



基础化学 (II)

化学热力学基础-7

王 帅

2025年4月3日

基础化学 (II) 课程安排

周	月	日	一	二	三	四	五	六
WK	Mth	Sun	Mon	Tue	Wed	Thu	Fri	Sat
	二月 FEB							1
		2	3	4	5	6	7	8
		9	10	11	12	13	14	15
1		16	17	18	19	20	21	22
2		23	24	25	26	27	28	
	三月 MAR							1
3		2	3	4	5	6	7	8
4		9	10	11	12	13	14	15
5		16	17	18	19	20	21	22
6		23	24	25	26	27	28	29
7		30	31					
	四月 APR			1	2	3	4	5
8		6	7	8	9	10	11	12
9		13	14	15	16	17	18	19
10		20	21	22	23	24	25	26
11		27	28	29	30			
	五月 MAY					1	2	3
12		4	5	6	7	8	9	10
13		11	12	13	14	15	16	17
14		18	19	20	21	22	23	24
15		25	26	27	28	29	30	31
	六月	1	2	3	4	5	6	7
16		8	9	10	11	12	13	14
17		15	16	17	18	19	20	21

期中考试
日期
选择

课程内容:

1. 元素化学 (3.5 周) 林海昕
2. 化学热力学基础 (4 周) 王帅
3. 相平衡+期中 (1.5+0.5 周) 王帅
4. 化学动力学基础 (2.5 周) 王帅
5. 电化学/Redox平衡 (3 周) 陈嘉嘉

化学热力学提纲

1. 化学热力学引言

2. 熵增加原理

3. 温度及其特性

4. 能量守恒定律

5. 可逆过程

6. 熵与热容

7. 吉布斯自由能

8. 化学反应变化

9. 化学平衡


$$\Delta S = q_{\text{可逆}}/T$$

$$\Delta_{\text{r}} G^{\circ} = \Delta_{\text{r}} H^{\circ} - T \Delta_{\text{r}} S^{\circ}$$

$$\Delta_{\text{r}} G^{\circ} = -RT \ln K$$

热力学基本状态函数

热力学第一定律

$$\Delta U = q + w$$

热平衡

力平衡

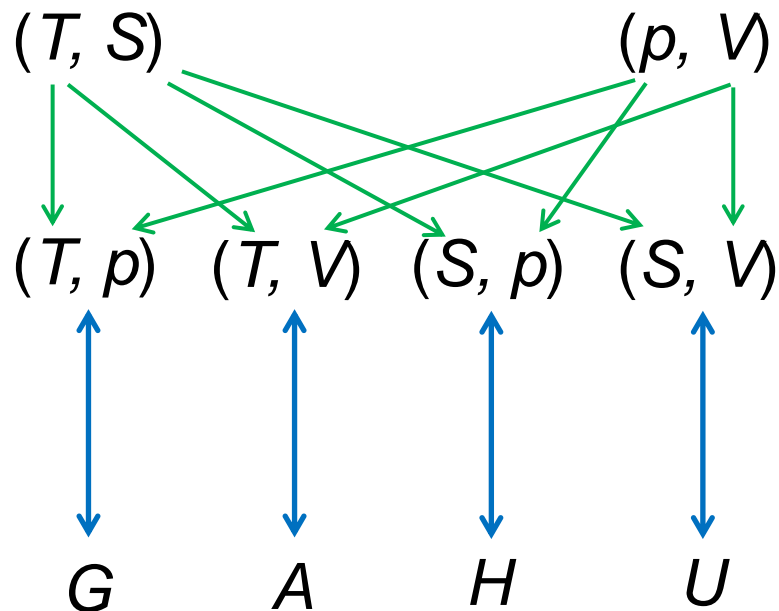
(T, S)

(p, V)

强度性质

广度性质

两对共轭状态函数



四个能量类函数与对应的
四套独立变量组

**组分不变，非机械功为零的封闭系统中状态函数变化量
需两个独立变量来确定**

热力学基本方程

$$dU = TdS - pdV$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n} \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,n}$$

$$dA = -SdT - pdV$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,n} \quad p = -\left(\frac{\partial A}{\partial V}\right)_{T,n}$$

$$dH = TdS + Vdp$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{p,n} \quad V = \left(\frac{\partial H}{\partial p}\right)_{S,n}$$

$$dG = -SdT + Vdp$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n} \quad V = \left(\frac{\partial G}{\partial p}\right)_{T,n}$$

麦克斯韦方程

将难以计算/观测的
状态函数转变为简单
常见的可观测量

$$\left(\frac{\partial P}{\partial S}\right)_{V,n} = -\left(\frac{\partial T}{\partial V}\right)_{S,n}$$

$$\left(\frac{\partial V}{\partial S}\right)_{P,n} = \left(\frac{\partial T}{\partial P}\right)_{S,n}$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \left(\frac{\partial S}{\partial V}\right)_{T,n}$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = -\left(\frac{\partial S}{\partial P}\right)_{T,n}$$

Gibbs自由能 vs 温度、压力

对于等压过程 ($dp = 0$), G 可表示为

$$dG = V dp - SdT = -S dT$$

Gibbs–Helmholtz方程: $\frac{d}{dT} \left(\frac{G}{T} \right) = -\frac{H}{T^2}$

对于等温过程 ($dT = 0$), G 可表示为

$$dG = V dp - SdT = V dp$$

$$G(p_2) - G(p_1) = nRT \ln \frac{p_2}{p_1}$$

以1 bar为标准态, 对理想气体有

$$G_{m,i}(p_i) = G_{m,i}^\circ + RT \ln \frac{p_i}{p^\circ}$$

混合体系的Gibbs自由能

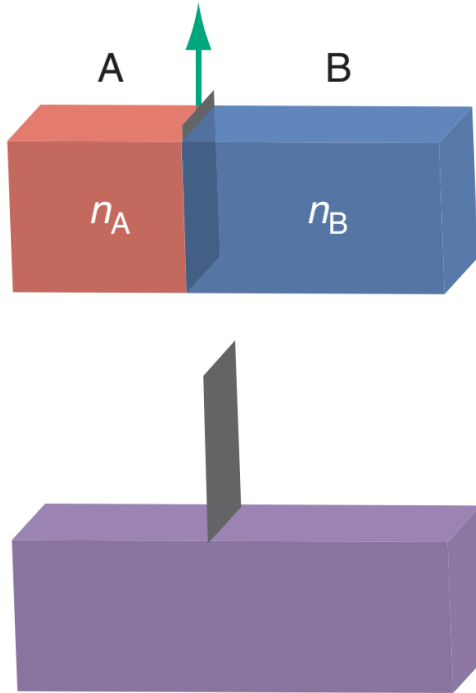


Fig. 19.11 Two (ideal) gases A and B are separated by a partition; there are n_A moles of A and n_B moles of B, and both are at the same pressure p . When the partition is removed, the gases mix spontaneously.

考虑两理想气体等温混合的 ΔG :

$$G_{\text{before mixing}} = \underbrace{n_A \left[G_{\text{m,A}}^{\circ} + RT \ln \left(\frac{p}{p^{\circ}} \right) \right]}_{\text{Gibbs energy of A}} + \underbrace{n_B \left[G_{\text{m,B}}^{\circ} + RT \ln \left(\frac{p}{p^{\circ}} \right) \right]}_{\text{Gibbs energy of B}}.$$

$$G_{\text{after mixing}} = \underbrace{n_A \left[G_{\text{m,A}}^{\circ} + RT \ln \left(\frac{p_A}{p^{\circ}} \right) \right]}_{\text{Gibbs energy of A}} + \underbrace{n_B \left[G_{\text{m,B}}^{\circ} + RT \ln \left(\frac{p_B}{p^{\circ}} \right) \right]}_{\text{Gibbs energy of B}}.$$



$$\Delta G_{\text{mix}} = n_A RT \ln \left(\frac{p_A}{p} \right) + n_B RT \ln \left(\frac{p_B}{p} \right)$$

$\Delta G_{\text{mix}} < 0$, 混合是自发过程!

化学势的引入

化学势，即偏摩尔吉布斯自由能 $\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n \neq n_i}$



$$(dG)_{p,T} = \sum_i \mu_i dn_i$$

完整的热力学基本方程 $dG = Vdp - SdT + \sum_i \mu_i dn_i$

理想气体: $\mu_i(p_i) = \mu_i^\circ + RT \ln \frac{p_i}{p^\circ}$

理想溶液: $\mu_i(c_i) = \mu_i^\circ + RT \ln \frac{c_i}{c^\circ}$

纯固体或液体: $\mu_i = \mu_i^\circ$

引入活度(activity)

$$\mu_i = \mu_i^\circ + RT \ln(a_i)$$

麦克斯韦方程完整版

$$dU = TdS - pdV + \sum_i \mu_i dn_i, \quad \mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n \neq n_i}$$

$$\left(\frac{\partial T}{\partial V}\right)_{S,n} = -\left(\frac{\partial P}{\partial S}\right)_{V,n}$$

$$\left(\frac{\partial \mu_i}{\partial S}\right)_{V,n} = \left(\frac{\partial T}{\partial n_i}\right)_{S,V,n \neq n_i}$$

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{S,n} = -\left(\frac{\partial P}{\partial n_i}\right)_{S,V,n \neq n_i}$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{V,n} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,V,n \neq n_i}$$

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{T,n} = -\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n \neq n_i}$$

$$\left(\frac{\partial T}{\partial P}\right)_{S,n} = \left(\frac{\partial V}{\partial S}\right)_{P,n}$$

$$\left(\frac{\partial \mu_i}{\partial S}\right)_{P,n} = \left(\frac{\partial T}{\partial n_i}\right)_{S,P,n \neq n_i}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{S,n} = \left(\frac{\partial V}{\partial n_i}\right)_{S,P,n \neq n_i}$$

$$\left(\frac{\partial S}{\partial P}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n \neq n_i}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n \neq n_i}$$

8. 化学反应变化

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

化学反应的标准自由能变化

对于化学反应： $aA + bB \rightleftharpoons cC + dD$

$$\Delta_r G^\circ = \underbrace{c \times G_{m,C}^\circ + d \times G_{m,D}^\circ}_{\text{products}} - \underbrace{[a \times G_{m,A}^\circ + b \times G_{m,B}^\circ]}_{\text{reactants}}$$

$$\Delta_r H^\circ = \underbrace{(cH_{m,C}^\circ + dH_{m,D}^\circ)}_{\text{products}} - \underbrace{(aH_{m,A}^\circ + bH_{m,B}^\circ)}_{\text{reactants}},$$

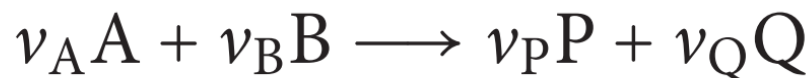
$$\Delta_r S^\circ = \underbrace{(cS_{m,C}^\circ + dS_{m,D}^\circ)}_{\text{products}} - \underbrace{(aS_{m,A}^\circ + bS_{m,B}^\circ)}_{\text{reactants}}.$$



$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

温度对反应焓/熵变的影响

在恒定压力下，反应的热容变化为



$$\Delta_r C_p^\circ = \nu_P C_{p,m}^\circ(P) + \nu_Q C_{p,m}^\circ(Q) - \nu_A C_{p,m}^\circ(A) - \nu_B C_{p,m}^\circ(B)$$

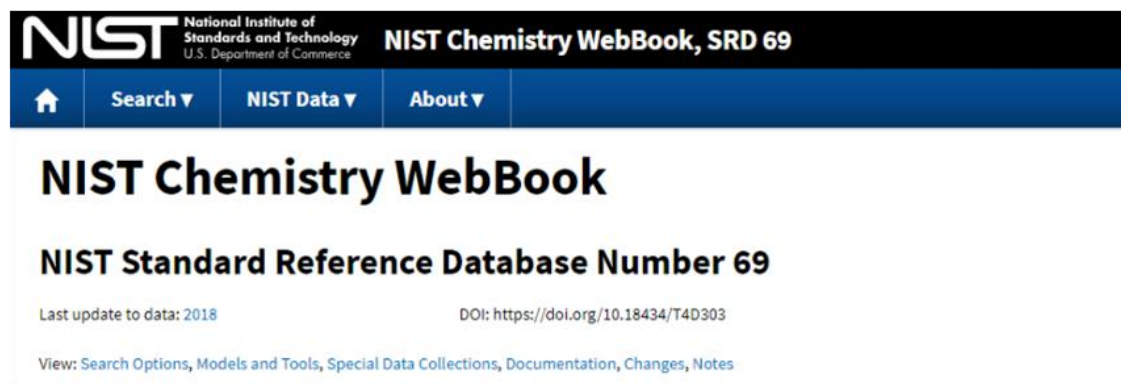
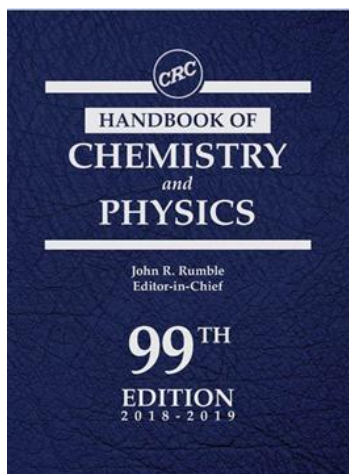
若假设**热容不随温度发生变化**，则有

$$\text{焓变} \left\{ \begin{array}{l} H_m(T_2) = H_m(T_1) + C_{p,m} [T_2 - T_1] \\ \Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \Delta_r C_p^\circ [T_2 - T_1] \end{array} \right.$$

$$\text{熵变} \left\{ \begin{array}{l} S_m(T_2) = S_m(T_1) + C_{p,m} \ln \frac{T_2}{T_1} \\ \Delta_r S^\circ(T_2) = \Delta_r S^\circ(T_1) + \Delta_r C_p^\circ \ln \frac{T_2}{T_1} \end{array} \right.$$

反应焓变、熵变的分析

- ❑ 化学键生成/断裂所产生的能量变化显著影响焓变
- ❑ 反应物/产物的物理状态也会影响焓变
- ❑ 化学反应的熵变主要取决于气体分子数目的变化
- ❑ 对应溶液反应，因溶剂化的影响，焓/熵的变化要复杂得多



<https://webbook.nist.gov/chemistry/>

热力学的标准状态

phase	definition of standard state
gas	the <i>pure</i> gas at a pressure of 1 bar and at the stated temperature
liquid	the <i>pure</i> liquid at the stated temperature
solid	the <i>pure</i> solid at the stated temperature
solution	an (ideal) solution with the solute at the standard concentration of 1 mol dm^{-3} , and at the stated temperature

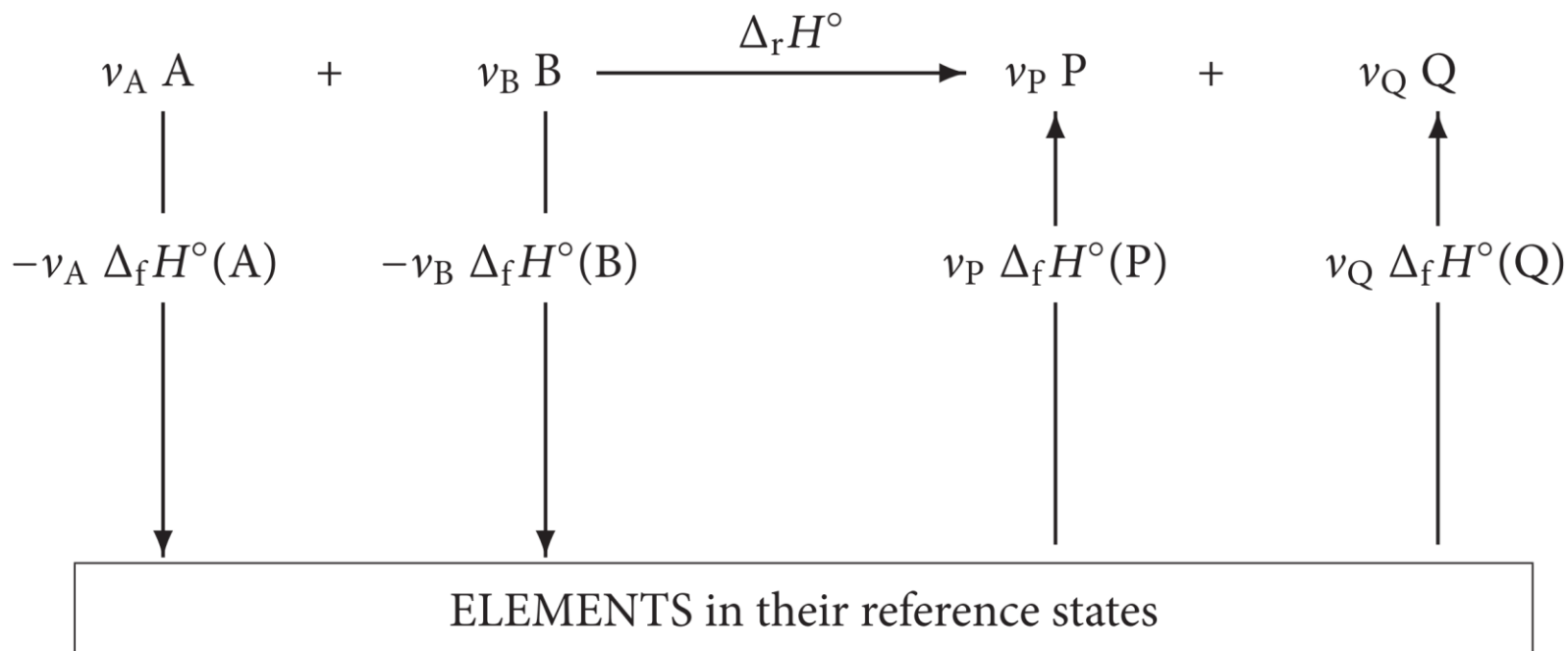
标准摩尔生成焓 ($\Delta_f H_m^\circ$; SI: $\text{kJ} \cdot \text{mol}^{-1}$) : 在标准压力 (100 kPa) 和一定温度下, 由元素最稳定的单质生成生成1 mol纯化合物时的反应焓变。

标准摩尔燃烧焓 ($\Delta_c H_m^\circ$; SI: $\text{kJ} \cdot \text{mol}^{-1}$) : 在标准压力 (100 kPa) 和一定温度下, 一摩尔物质完全燃烧时的反应焓变。

标准摩尔熵 (S_m° ; SI: $\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) : 常见单质和化合物在标准状态下的熵值可直接查表获得。

反应热加成性定律

Hess定律：一个反应，在定压或定容条件下，不论是一步完成还是分几步完成，其反应热是相同的，即总反应方程式的焓变等于各部分分步反应按一定系数比加和的焓变。

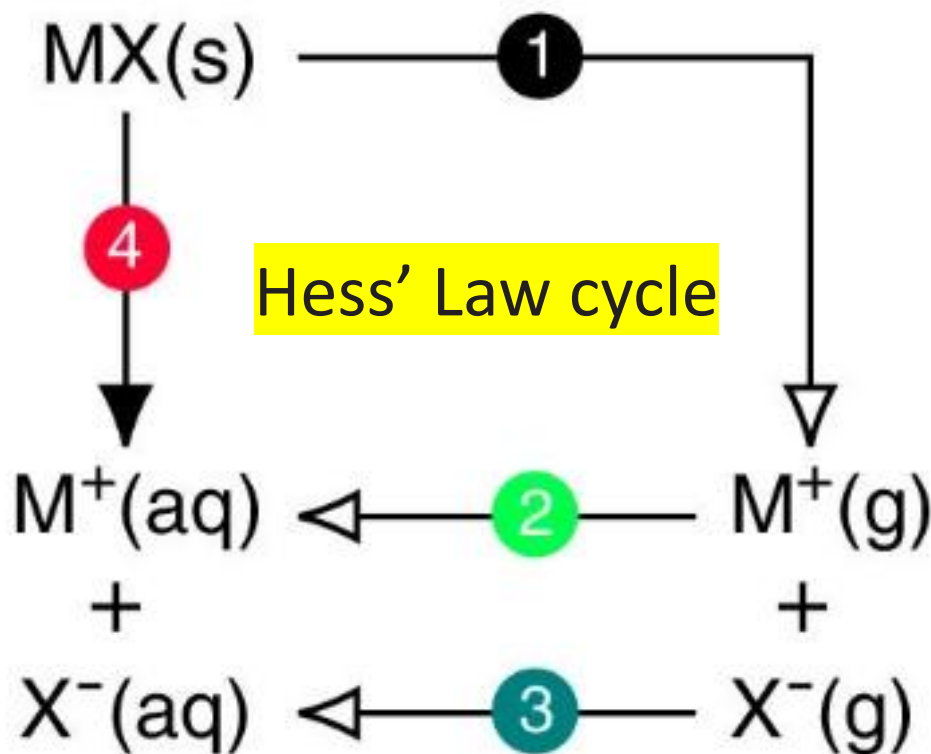


$$\Delta_r H^\circ = \nu_P \Delta_f H^\circ(P) + \nu_Q \Delta_f H^\circ(Q) - \nu_A \Delta_f H^\circ(A) - \nu_B \Delta_f H^\circ(B)$$

应用：离子化合物的溶解

离子化合物在水中溶解： $\text{MX}(\text{s}) \rightleftharpoons \text{M}^+(\text{aq}) + \text{X}^-(\text{aq})$

为何NaCl易溶，LiF难溶？



1: 气相解离

2: M^+ 溶剂化

3: X^- 溶剂化

4: 溶解过程

应用：伯恩-哈珀循环

Determination of ΔH for Reactions of the Born–Haber Cycle

Richard S. Treptow

Department of Chemistry and Physics, Chicago State University, Chicago, IL 60628

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This paper reviews the experimental methods used to determine ΔH for the various steps of the Born–Haber cycle. The methods employed are surprisingly varied; they include several forms of spectroscopy and calorimetry. The cycle for the formation of sodium chloride will be used for the purpose of illustration. It will be constructed using the best available data from the current literature. We will take particular care to specify the standard state of each species in the cycle and to assign every reaction its proper enthalpy change, rather than its energy change. In other words, the cycle will be thermodynamically correct.

Table 2. ΔH for Steps in the Born–Haber Cycle for NaCl

Step	ΔH (kJ mol ⁻¹)	Method
Atomization of Na(s)	107.3	Ice calorimetry and vapor pressure measurement
Dissociation of 1/2 Cl ₂ (g)	121.3	Molecular spectroscopy
Ionization of Na(g)	502.0	Atomic spectroscopy
Electron attachment to Cl(g)	-355.2	Negative ion spectroscopy
Compound formation from the elements	-411.1	Several calorimetric methods combined
Lattice formation from ions	-786.5	Hess's law calculation

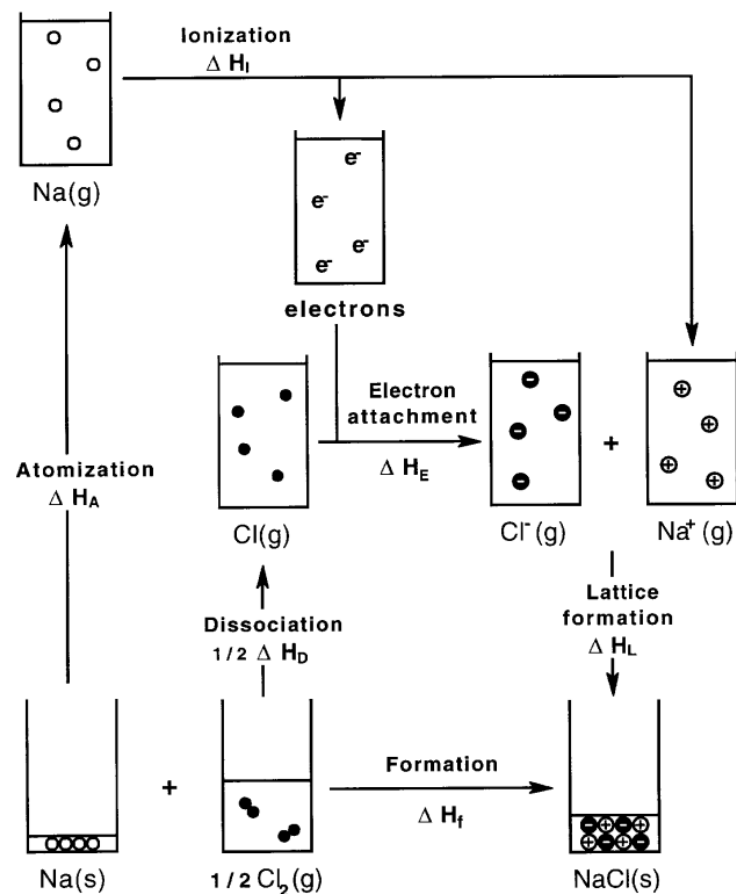


Figure 1. Born–Haber cycle for formation of sodium chloride at standard conditions.

9. 化学平衡

$$\Delta_{\text{r}}G^{\circ} = -RT \ln K$$

实验可测量量

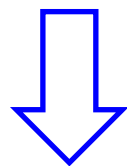
反应平衡常数

对于反应平衡： $\nu_A A + \nu_B B \dots \rightleftharpoons \nu_P P + \nu_Q Q \dots$

平衡常数定义

$$K = \frac{[P]^{\nu_P} [Q]^{\nu_Q} \dots}{[A]^{\nu_A} [B]^{\nu_B} \dots}$$

单位取决于
反应计量系数



标准平衡常数
(无量纲)

$$K_p = \frac{\left(\frac{p_P}{p^\circ}\right)^{\nu_P} \left(\frac{p_Q}{p^\circ}\right)^{\nu_Q} \dots}{\left(\frac{p_A}{p^\circ}\right)^{\nu_A} \left(\frac{p_B}{p^\circ}\right)^{\nu_B} \dots}$$

$$K_c = \frac{\left(\frac{c_P}{c^\circ}\right)^{\nu_P} \left(\frac{c_Q}{c^\circ}\right)^{\nu_Q} \dots}{\left(\frac{c_A}{c^\circ}\right)^{\nu_A} \left(\frac{c_B}{c^\circ}\right)^{\nu_B} \dots}$$

反应平衡常数

phase	definition of standard state
gas	the <i>pure</i> gas at a pressure of 1 bar and at the stated temperature
liquid	the <i>pure</i> liquid at the stated temperature
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solution	an (ideal) solution with the solute at the standard concentration of 1 mol dm ⁻³ , and at the stated temperature

反应中出现的固相和液相等凝聚态均对平衡常数无贡献：

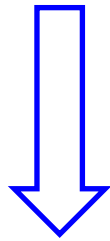


$$K_p = \frac{(p_{\text{CO}}/p^\circ)(p_{\text{H}_2}/p^\circ)}{(p_{\text{H}_2\text{O}}/p^\circ)} = \frac{p_{\text{CO}}p_{\text{H}_2}}{p_{\text{H}_2\text{O}}p^\circ}$$

平衡常数的溯源

对于反应平衡： $\nu_A A + \nu_B B \rightleftharpoons \nu_P P + \nu_Q Q$

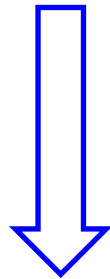
等温等压



$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

$$\Delta_r G = \nu_P \mu_P + \nu_Q \mu_Q - \nu_A \mu_A - \nu_B \mu_B$$

若为气相反应



$$\mu_i(p_i) = \mu_i^\circ + RT \ln \frac{p_i}{p^\circ}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{\left(\frac{p_P}{p^\circ}\right)^{\nu_P} \left(\frac{p_Q}{p^\circ}\right)^{\nu_Q}}{\left(\frac{p_A}{p^\circ}\right)^{\nu_A} \left(\frac{p_B}{p^\circ}\right)^{\nu_B}}$$

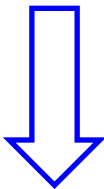
← 逸度商
(Q_f)

平衡常数的溯源

对于反应平衡： $\nu_A A + \nu_B B \rightleftharpoons \nu_P P + \nu_Q Q$

因为平衡时 $\Delta_r G = 0$

于是 $0 = \Delta_r G^\circ + RT \ln \left[\frac{\left(\frac{p_P}{p^\circ}\right)^{\nu_P} \left(\frac{p_Q}{p^\circ}\right)^{\nu_Q}}{\left(\frac{p_A}{p^\circ}\right)^{\nu_A} \left(\frac{p_B}{p^\circ}\right)^{\nu_B}} \right]_{\text{eq.}}$ $\leftarrow K_p$


$$\Delta_r G^\circ = -RT \ln K_p$$

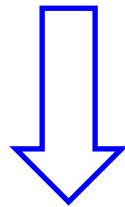
当反应在溶液中进行时，易得 $\Delta_r G^\circ = -RT \ln K_c$

平衡常数的溯源

对于包含固体的化学平衡：



$$\Delta_{\text{r}}G = \mu(\text{CO}_2) + \mu(\text{CaO}) - \mu(\text{CaCO}_3)$$



$$\mu_i(p_i) = \mu_i^\circ + RT \ln \frac{p_i}{p^\circ}$$

$$\Delta_{\text{r}}G = [\mu^\circ(\text{CO}_2) + \mu^\circ(\text{CaO}) - \mu^\circ(\text{CaCO}_3)] + RT \ln \frac{p_{\text{CO}_2}}{p^\circ}$$

平衡时： $\Delta_{\text{r}}G^\circ = -RT \ln \frac{p_{\text{CO}_2, \text{eq.}}}{p^\circ} \leftarrow K_p$

关于 $\Delta G^\circ = -RT \ln K$

对于反应平衡: $\nu_A A + \nu_B B \dots \rightleftharpoons \nu_P P + \nu_Q Q \dots$

两种平衡
常数

$$K_p = \frac{\left(\frac{p_P}{p^\circ}\right)^{\nu_P} \left(\frac{p_Q}{p^\circ}\right)^{\nu_Q} \dots}{\left(\frac{p_A}{p^\circ}\right)^{\nu_A} \left(\frac{p_B}{p^\circ}\right)^{\nu_B} \dots} \quad K_c = \frac{\left(\frac{c_P}{c^\circ}\right)^{\nu_P} \left(\frac{c_Q}{c^\circ}\right)^{\nu_Q} \dots}{\left(\frac{c_A}{c^\circ}\right)^{\nu_A} \left(\frac{c_B}{c^\circ}\right)^{\nu_B} \dots}$$

根据 $pV = nRT$, 有 $p = cRT$, 即 $K_p = K_c (c^\circ RT/p^\circ)^{\Delta \nu}$

问题: 对于 $\Delta G^\circ = -RT \ln K$, 计算 ΔG° 时应该用 K_p 还是 K_c ?

平衡常数的一般性定义

$$K = \frac{(a_P)^{\nu_P} (a_Q)^{\nu_Q}}{(a_A)^{\nu_A} (a_B)^{\nu_B}}$$

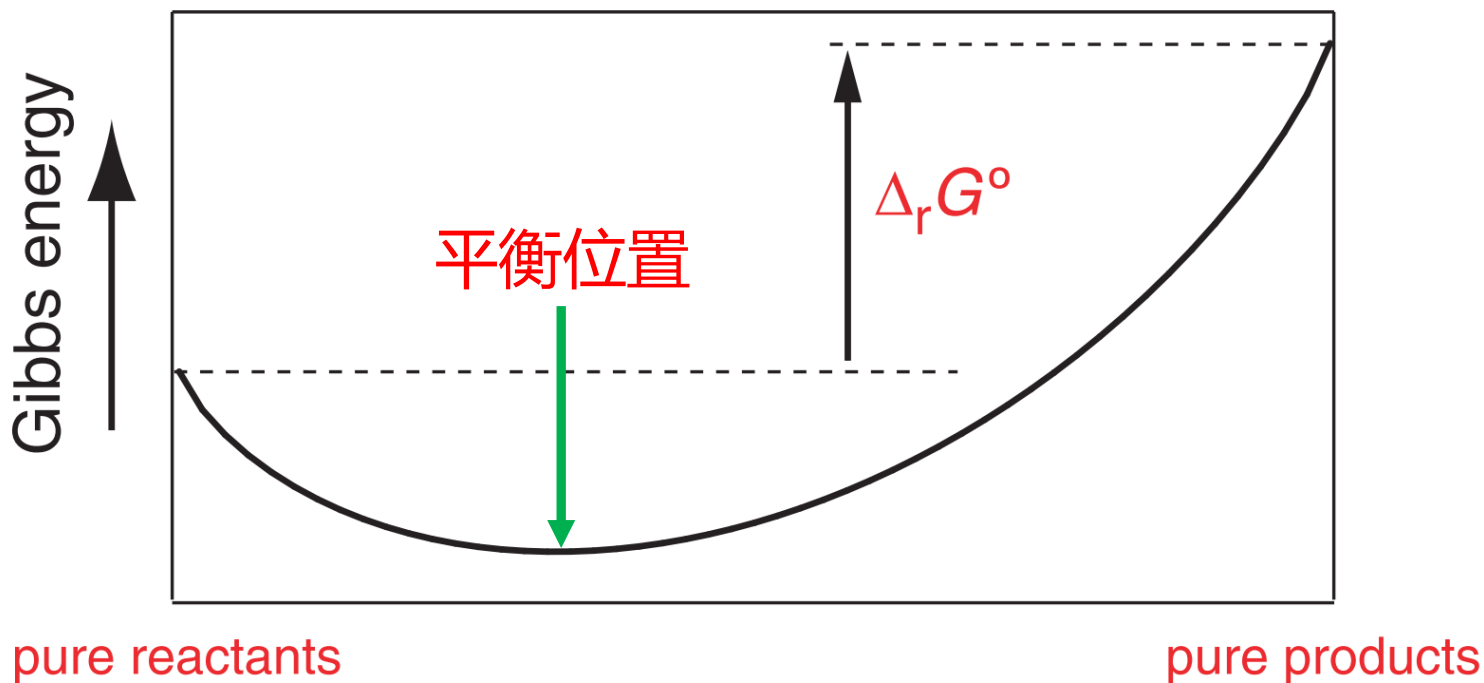
理想气体: $a_i = p/p^\circ$

理想溶液: $a_i = c/c^\circ$

纯固体或液体: $a_i = 1$

化学平衡的本质

根据 $\Delta_r G^\circ = -RT \ln K$ 可知，即使 $\Delta_r G^\circ \gg 0$ ，总会有一些反应物转化为产物以建立化学平衡。这是否与自发反应过程对 $\Delta_r G^\circ < 0$ 的要求相矛盾？



化学平衡的本质

考虑化学平衡 $A \rightleftharpoons B$ ，因反应物的消耗与产物的生成遵循化学计量比，引入反应进度 (ξ) 代表系统中归一化的产物产量：

$$dn_A = -d\xi, \quad dn_B = +d\xi$$

希腊字母的读音

序号	大写	小写	国际音标[推荐]	英文	汉字注音	常用指代意义
1	A	α	/ˈælfə/	alpha	阿尔法	角度，系数，角加速度
2	B	β	/ˈbi:tə/ /ˈbeɪtə/	beta	贝塔/毕塔	磁通系数，角度，系数
3	Γ	γ	/ˈgæmə/	gamma	伽玛/甘玛	电导系数，角度，比热容比
4	Δ	δ	/ˈdeltə/	delta	德尔塔/岱欧塔	变化量，化学反应中的加热，屈光度，一元二次方程中的判别式
5	E	ϵ	/ˈepsɪlɒn/	epsilon	艾普西龙	对数之基数，介电常数
6	Z	ζ	/ˈzi:tə/	zeta	泽塔	系数，方位角，阻抗，相对黏度
7	H	η	/ˈi:tə/	eta	伊塔/诶塔	迟滞系数，效率
8	Θ	θ	/ˈθi:tə/	theta	西塔	温度，角度
9	I	ι	/aɪˈəʊtə/	iota	埃欧塔	微小，一点
10	K	κ	/ˈkæpə/	kappa	堪帕	介质常数，绝热指数
11	Λ	λ	/ˈlæmdə/	lambda	兰姆达	波长，体积，导热系数； 强度
12	M	μ	/mju:/	mu	谬/穆	磁导系数，微，动摩擦系（因）数，流体动力黏度； 数学期望

希腊字母的读音

13	N	ν	/nju:/	nu	拗/奴	磁阻系数，流体运动粘度光子频率，化学计量数
14	Ξ	ξ	希腊: /ksi/ 英美: /'zaɪ/或/'ksaɪ/	xi	可西/赛	随机变量，（小）区间内的一个未知特定值
15	O	ο	/əu'maɪkrən/ /'ɑmɪˌkrən/	omicron	欧 (阿~) 米可荣	高阶无穷小函数
16	Π	π	/paɪ/	pi	派	圆周率， $\pi(n)$ 表示不大于n的质数个数
17	P	ρ	/rəu/	rho	柔/若	电阻系数，柱坐标和极坐标中的极径，密度
18	Σ	σ	/'sɪgmə/	sigma	西格玛	总和，表面密度，跨导，正应力； 标准差
19	T	τ	/tɔ:/ /taʊ/	tau	套/驼	时间常数，切应力， 2π （两倍圆周率）
20	Υ	υ	/'ɪpsɪlən/ /'ʌpsɪlən/	upsilon	宇 (阿~) 普西龙	位移
21	Φ	φ	/faɪ/	phi	弗爱/弗忆	磁通，角，透镜焦度，热流量
22	X	χ	/kaɪ/	chi	凯/柯义	统计学中有卡方(χ^2)分布
23	Ψ	ψ	/psaɪ/	psi	赛/普赛/普西	角速，介质电通量， ψ 函数
24	Ω	ω	/'əʊmɪgə/ /ou'mega/	omega	欧米伽/欧枚嘎	欧姆，角速度，交流电的电角度，化学中的质量分数； 概率论：必然事件、样本空间；

化学平衡的本质

考虑化学平衡 $A \rightleftharpoons B$ ，因反应物的消耗与产物的生成遵循化学计量比，引入反应进度 (ξ) 代表系统中归一化的产物产量：

$$dn_A = -d\xi, \quad dn_B = +d\xi$$

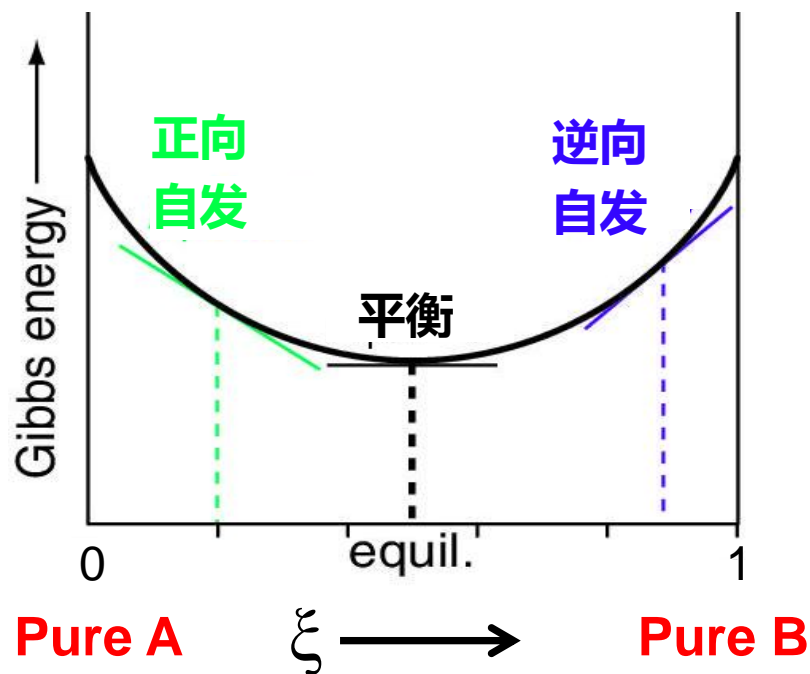
于是有：

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$= -\mu_A d\xi + \mu_B d\xi$$

$$= (\mu_B - \mu_A) d\xi$$

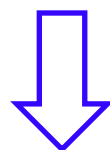
$$\left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \mu_B - \mu_A$$



化学平衡的本质

若A和B均为理想气体, $A(g) \rightleftharpoons B(g)$

$$G = n_A \left[G_{m,A}^{\circ} + RT \ln \left(\frac{p_A}{p^{\circ}} \right) \right] + n_B \left[G_{m,B}^{\circ} + RT \ln \left(\frac{p_B}{p^{\circ}} \right) \right]$$

 $n = n_A + n_B, p = p_A + p_B$
 $\xi = n_B/n = x_B$

$$G/n = (1 - x_B) \left[G_{m,A}^{\circ} + RT \ln \left(\frac{(1 - x_B)p}{p^{\circ}} \right) \right] + x_B \left[G_{m,B}^{\circ} + RT \ln \left(\frac{x_B p}{p^{\circ}} \right) \right]$$
$$= (1 - x_B) G_{m,A}^{\circ} + x_B G_{m,B}^{\circ} + (1 - x_B) RT \ln \left(\frac{(1 - x_B)p}{p^{\circ}} \right) + x_B RT \ln \left(\frac{x_B p}{p^{\circ}} \right)$$

单纯由A向B转化所带来的自由能变化 (无A与B间混合)

单纯由理想气体A与B之间混合所带来的自由能变化

混合体系的Gibbs自由能

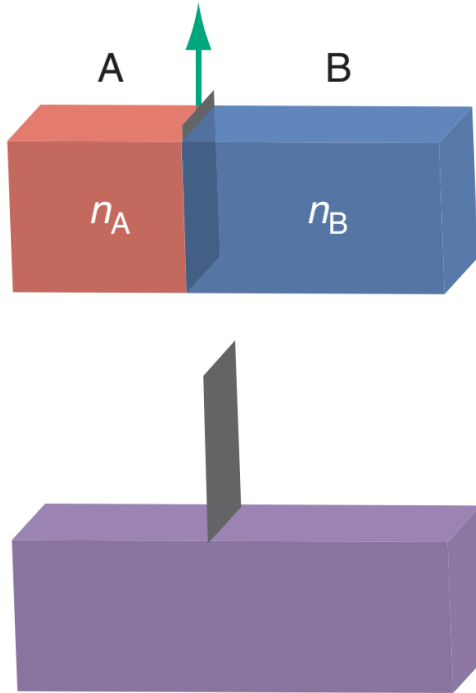


Fig. 19.11 Two (ideal) gases A and B are separated by a partition; there are n_A moles of A and n_B moles of B, and both are at the same pressure p . When the partition is removed, the gases mix spontaneously.

考虑两理想气体等温混合的 ΔG :

$$G_{\text{before mixing}} = \underbrace{n_A \left[G_{\text{m,A}}^{\circ} + RT \ln \left(\frac{p}{p^{\circ}} \right) \right]}_{\text{Gibbs energy of A}} + \underbrace{n_B \left[G_{\text{m,B}}^{\circ} + RT \ln \left(\frac{p}{p^{\circ}} \right) \right]}_{\text{Gibbs energy of B}}.$$

$$G_{\text{after mixing}} = \underbrace{n_A \left[G_{\text{m,A}}^{\circ} + RT \ln \left(\frac{p_A}{p^{\circ}} \right) \right]}_{\text{Gibbs energy of A}} + \underbrace{n_B \left[G_{\text{m,B}}^{\circ} + RT \ln \left(\frac{p_B}{p^{\circ}} \right) \right]}_{\text{Gibbs energy of B}}.$$

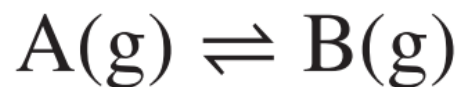


$$\Delta G_{\text{mix}} = n_A RT \ln \left(\frac{p_A}{p} \right) + n_B RT \ln \left(\frac{p_B}{p} \right)$$

$\Delta G_{\text{mix}} < 0$, 混合是自发过程!

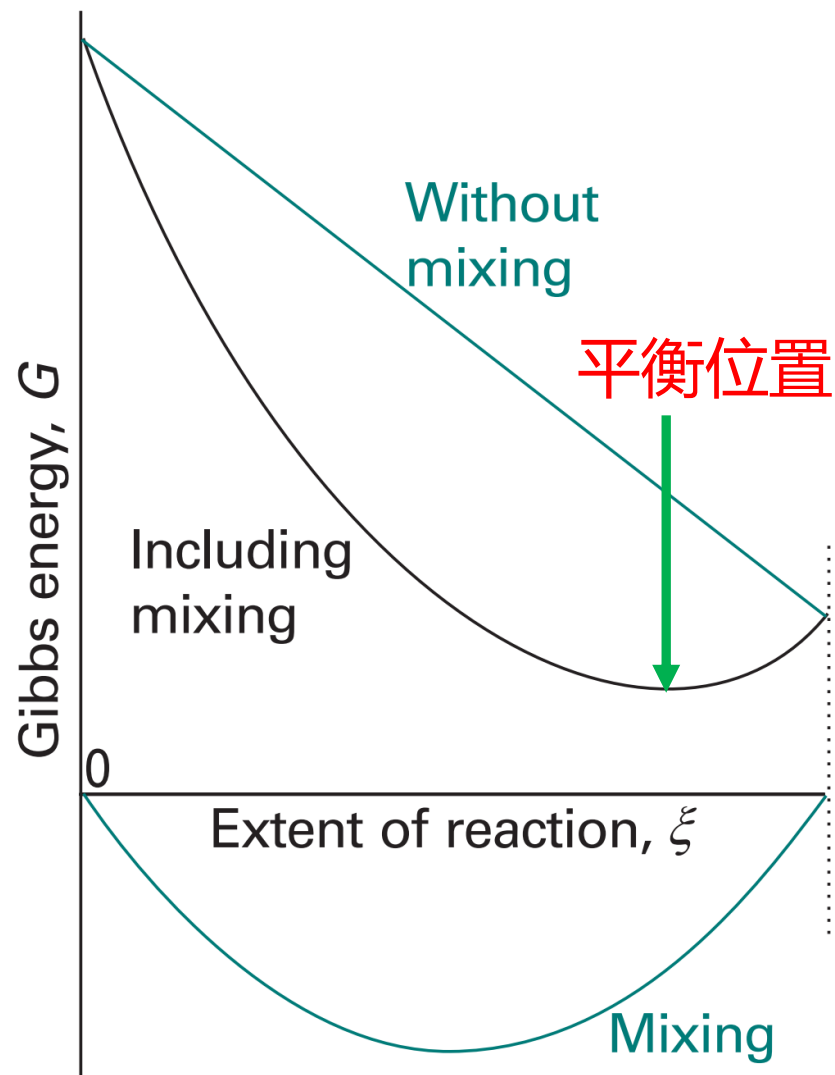
化学平衡的本质

若A和B均为理想气体,



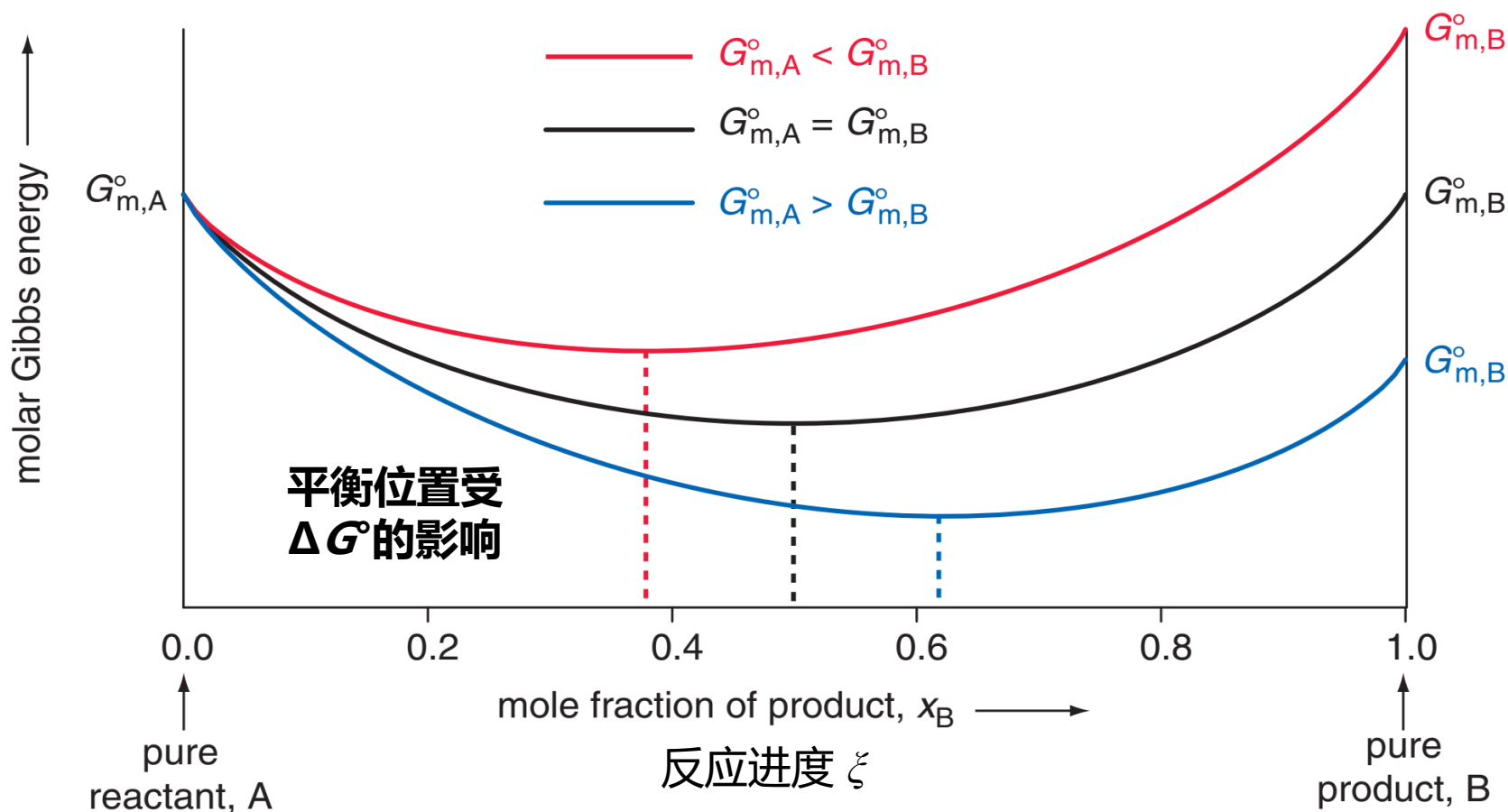
$$G = \underbrace{n_A \left[G_{m,A}^{\circ} \right]}_{\text{without mixing}} + \underbrace{RT \ln \left(\frac{p_A}{p^{\circ}} \right)}_{\text{Mixing}} + \underbrace{n_B \left[G_{m,B}^{\circ} \right]}_{\text{without mixing}} + \underbrace{RT \ln \left(\frac{p_B}{p^{\circ}} \right)}_{\text{Mixing}}$$

化学平衡的存在纯粹是因为理想气体混合自由能的贡献!



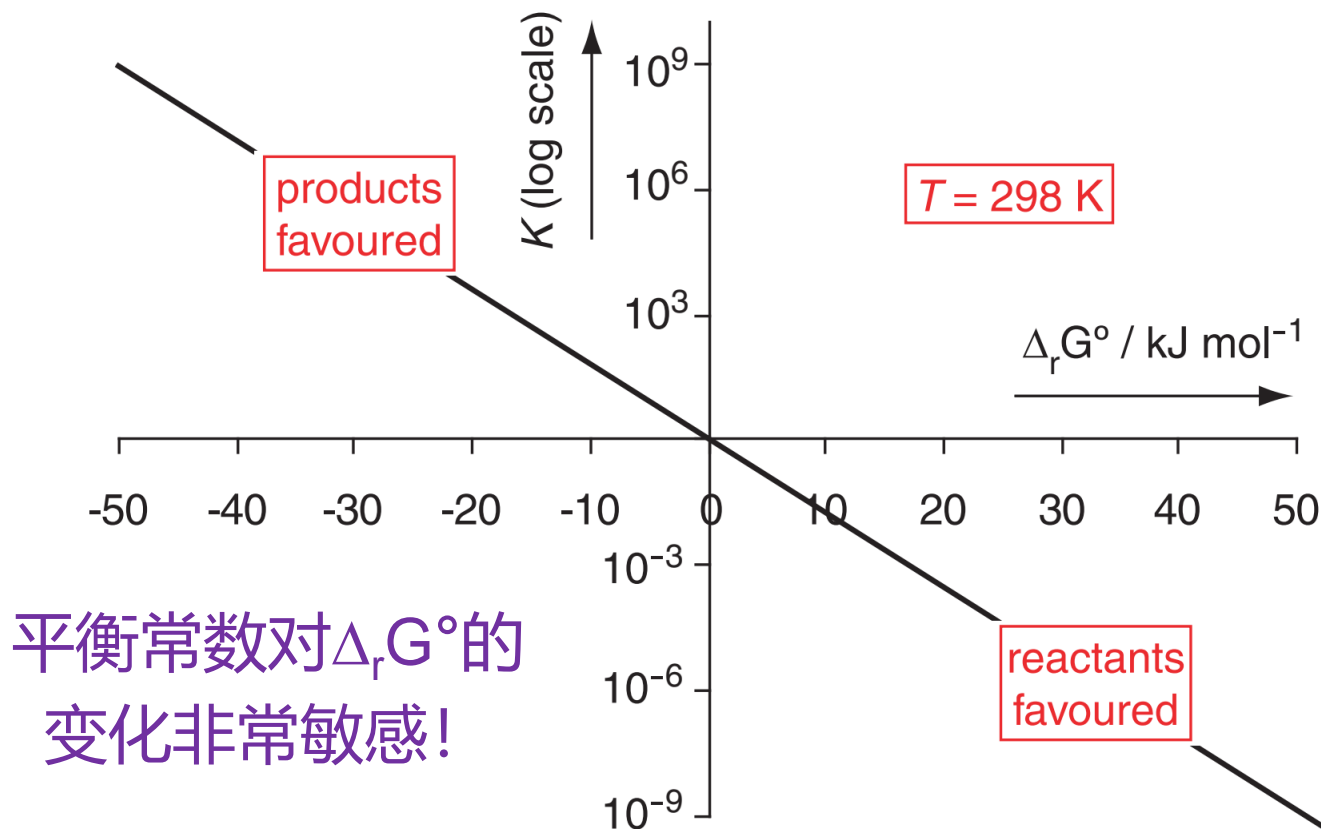
化学平衡的本质

$$G/n = (1 - x_B)[G_{m,A}^\circ + RT\ln(\frac{(1-x_B)p}{p^\circ})] + x_B[G_{m,B}^\circ + RT\ln(\frac{x_B p}{p^\circ})]$$



自由能与平衡常数的关系

$$\Delta_r G^\circ = -RT \ln K \Rightarrow K = \exp\left(\frac{-\Delta_r G^\circ}{RT}\right)$$



化学平衡的调控

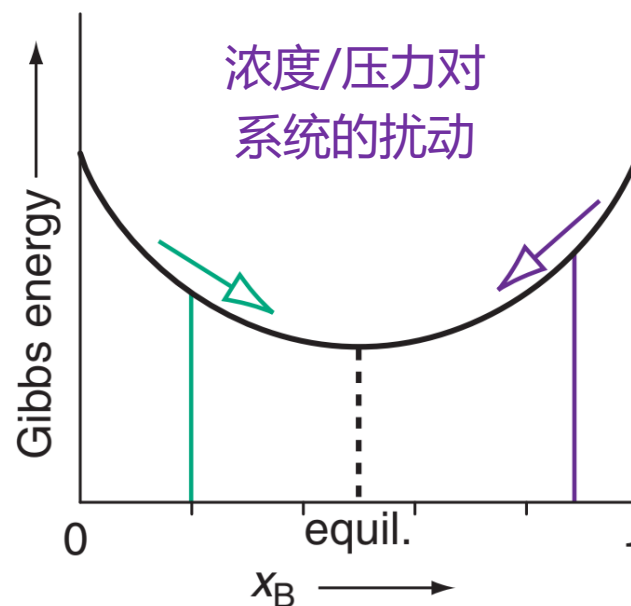
Le Chatelier's principle:

If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium.



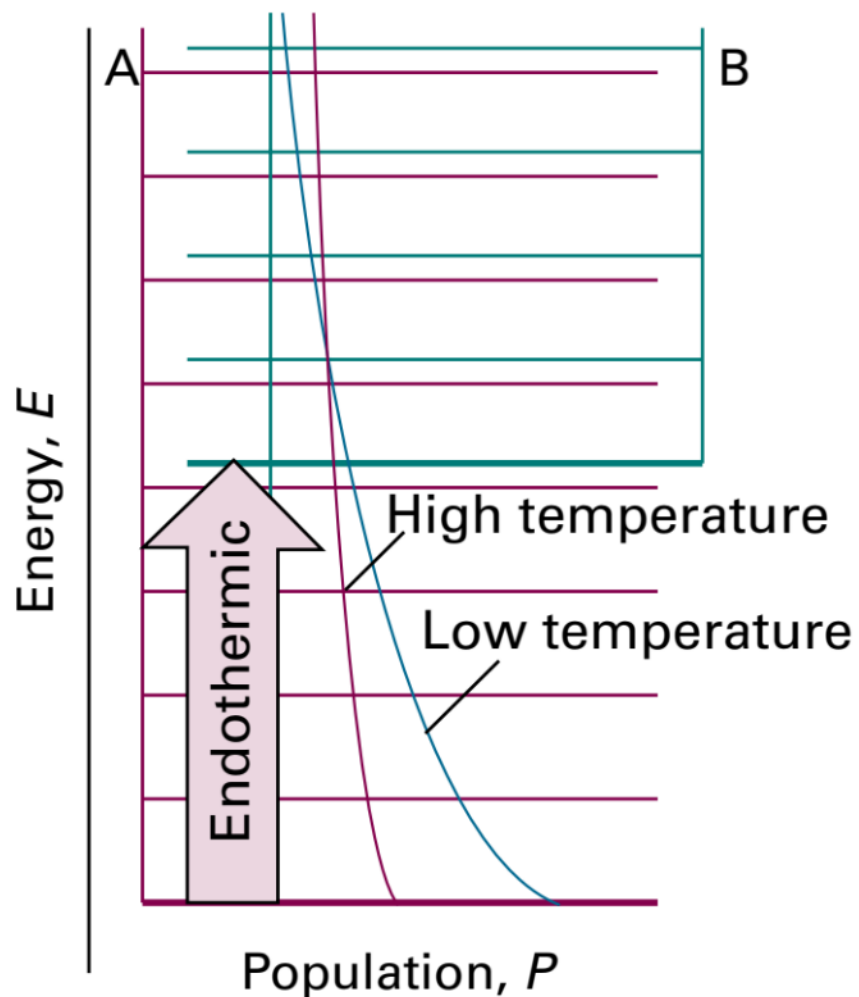
$$K = \frac{[P]^{\nu_P} [Q]^{\nu_Q} \dots}{[A]^{\nu_A} [B]^{\nu_B} \dots}$$

浓度/压力改变仅影响相对组成，而温度改变则会影响平衡点的位置。

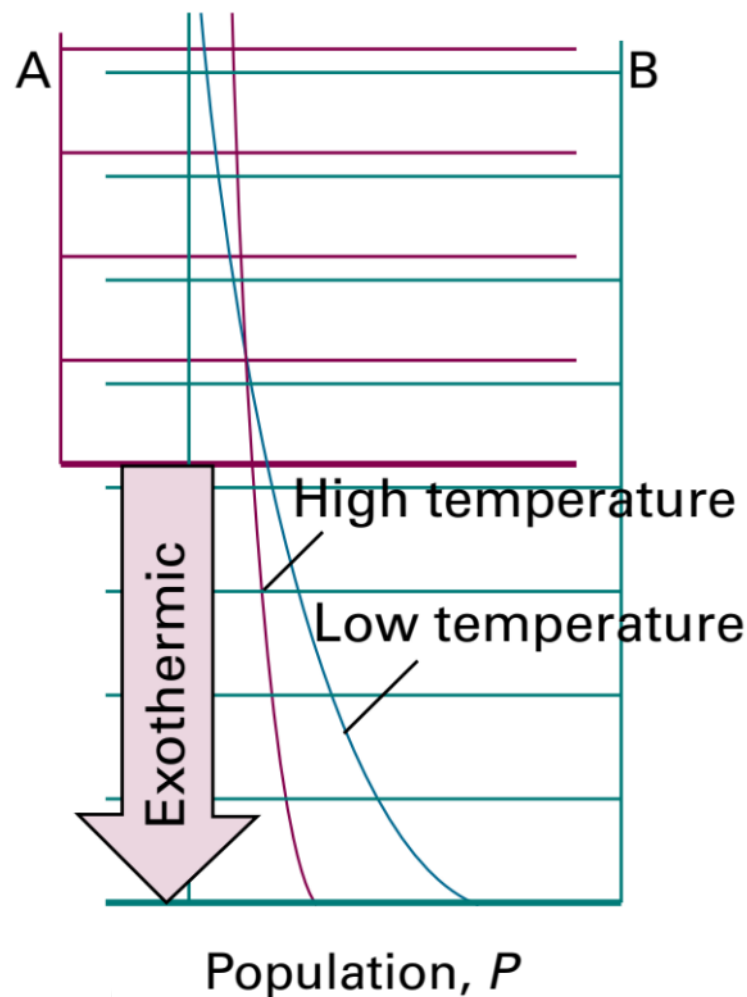


温度对化学平衡的影响

(1) 吸热反应的Boltzmann分布



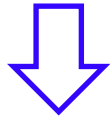
(2) 放热反应的Boltzmann分布



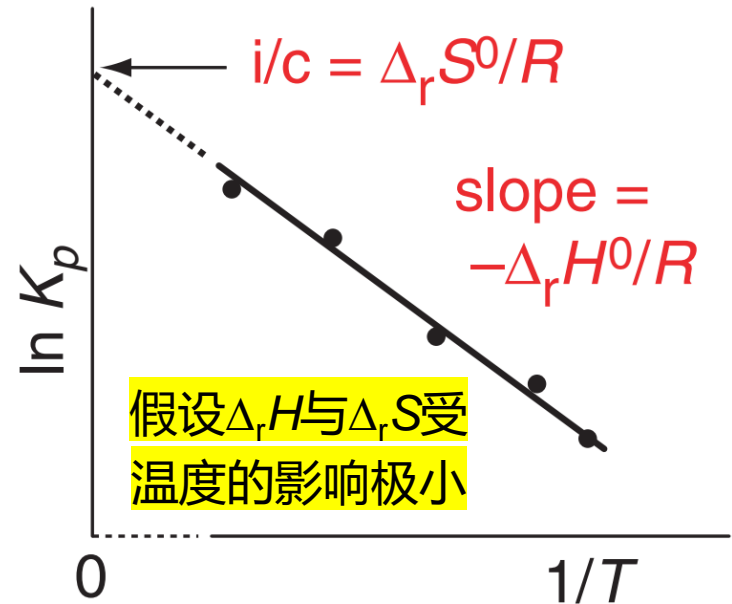
温度对化学平衡的影响

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$



$$\ln K = \frac{-\Delta_r H^\circ}{R} \frac{1}{T} + \frac{\Delta_r S^\circ}{R}$$

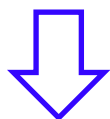


- For an endothermic reaction ($\Delta_r H^\circ > 0$), the term $-\Delta_r H^\circ / T$ is negative and so increasing T makes the term less negative. As a result $\ln K$ increases and so does K .
- For an exothermic reaction ($\Delta_r H^\circ < 0$), the term $-\Delta_r H^\circ / T$ is positive and so increasing T makes the term less positive. As a result $\ln K$ decreases and so does K .

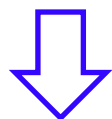
温度对化学平衡的影响

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$



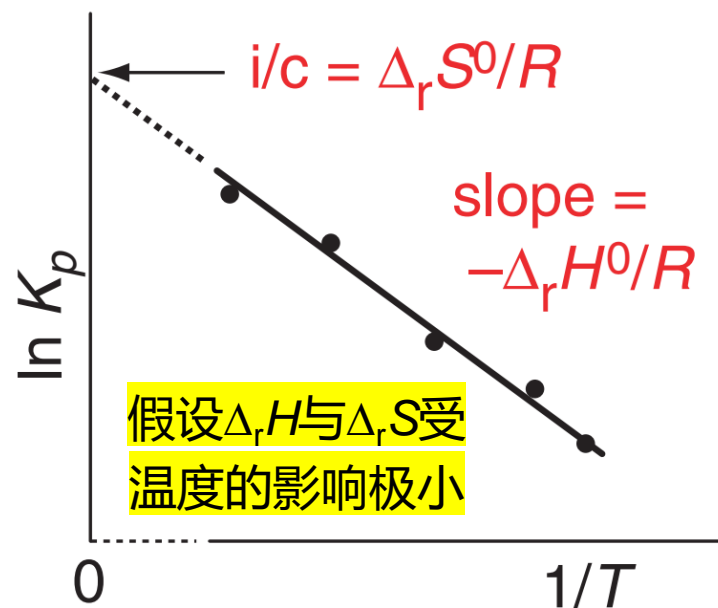
$$\ln K = \frac{-\Delta_r H^\circ}{R} \frac{1}{T} + \frac{\Delta_r S^\circ}{R}$$



van 't Hoff
方程

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

$$\ln K(T_2) - \ln K(T_1) = -\frac{\Delta_r H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$



Gibbs–Helmholtz方程

$$\frac{d}{dT} \left(\frac{G}{T} \right) = -\frac{H}{T^2}$$

温度对化学平衡的影响

The Temperature Dependence of ΔG° and the Equilibrium Constant, K_{eq} ; Is There a Paradox?

Frances H. Chapple

Department of Chemistry, Willamette University, Salem, Oregon 97301

Journal of Chemical Education • Vol. 75 No. 3 March 1998

Table 1. Effect of Temperature on ΔG° and K_{eq}

ΔH° (kJ)	ΔS° (J/K)	$T = 273 \text{ K}$		$T = 373 \text{ K}$	
		ΔG° (kJ)	K_{eq}	ΔG° (kJ)	K_{eq}
3	10	0.27	0.89	-0.73	1.27
-3	-10	-0.27	1.13	0.73	0.79
3	-10	5.73	0.08	6.73	0.11
-3	10	-5.73	12.49	-6.73	8.76

Note: Calculations of ΔG° and K_{eq} are based on the assumption that ΔH° and ΔS° are temperature independent.

温度对化学平衡的影响

That it is the sign of ΔS° that determines whether ΔG° increases or decreases with temperature is clear both from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and from the differential of this equation,

$$\begin{aligned}(\partial \Delta G^\circ / \partial T)_p &= (\partial \Delta H^\circ / \partial T)_p - \Delta S^\circ - T(\partial \Delta S^\circ / \partial T)_p \\ &= \Delta C_p - \Delta S^\circ - T(\Delta C_p / T) = -\Delta S^\circ\end{aligned}$$

When the standard-state spontaneity of a reaction (ΔG) is of concern...

The solution to the apparent discrepancy lies in the fact that K_{eq} is related to ΔG° by the equation $\ln K_{\text{eq}} = -\Delta G^\circ / RT$. It is thus the temperature dependence of $\Delta G^\circ / T$, and not of ΔG° alone, that determines whether K_{eq} increases or decreases with temperature. The Gibbs–Helmholtz equation

$$(\partial(\Delta G^\circ / T) / \partial(1/T))_p = \Delta H^\circ$$

and the derived equation

$$(\partial \ln K_{\text{eq}} / \partial(1/T))_p = -\Delta H^\circ / R$$

When considering the effect of temperature on equilibrium concentrations of products and reactants...

平衡浓度/压力的计算

考虑在气相发生的分解反应: $A_2(g) \rightleftharpoons 2 A(g)$

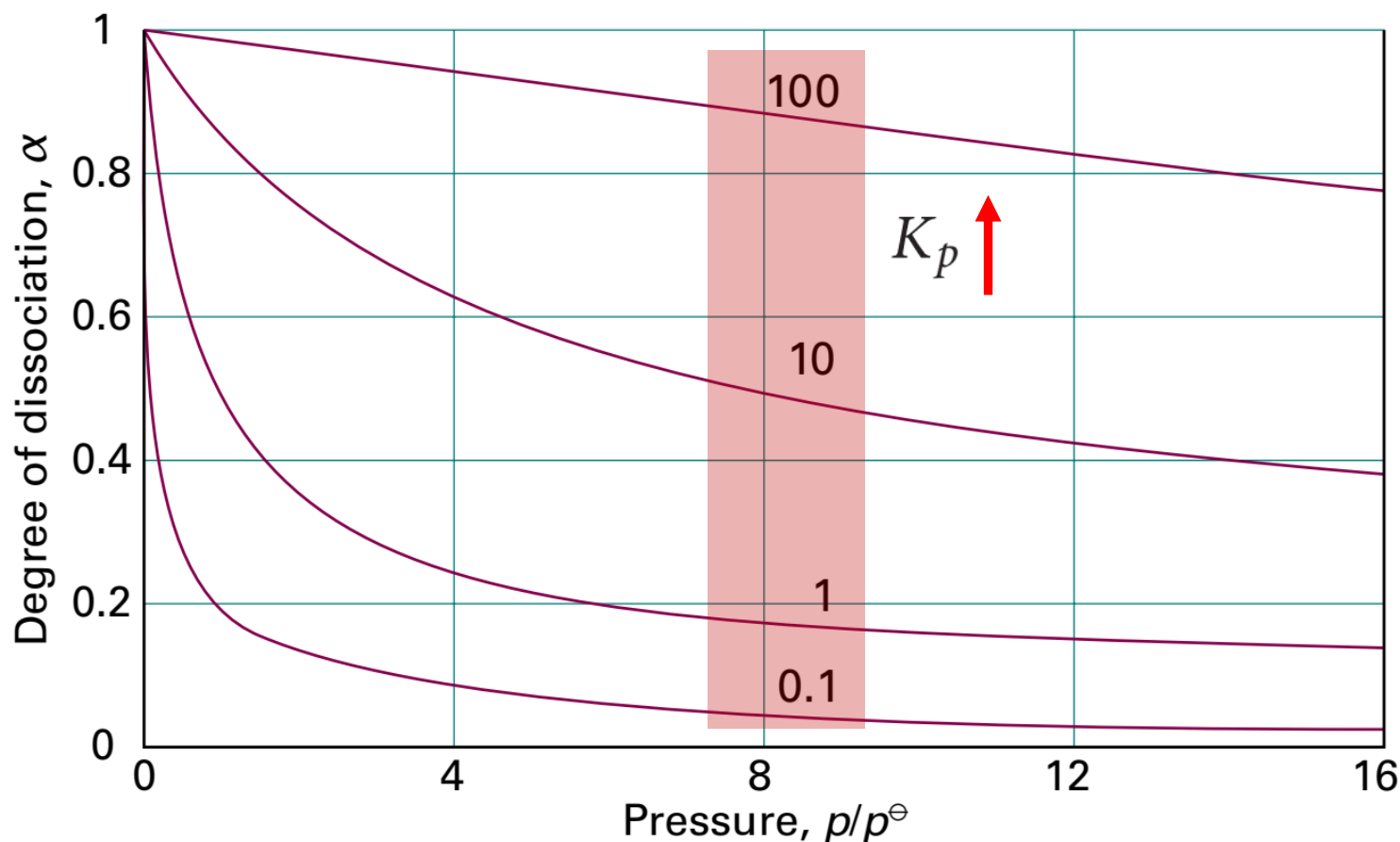
line	quantity	$A_2(g)$	\rightleftharpoons	$2A(g)$
1	initial moles	n_0		0
2	moles at equil.	$n_0(1 - \alpha)$		$2 \times n_0\alpha$
3	mole fractions	$(1 - \alpha)/(1 + \alpha)$		$(2\alpha)/(1 + \alpha)$
4	partial pressures	$p \times (1 - \alpha)/(1 + \alpha)$		$p \times 2\alpha/(1 + \alpha)$

$$K_p = \frac{(p_A/p^\circ)^2}{(p_{A_2}/p^\circ)} = \frac{4\alpha^2}{(1 + \alpha)^2} \frac{(1 + \alpha)}{(1 - \alpha)} \frac{p_{\text{tot}}^2}{p_{\text{tot}}} \frac{p^\circ}{(p^\circ)^2}$$

$$= \frac{4\alpha^2}{(1 - \alpha^2)} \frac{p_{\text{tot}}}{p^\circ} \quad \Rightarrow \quad K_p = 4\alpha^2 \frac{p_{\text{tot}}}{p^\circ} \quad (\text{当 } \alpha \ll 1 \text{ 时})$$

平衡浓度/压力的计算

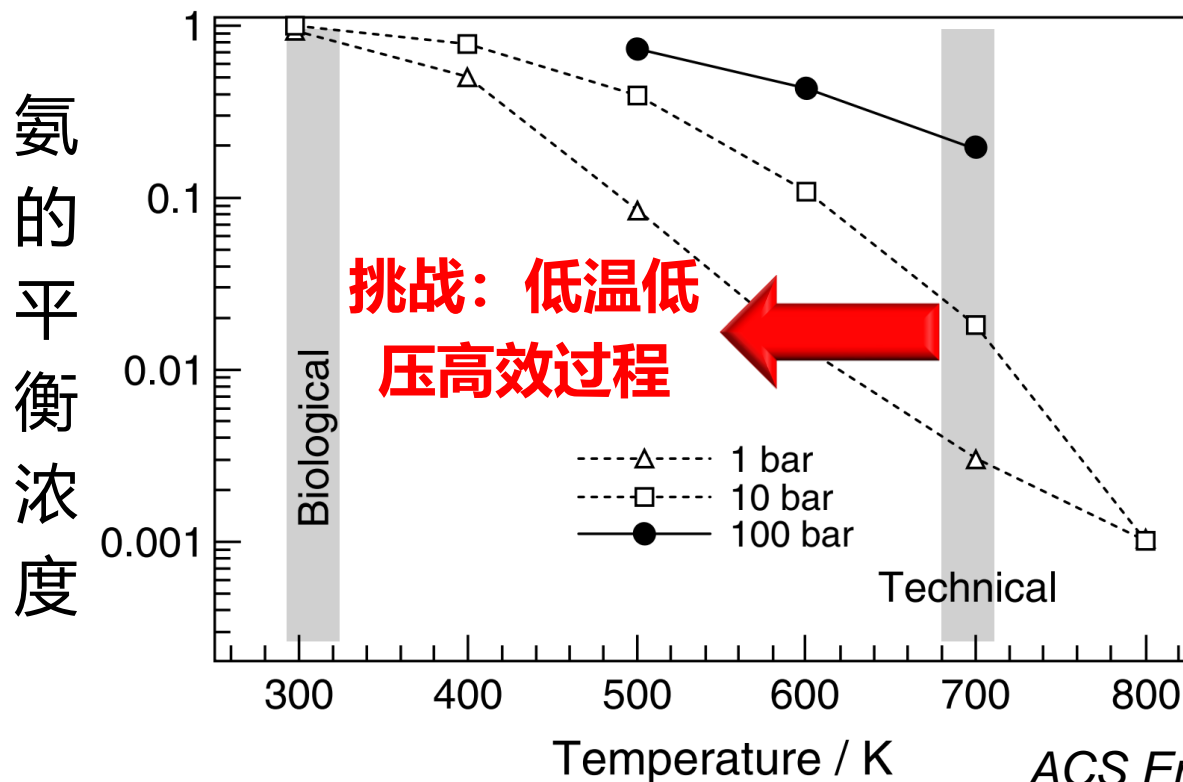
气相反应: $A_2(g) \rightleftharpoons 2 A(g)$ $K_p = \frac{4\alpha^2}{(1-\alpha^2)} \frac{p_{\text{tot}}}{p^\ominus}$



化学平衡原理的实际应用



N_2 的高键能和非极性特征导致其通常需要高温活化



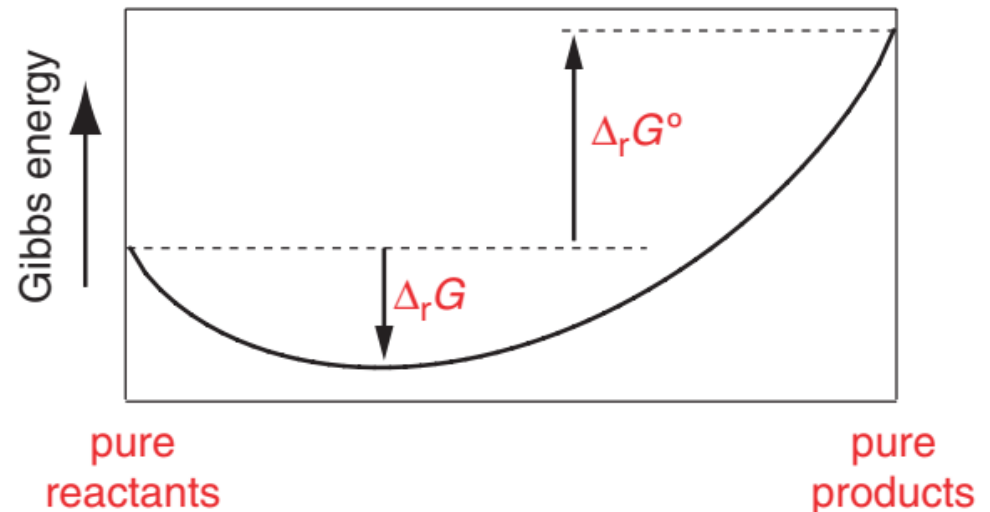
工业合成氨过程在
高温高压下进行
400-550°C
150-250 bar

本章小结

- ✓ The value of the equilibrium constant is determined by $\Delta_r G^\circ$.
- ✓ The temperature dependence of the equilibrium constant is given by the van 't Hoff equation.
- ✓ Standard enthalpies and entropies of reaction can be converted from one temperature to another using heat capacities.

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$



化学热力学提纲

1. 化学热力学引言

2. 熵增加原理

3. 温度及其特性

4. 能量守恒定律

5. 可逆过程

6. 熵与热容

7. 吉布斯自由能

8. 化学反应变化

9. 化学平衡

$$\Delta S = q_{\text{可逆}}/T$$

化学体系

$$\Delta_{\text{r}} G^{\circ} = \Delta_{\text{r}} H^{\circ} - T \Delta_{\text{r}} S^{\circ}$$

等温等压

$$\Delta_{\text{r}} G^{\circ} = -RT \ln K$$

本周作业： 4道题

第一题： 室温（300 K）条件下， $\text{H}_2\text{O}(\text{g})$ 和 $\text{CO}(\text{g})$ 的摩尔生成吉布斯自由能分别是 -228 kJ/mol 和 -137 kJ/mol。请计算给定条件下，水煤气反应的标准反应吉布斯自由能和反应平衡常数。



第二题： 若 $\text{N}_2\text{O}_4(\text{g})$ 和 $\text{NO}_2(\text{g})$ 均理想气体，请计算这两种物质的平衡常数，以及在平衡时系统的混合熵。假定反应在 298 K、1 bar 下进行，反应起始为 2 mol N_2O_4 。已知：

$$\Delta_f G_m^\ominus(\text{N}_2\text{O}_4) = 97.89 \text{ kJ/mol} \quad \Delta_f G_m^\ominus(\text{NO}_2) = 51.31 \text{ kJ/mol}$$

第三题： 将下面的数据用 Excel 作图，计算给定反应， $\text{Ag}_2\text{CO}_3(\text{固}) \rightarrow \text{Ag}_2\text{O}(\text{固}) + \text{CO}_2(\text{气})$ ，在各个温度的标准反应热。然后，请计算各温度点的标准反应熵。所需数据如下。

T (K)	350	400	450	500
K	0.0004	0.014	0.186	1.48

本周作业：4道题

第四题：

298 K 时, 反应 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ 的 $K_p^\ominus = 0.155$ 。

(1) 求总压为 p^\ominus 时 $\text{N}_2\text{O}_4(\text{g})$ 的解离度。

(2) 求总压为 $\frac{1}{2}p^\ominus$ 时 $\text{N}_2\text{O}_4(\text{g})$ 的解离度。

(3) 求总压为 p^\ominus 、解离前 $\text{N}_2\text{O}_4(\text{g})$ 和 $\text{N}_2(\text{g})$ (惰性气体) 的摩尔比为 1:1 时 $\text{N}_2\text{O}_4(\text{g})$ 的解离度。