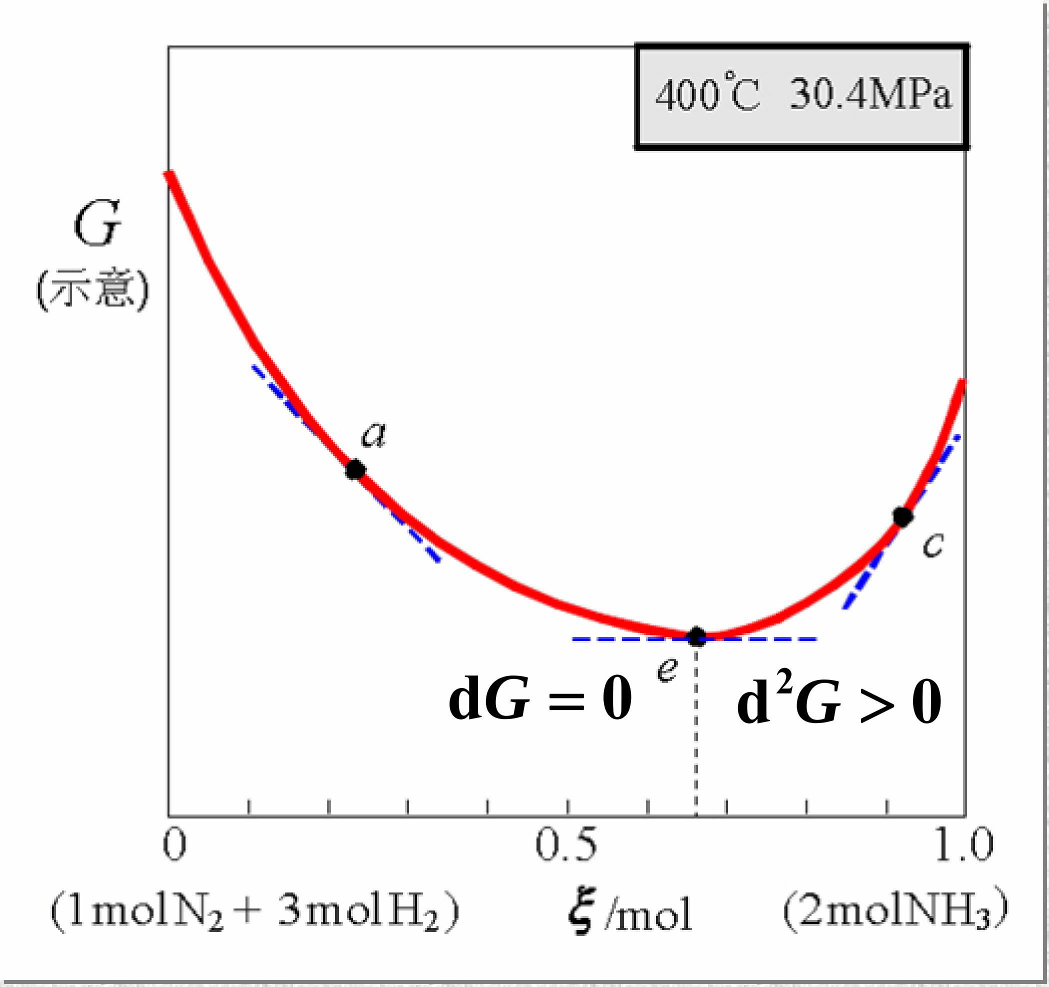
$p_{外} = p$

$p_{外} > p$

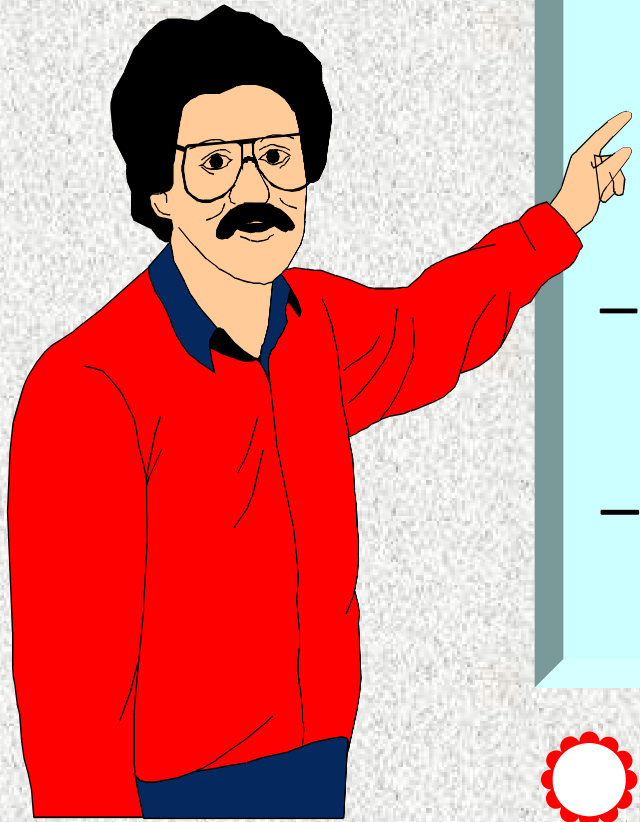
$$\mathrm{d}S - \frac{\text{đ}Q}{T_{环}} \geq 0$$



$$\mathrm{d}S_{U,V,W'=0} \geq 0$$


400℃ 30.4MPa
G
(示意)
a
c
e
dG = 0
d²G > 0
0
0.5
1.0
(1molN₂ + 3molH₂)
ξ /mol
(2molNH₃)

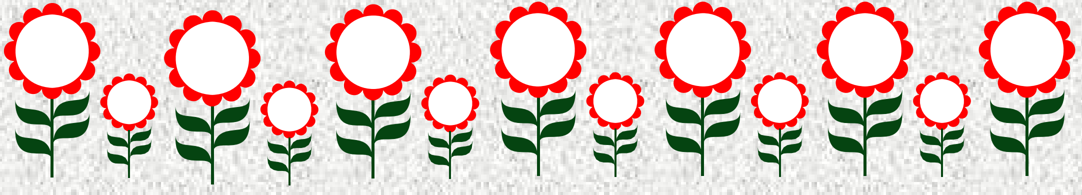
$$dG_{T,p,W'=0} \leq 0$$



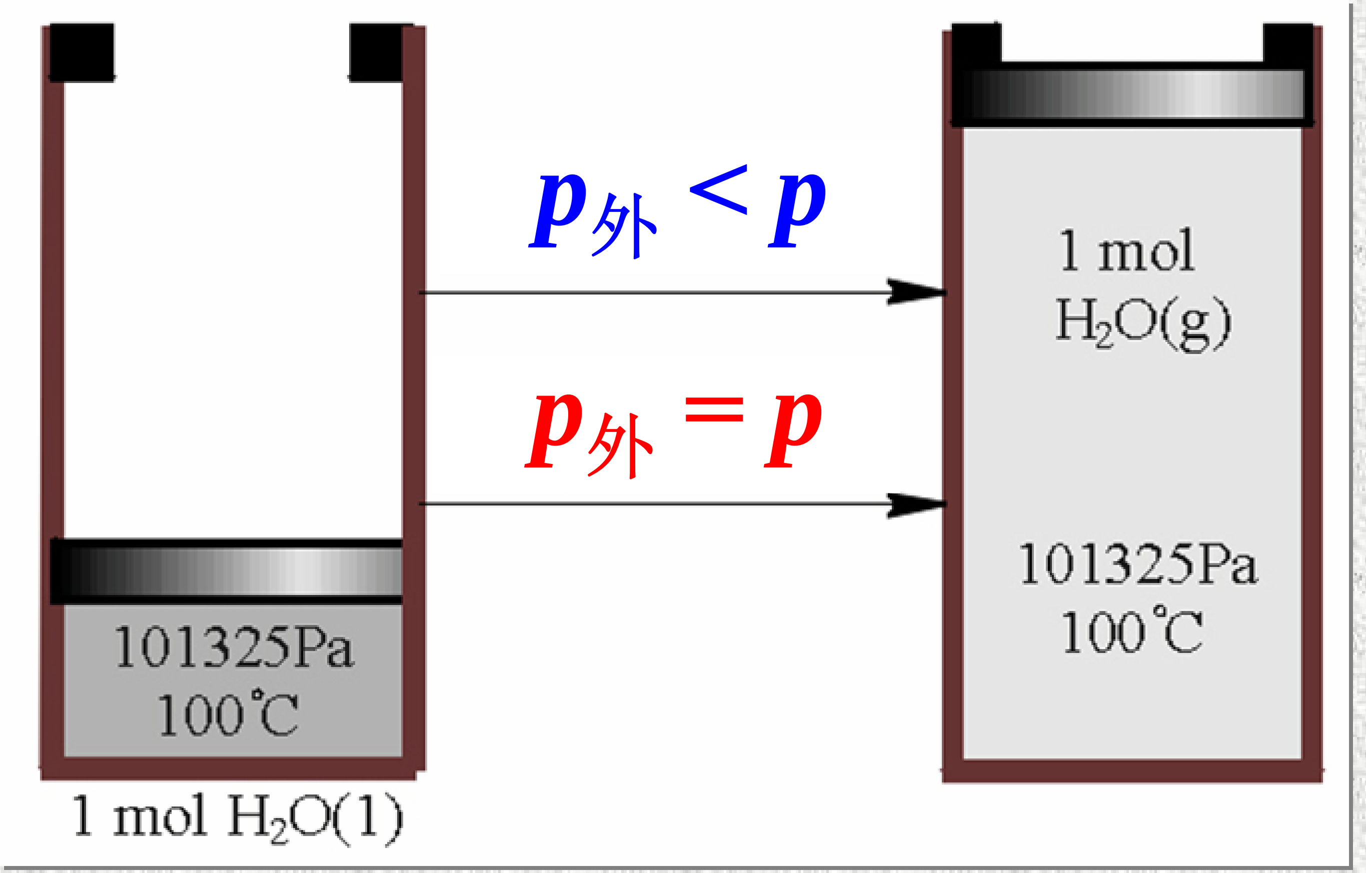
$$\mathrm{d}S \geq \frac{\text{đ}Q}{T_{环}} \qquad \mathrm{d}S_{U,V,W'=0} \geq 0$$

$$-\mathrm{d}A_{T,V} \geq -\text{đ}W' \qquad \mathrm{d}A_{T,V,W'=0} \leq 0$$

$$-\mathrm{d}G_{T,p} \geq -\text{đ}W' \qquad \mathrm{d}G_{T,p,W'=0} \leq 0$$



上一页 下一页 节首



$p_{外} < p$

$p_{外} = p$

2-14 单元系统的相平衡

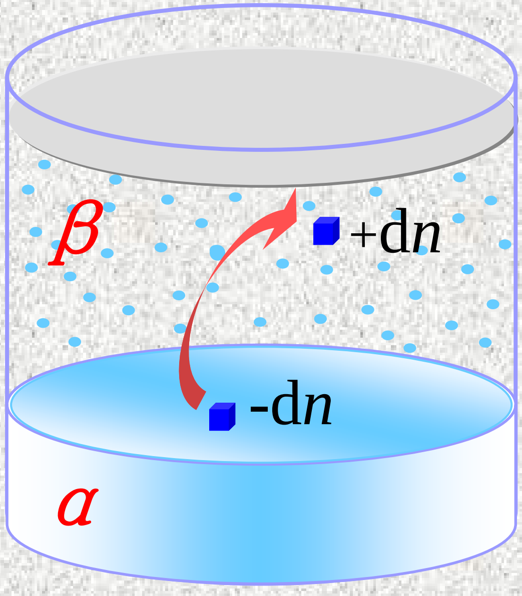
物理化学多媒体课堂教学软件 V1.0版

$$\mathrm{d}G_{T,p,W'=0} = [G_{\mathrm{m}}(\beta) - G_{\mathrm{m}}(\alpha)]\mathrm{d}n$$

<0 $G_{\mathrm{m}}(\beta) < G_{\mathrm{m}}(\alpha)$ 不可逆过程

$=0$ $G_{\mathrm{m}}(\beta) = G_{\mathrm{m}}(\alpha)$ 可逆过程

$T \rightarrow T+\mathrm{d}T$ $\Rightarrow$ $p \rightarrow p+\mathrm{d}p$



$$\begin{array}{c} G_{\mathrm{m}}(\alpha)+\mathrm{d}G_{\mathrm{m}}(\alpha) \\ \| \\ G_{\mathrm{m}}(\beta)+\mathrm{d}G_{\mathrm{m}}(\beta) \end{array} \Rightarrow \boxed{\mathrm{d}G_{\mathrm{m}}(\alpha) = \mathrm{d}G_{\mathrm{m}}(\beta)}$$

$$\mathrm{d}G_\mathrm{m}(\alpha) = -S_\mathrm{m}(\alpha)\mathrm{d}T + V_\mathrm{m}(\alpha)\mathrm{d}p$$

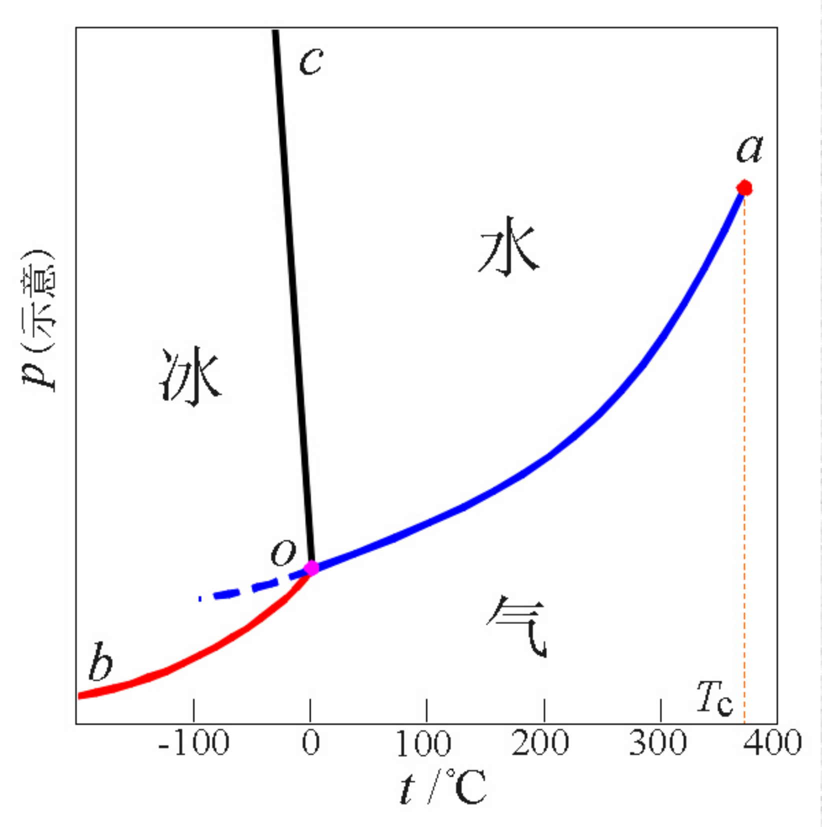
$$\mathrm{d}G_\mathrm{m}(\beta) = -S_\mathrm{m}(\beta)\mathrm{d}T + V_\mathrm{m}(\beta)\mathrm{d}p$$

$$-S_\mathrm{m}(\alpha)\mathrm{d}T + V_\mathrm{m}(\alpha)\mathrm{d}p = -S_\mathrm{m}(\beta)\mathrm{d}T + V_\mathrm{m}(\beta)\mathrm{d}p$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_\mathrm{m}(\beta) - S_\mathrm{m}(\alpha)}{V_\mathrm{m}(\beta) - V_\mathrm{m}(\alpha)} = \frac{\Delta_{相变} S_\mathrm{m}}{\Delta_{相变} V_\mathrm{m}} = \frac{\Delta_{相变} H_\mathrm{m}}{T\Delta_{相变} V_\mathrm{m}}$$

克拉佩龙–克劳修斯方程

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{相变}H_m}{T\Delta_{相变}V_m}}$$



$$\frac{\mathrm{d}p}{\mathrm{d}T}>0$$

$$\Delta_{\mathrm{Vap}}H_m>0$$

$$\Delta_{\mathrm{Vap}}V_m>0$$

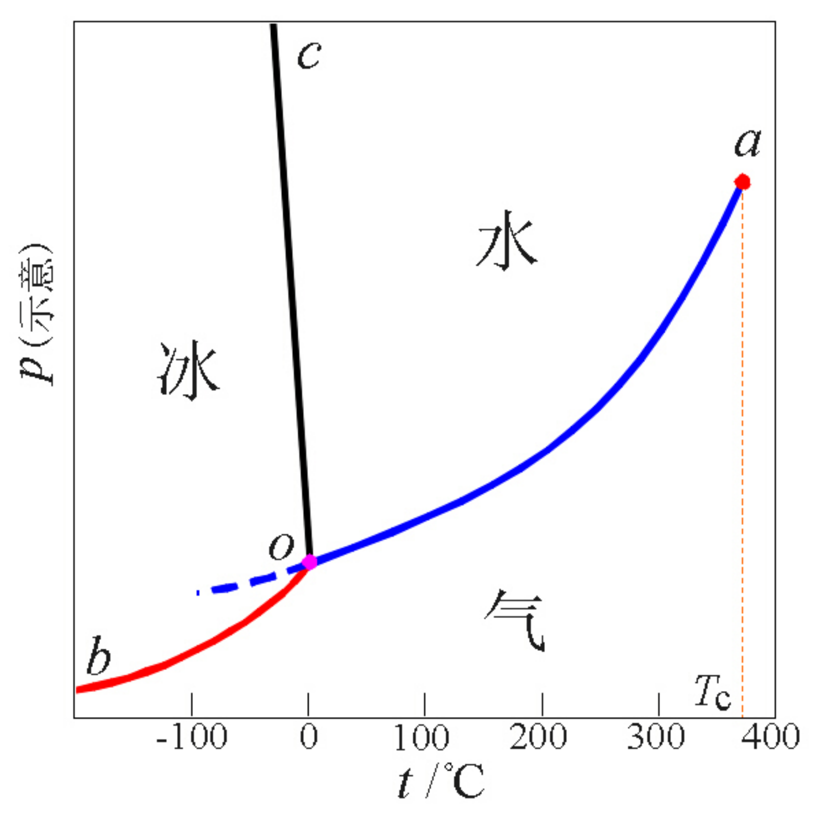
$$V(\mathrm{g})>V(\mathrm{l})$$

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{相变}H_{\mathrm{m}}}{T\Delta_{相变}V_{\mathrm{m}}}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T}<0$$

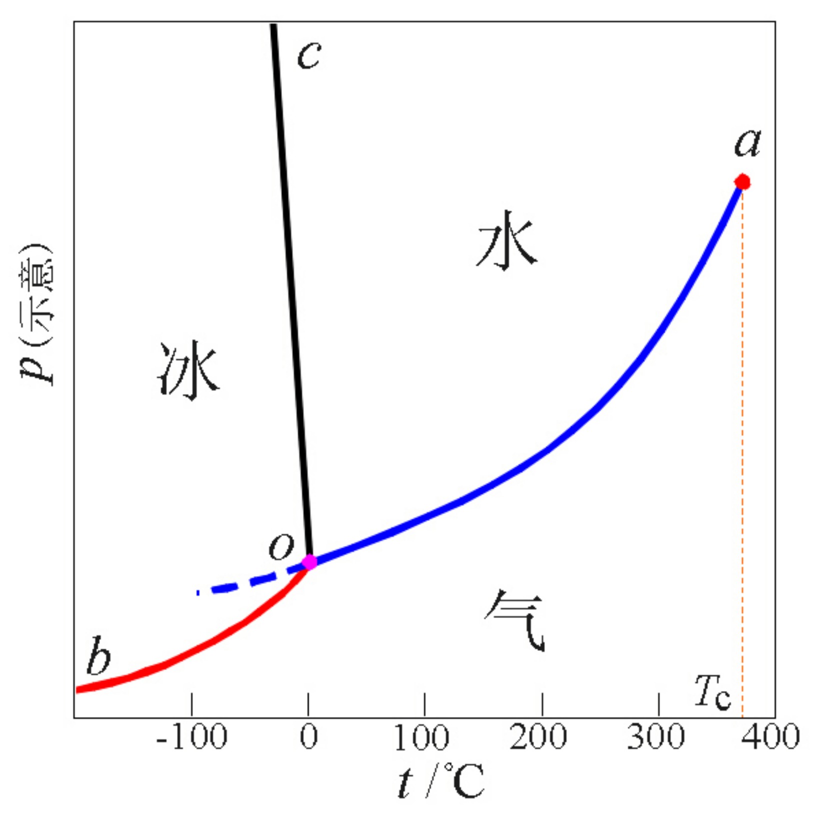
$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}>0$$

$$\Delta_{\mathrm{fus}}V_{\mathrm{m}}<0$$



$$V(\mathrm{s})>V(\mathrm{l})$$

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta_{\text{相变}}H_{\mathrm{m}}}{T\Delta_{\text{相变}}V_{\mathrm{m}}}$$



$$\frac{\mathrm{d}p^*}{\mathrm{d}T}=\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{TV_{\mathrm{m}}(\mathrm{g})}$$

$$=\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}p^*}{RT^2}$$

$$\ln\{p^*\}=-\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{RT}+C$$

VLE，VSE
g—idgas
△*H*—Const.

例1 酚的精制采取减压蒸馏方法。已知酚的正常沸点为181.9℃，如真空度为86.7kPa，酚的沸点应为多少？已知酚的蒸发热为 $48.1\times10^{3}\,\mathrm{J\cdot mol^{-1}}$, 外压为100.0kPa。

解:

$$T_1, \ p_1 \xrightarrow{\Delta H} T_2, \ p_2$$

$$p_1^{*}=101.3\mathrm{kPa} \qquad T_1=(181.9+273.2)\mathrm{K}=455.1\mathrm{K}$$

$$p_2^{*}=(100.0-86.7)\mathrm{kPa}=13.3\mathrm{kPa}$$

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}}=48.1\times10^{3}\,\mathrm{J\cdot mol^{-1}} \quad \Rightarrow \quad T_2=?$$

$$\ln(13.3/101.3)=-(48.1\times10^{3}/8.3145)[1/(T_2/\mathrm{K})-1/455.1]$$

$$T_2=392.4\mathrm{K}\rightarrow 119.2℃,$$

2-15 能量的有效利用

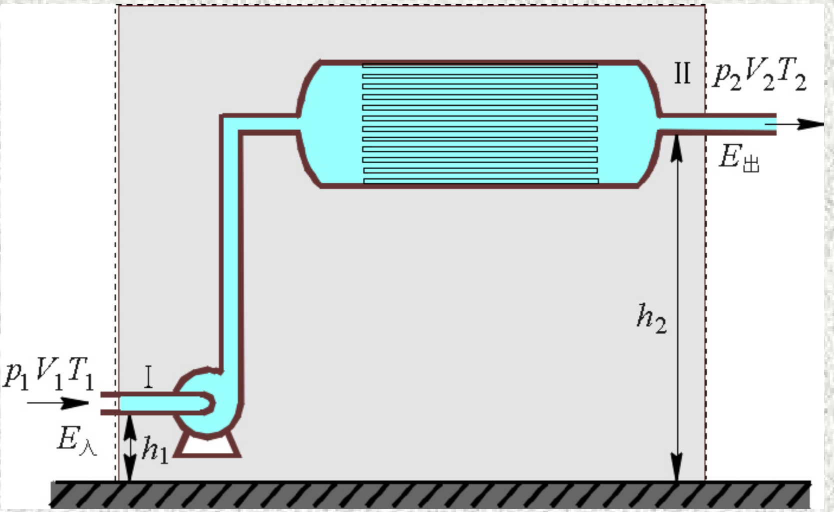
物理化学多媒体课堂教学软件 V1.0版

1. 能量衡算

$$E_{入} = U_1 + E_{k1} + E_{p1}$$

$$E_{出} = U_2 + E_{k2} + E_{p2}$$

$$E_{传递} = p_1V_1 - p_2V_2 + W_{轴} + Q$$



$$U_1 + E_{k1} + E_{p1} - U_2 - E_{k2} - E_{p2} + Q + p_1V_1 - p_2V_2 + W_{轴} = 0$$

$$\Delta H = Q + W_{轴}$$

敞开系统的热力学第一定律

◆稳定流动 ◆忽略动能势能

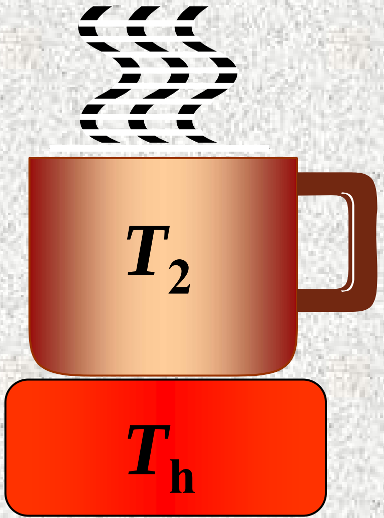
$$\Delta H = Q$$

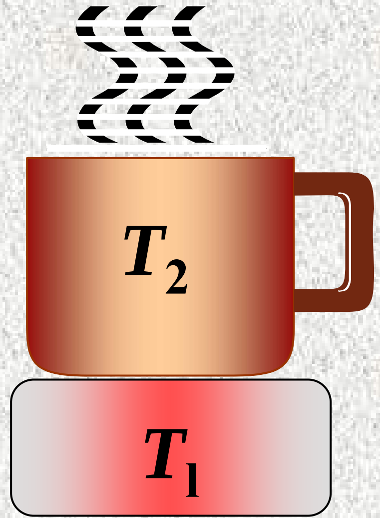
◆不做非其它功

2. 能量的品位和能量的有效利用

第一定律效率

$$\eta_{\mathrm{I}} = E_{\text{获得}} / E_{\text{输入}}$$

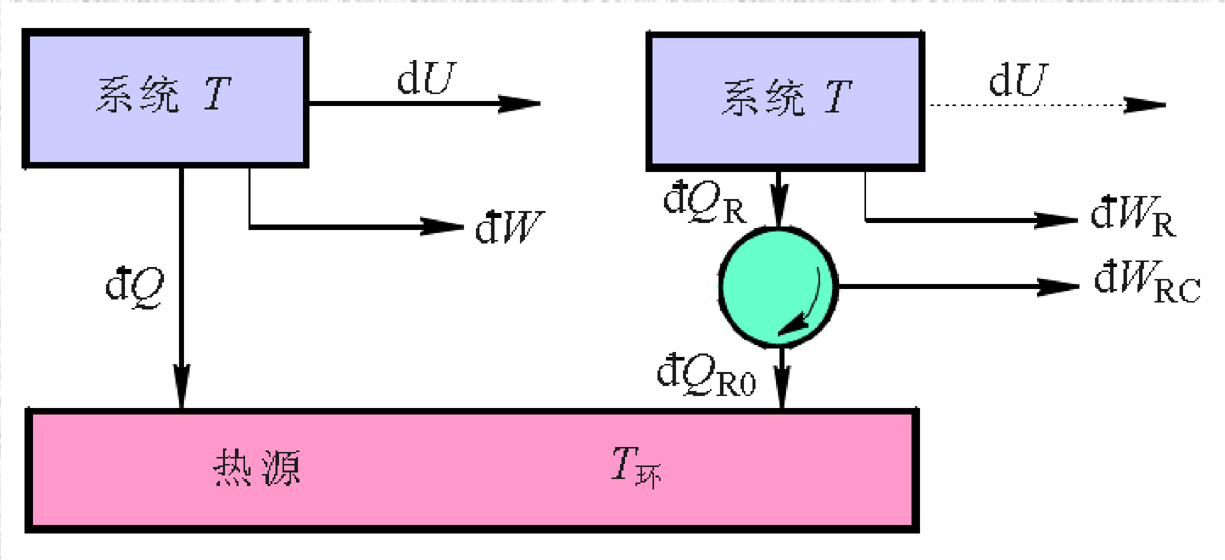




$$\mathrm{d}S = \frac{\text{đ}Q_{\mathrm{R}}}{T}$$

$$\mathrm{d}S_{\text{环}} = -\frac{\text{đ}Q_{\mathrm{R0}}}{T_{\text{环}}}$$

$$\mathrm{d}S = -\mathrm{d}S_{\text{环}}$$



$$\text{đ}Q + \text{đ}W = \text{đ}Q_{\mathrm{R0}} + \text{đ}W_{\mathrm{R}} + \text{đ}W_{\mathrm{RC}} = \mathrm{d}U$$

$$T_{\text{环}}\mathrm{d}S - \text{đ}Q = \text{đ}Q_{\mathrm{R0}} - \text{đ}Q = -\text{đ}W_{\mathrm{R}} - \text{đ}W_{\mathrm{RC}} + \text{đ}W$$

$$= -\text{đ}W_{\text{理想}} + \text{đ}W = \text{đ}W_{\text{损失}}$$

功损失

$$\boxed{W_{\text{损失}} = -W_{\text{理想}} + W}$$

有效能和有效能分析

$$W_{\text{理想}} = W_{\text{R,轴}} + W_{\text{RC}} \qquad T_{\text{环}}\mathrm{d}S - \text{đ}Q = -\text{đ}W_{\text{理想}} + \text{đ}W_{\text{轴}}$$

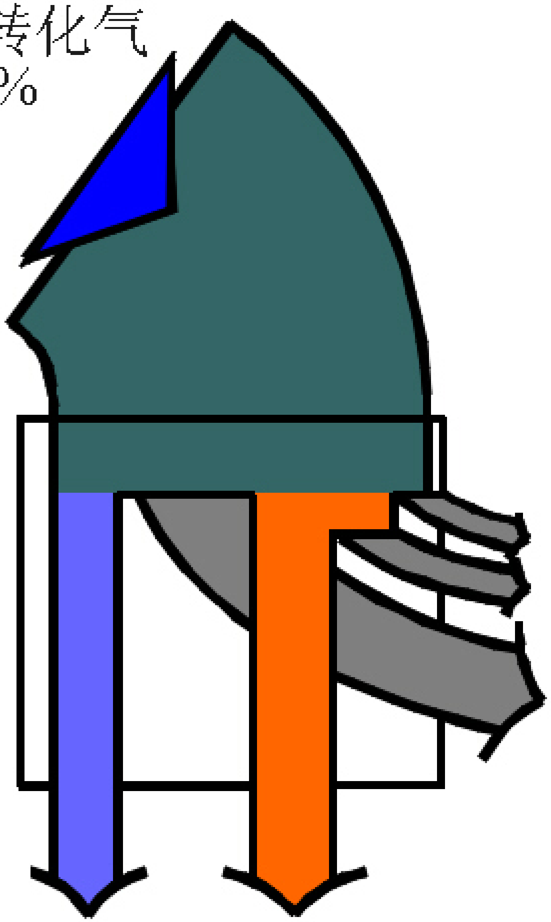
取 $T_{\text{环}} = 298.15\ \mathrm{K}$

$$\text{đ}W_{\text{理想}} = -T_0\mathrm{d}S + \mathrm{d}H + \mathrm{d}E_{\mathrm{k}} + \mathrm{d}E_{\mathrm{p}} = \mathrm{d}(H - T_0 S + E_{\mathrm{k}} + E_{\mathrm{p}})$$

$$\boxed{\begin{aligned} E_{\mathrm{X}} &\overset{\text{def}}{=\!=} -W_{\text{理想}}\ (\text{与标准环境达到平衡}) \\ &= -(H_0 - H) + T_0(S_0 - S) + E_{\mathrm{k}} + E_{\mathrm{p}} \end{aligned}}$$

第二定律效率 $\eta_{\mathrm{EX}} \overset{\text{def}}{=\!=} E_{\mathrm{Xf}} / E_{\mathrm{Xi}}$

上一页 下一页 节首



二段转化气
100%

低温转化气
21.9%

轴功
27.5%

冷凝器损失	5.4%
透平损失	12.5%
废热锅炉损失	32.7%
总损失	50.6%
总效率	49.4%

上一页　下一页　节首