

Catalysis and Adsorption

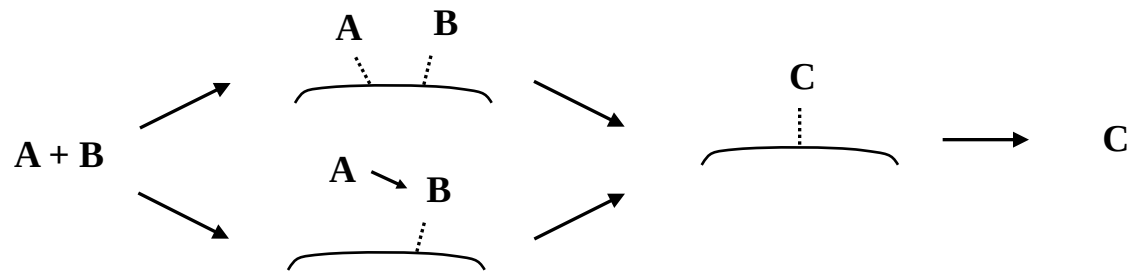
Theory and Applications

촉매작용과 흡착

촉매작용

1. 반응은 표면에 **흡착한 물질** 사이에서 일어남.
2. 그래서 흡착은 촉매 작용의 **핵심 단계**임.
3. 촉매의 성능은 반응물의 **흡착열과 흡착 형태**에 따라 크게 달라짐.

반응기구

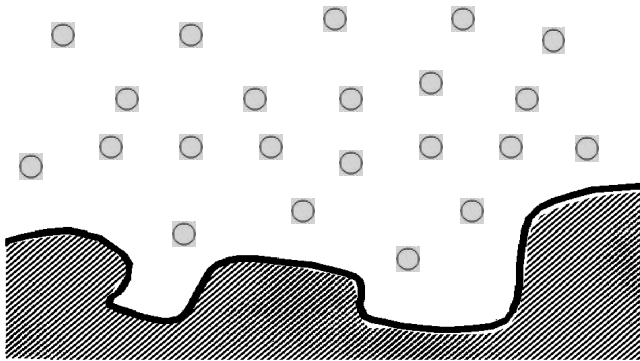


촉매작용에서 흡착의 역할

1. 흡착하여 **활성화된 반응물** 생성 : 개수와 세기
2. **새로운 반응경로**의 생성 : 활성화에너지의 감소
⇒ 활성과 선택성이 높아짐

흡착의 정의

흡착 : 계면에서 특정 물질의 농도가 증가하는 현상



The surface of solid

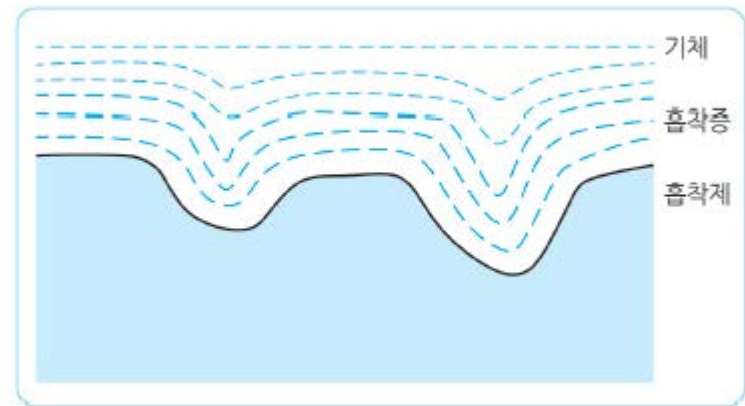


그림 2-1 고체 표면에서 흡착층의 단면도 점선의 굵기는 흡착한 물질의 농도를 나타낸다.

* 표면에서 농도가 증가하면 '흡착'이고, 감소하면 '탈착'임.

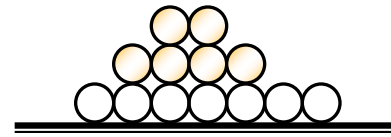
흡착과 흡수

흡착

— 계면에서 일어나는 현상



단분자층 흡착



다분자층 흡착

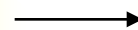
흡수

— 계 전체에서 균일하게 흡수되는 물질의 농도가 증가하거나
충격의 영향이 나타나는 현상

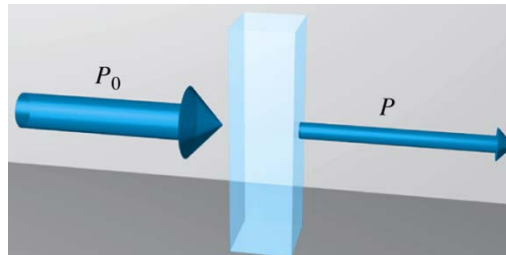
water

+

sponge



water in sponge

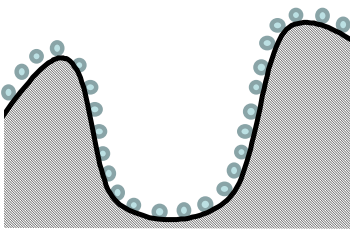


* 빛이 용액에 흡수되었음.

$$I_0 \rightarrow I$$

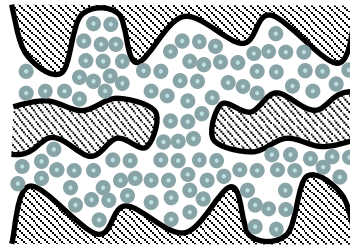
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흡착과 흡수의 분류



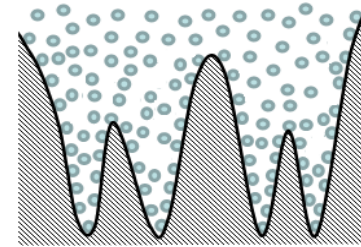
흡착

- * 고체의 표면과 내부가 명확하게 구분되고
표면에서 반응 농도가
증가함.



흡수

- * 흡수되는 물질의 농도가
균일하게 (거시적으로)
고체 내부에서 증가함.



수착(收着)

- * 세공이 너무 작거나
촘촘하여 구별하기
어려운 경우
흡수나 흡착 대신
수착이라는 용어를 씀.

주요 용어

◆ 흡착 (Adsorption)

- 고체·액체 표면에 특정 물질이 달라붙는 현상
- 흡착하는 물질의 끓는점보다 높거나 포화증기압보다 낮은 조건에서 두 상의 경계면에서 어떤 물질의 농도가 증가하는 현상

◆ 흡착제 (Adsorbent)

- 기체나 녹아 있는 물질들을 흡착하는 물질(고체, 액체)
- 예: 숯, 활성탄, 규조토, zeolite, silica, alumina, titania, bentonite, 녹말 등

◆ 흡착물(피흡착제) (Adsorbate)

- 흡착제에 달라붙은 물질

◆ 탈착 (Desorption)

- 흡착했던 물질이 표면원자로부터 떨어지는 현상
- 두 상의 경계면에 흡착된 어떤 물질의 농도가 감소하는 현상:
온도↑, 기체의 압력↓ ⇒ 탈착 ↑

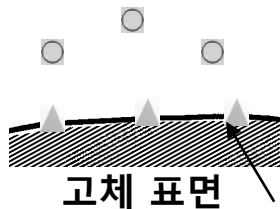
- ◆ 흡착과 탈착은 기체분자의 운동에너지와 흡착세기(기체분자와 표면원자 사이의 인력)의 상대적인 크기에 따라서 결정됨 (운동에너지 > 흡착세기 ⇒ 탈착)

흡착의 원동력

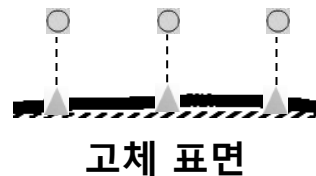
자발적으로 흡착되려면

◆ $\Delta G < 0$

흡착 전



흡착 상태



분자의 자유도가
줄어들면서 흡착됨.
 $\Rightarrow \Delta S < 0$

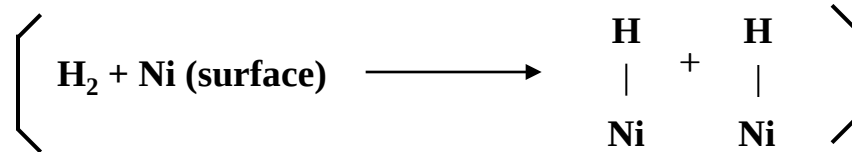
◆ $\Delta G = \Delta H - T\Delta S$

◆ 자발적인 흡착에서는 ΔG 가 음수이어야 하고, $-T\Delta S$ 는 양수이어야 하므로 ($\Delta S < 0$)
 ΔH 는 음수($\Delta H < 0$), - 발열흡착

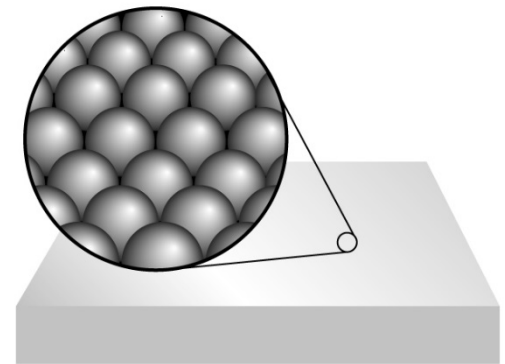
◆ 기체 분자가 흡착하면서 운동에너지가 흡착열로 방출됨.

특수한 흡착

분자가 나뉘어 흡착하면(해리흡착, 나뉘어 흡착)

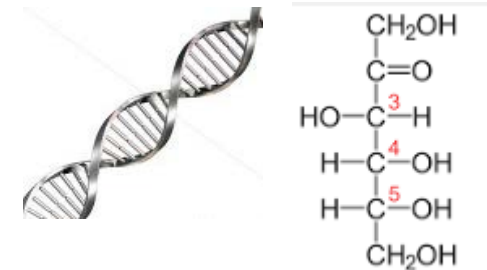


- ◆ 해리되면 $\Delta S > 0$ ($-T\Delta S < 0$) 일 수도 있어
특별한 조건에서는 흡열흡착 ($\Delta H > 0$) 도 가능함.



특수한 흡착물

- ◆ 단백질의 흡착 :
단백질의 구조가 달라짐(나선형, 무정형, 코일형 등).
- ◆ 큰 극성물질의 흡착 과정에서 물의 배제
물의 배제 과정에서 엔트로피 증가 ($\Delta S > 0$)



흡착과 탈착

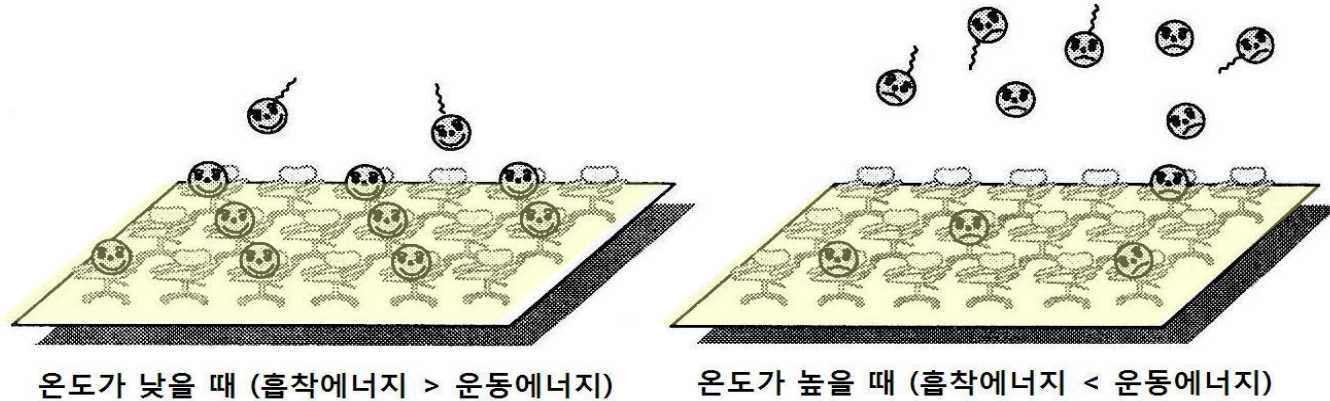


그림 2-2. 온도에 따른 흡착과 탈착.

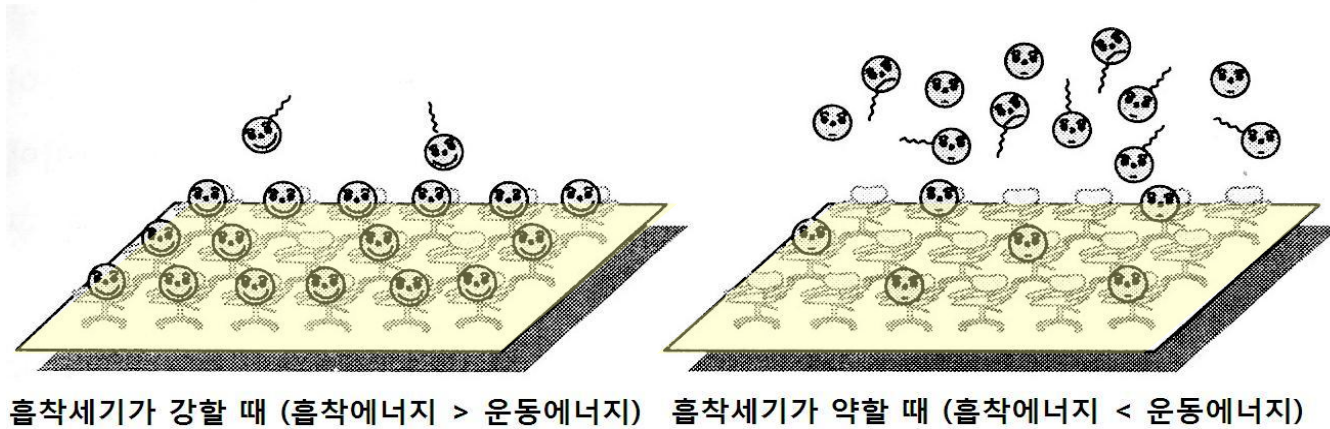


그림 2-3. 흡착세기에 따른 흡착과 탈착.

원동력에 따른 흡착의 분류

◆ 흡착 상태가 안정해지는 이유 (엔탈피 감소 원인)?

- 물리 흡착 (Physical adsorption) – 반데르 발스 힘 (물리적 상호작용:
쌍극자 – 쌍극자, 쌍극자 – 유도된 쌍극자, 분산력)
- 화학 흡착 (Chemical adsorption) – 화학결합의 생성

◆ 물리와 화학의 대상 – 물리 화학은?

흡착의 퍼텐셜 곡선

◆ 퍼텐셜의 개념 :

양이온과 음이온 사이 거리 변화에 따른 상호작용 차이로 설명.

◆ 물리 흡착

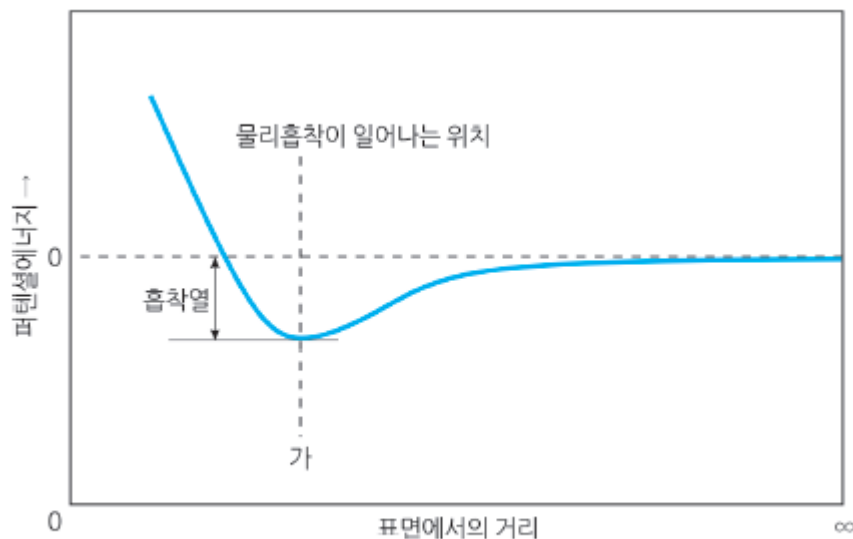


그림 2-2 물리흡착 과정에서 계의 퍼텐셜에너지 변화[1]

◆ 화학 흡착

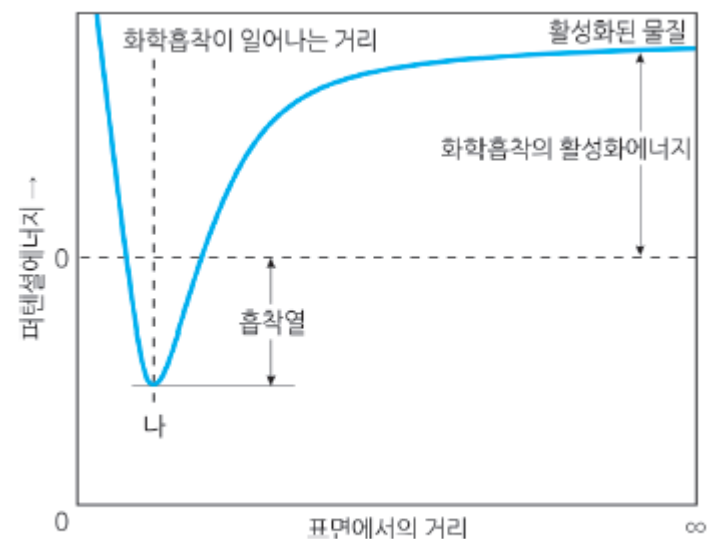


그림 2-3 화학흡착 과정에서 계의 퍼텐셜에너지 변화[2]

물리흡착과 화학흡착의 엔탈피

Table 23.1* Maximum observed enthalpies of physisorption

Adsorbate	$\Delta_{\text{ad}}H^\ominus/(\text{kJ mol}^{-1})$
CH ₄	-21
H ₂	-84
H ₂ O	-59
N ₂	-21

Table 23.2* Enthalpies of chemisorption, $\Delta_{\text{ad}}H^\ominus/(\text{kJ mol}^{-1})$

Adsorbate	Adsorbent (substrate)		
	Cr	Fe	Ni
C ₂ H ₄	-427	-285	-243
CO		-192	
H ₂	-188	-134	
NH ₃		-188	-155

◆ 화학흡착의 엔탈피는 일반적으로 물리흡착에 비해 **상당히 큼!**

흡착상태에 근거한 흡착 분류

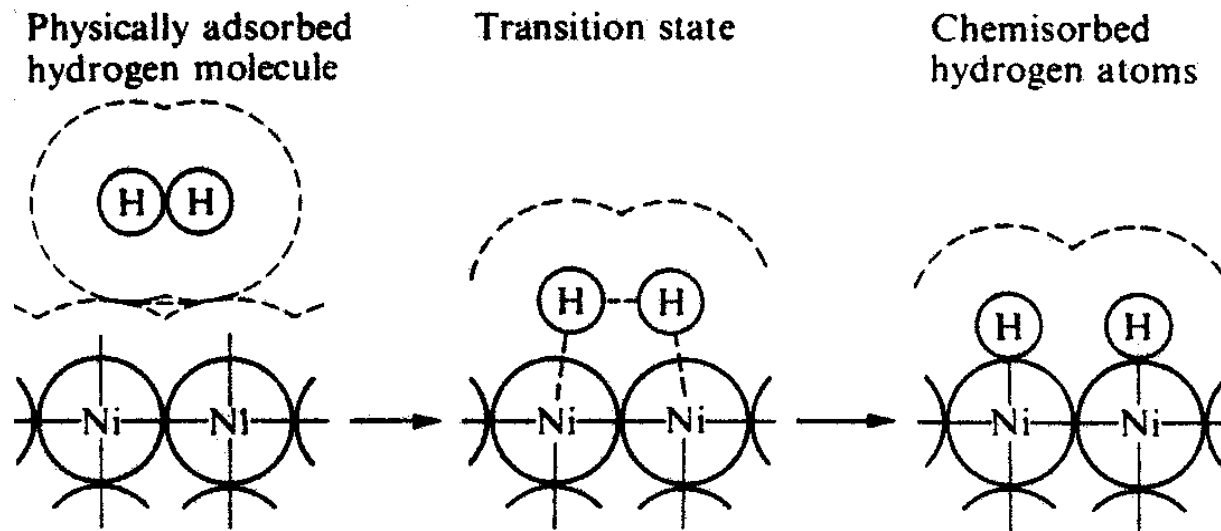
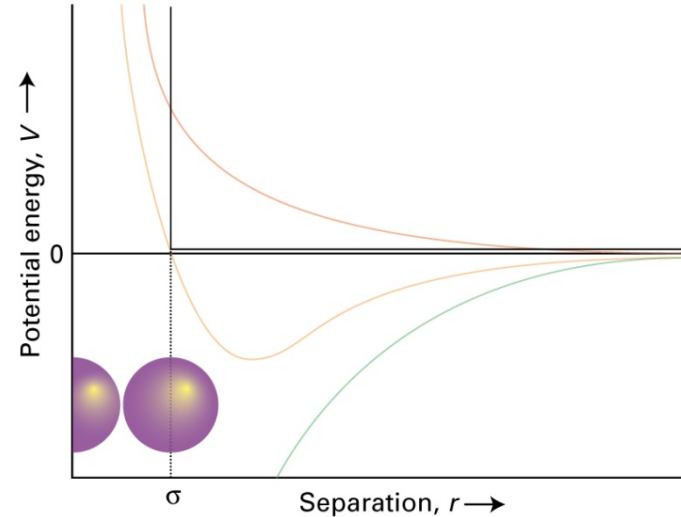
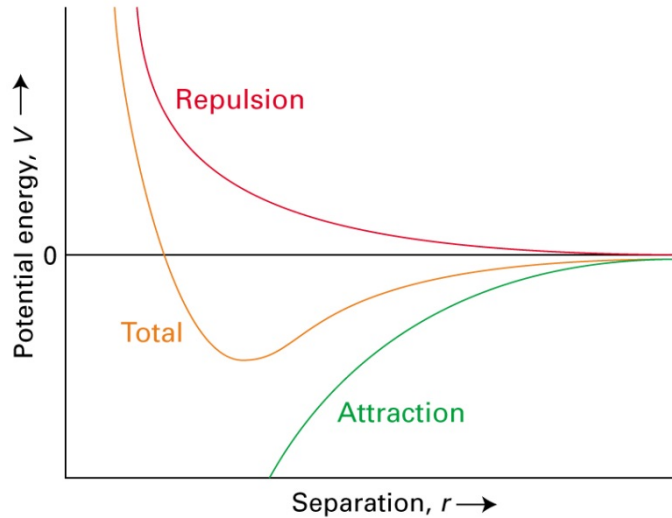


FIG. 3.3. Chemisorption of a hydrogen molecule on a nickel surface.

[G.C. Bond, "Heterogeneous Catalysis", 2nd Ed., Oxford Science Publications (1987) p28]

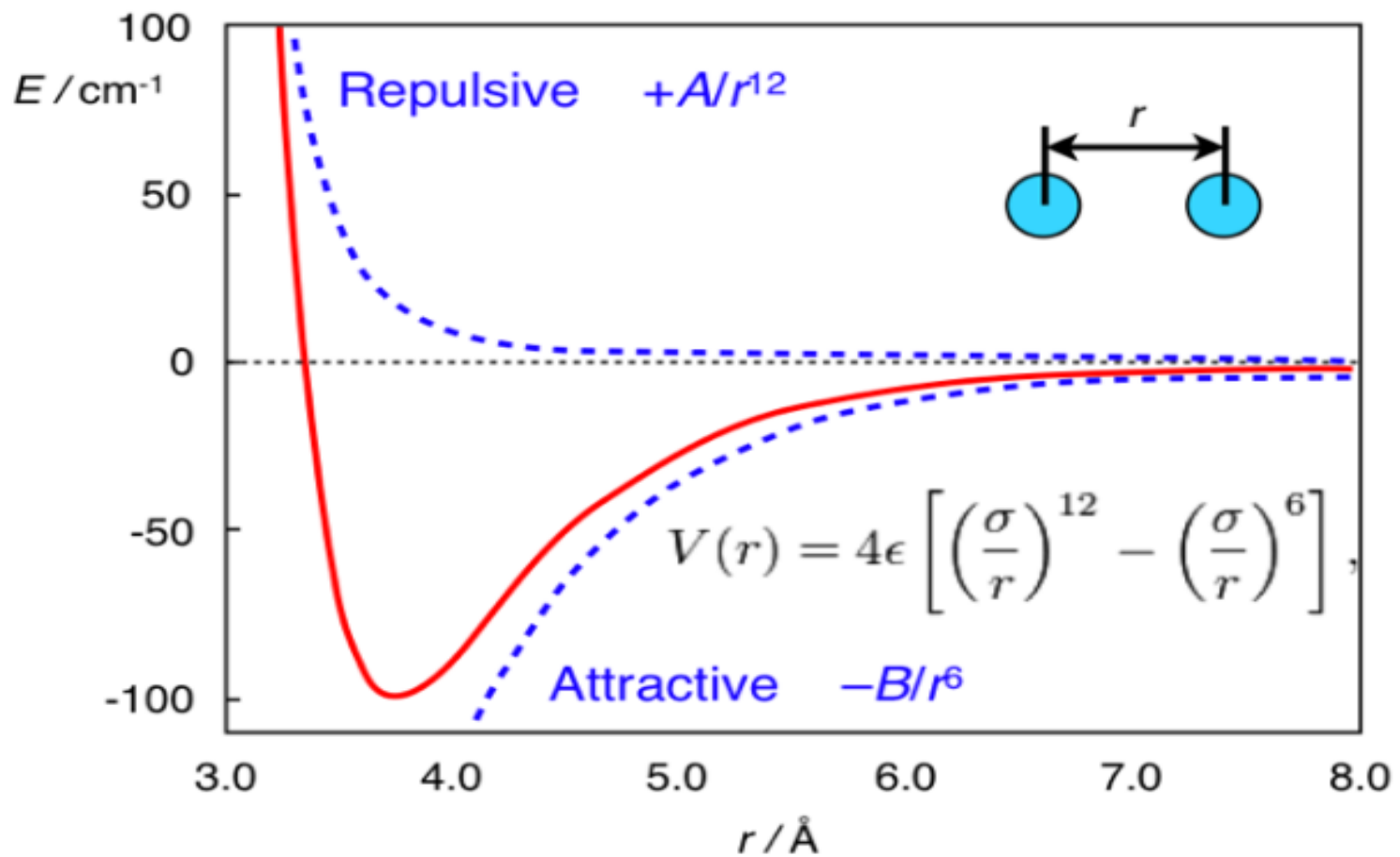
◆ 분자와 원자 궤도, 수소 원자간 거리, 표면과 수소 원자 사이 거리 - 구분 근거

퍼텐셜 에너지



[P. Atkins & J. de Paula, "Element of Physical Chemistry", Fifth Ed., Oxford University Press (2009)]

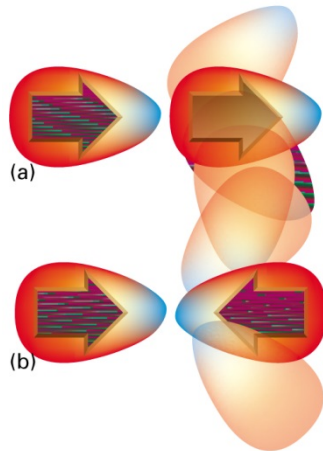
- ◆ 퍼텐셜은 거리의 함수
- ◆ 음과 양의 의미
- ◆ 전체 퍼텐셜이 실제 작용하는 값
- ◆ 예: Lennard-Jones potential, Morse potential, hard-sphere potential, Kihara potential, ...



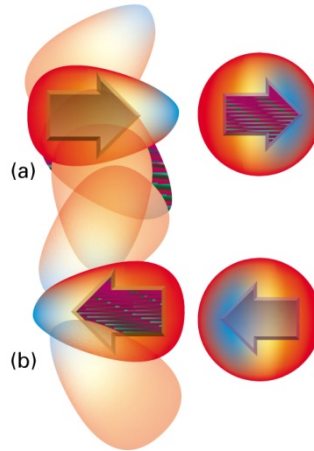
- ◆ 가장 널리 사용되는 퍼텐셜
- ◆ 실제 상황을 잘 근사할 수 있음.

물리적 인력

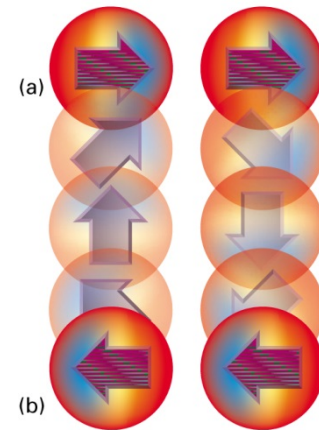
◆ 반데르 발스 힘



쌍극자 - 쌍극자
상호작용 :
강함.



쌍극자 - 유도된
쌍극자 상호작용



분산력 :
평균값이 0이 아님.
* 머무르는 시간 차이

퍼텐셜에 근거한 흡착 분류

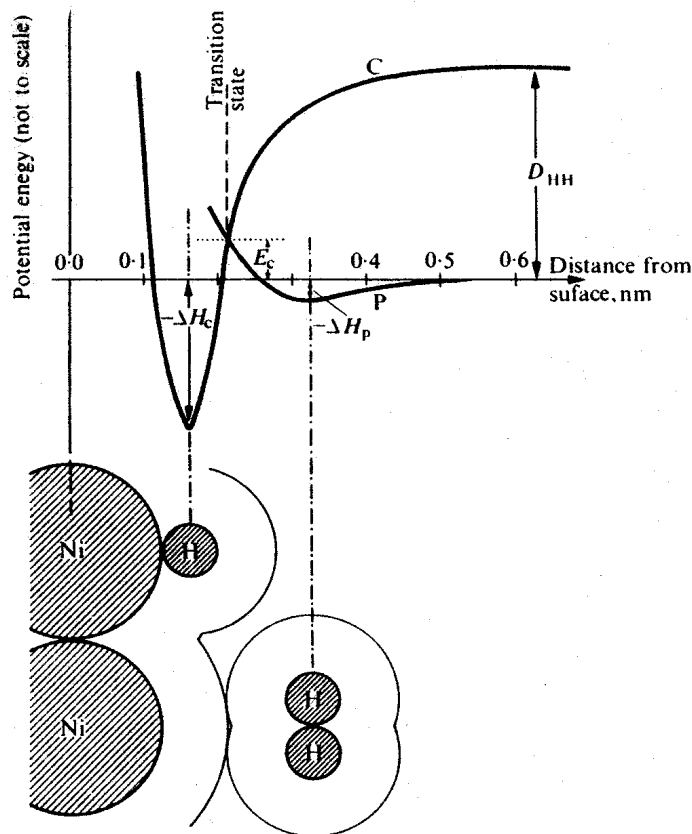


FIG. 3.2. Potential-energy curves for the adsorption of hydrogen on nickel, and pictorial representation of the adsorbed states.

거리	퍼텐셜 에너지
∞	0
r_p	$-\Delta H_p$
r_t	E_c
r_c	$-\Delta H_c$

$$r_{\text{Ni}} + r_{\text{H}} = 0.125 \text{ nm} + 0.035 \text{ nm} = 0.16 \text{ nm}$$

$$\begin{aligned}
 & r_{\text{Ni}} + r_{\text{Ni,vdW}} + r_{\text{H}} + r_{\text{H,vdW}} \\
 &= 0.125 \text{ nm} + 0.08 \text{ nm} + 0.035 \text{ nm} + 0.08 \text{ nm} \\
 &= 0.32 \text{ nm}
 \end{aligned}$$

[G.C. Bond, "Heterogeneous Catalysis", 2nd Ed., Oxford Science Publications (1987) p27]

- ◆ 활성화에너지, 흡착한 물질과 표면의 거리, 흡착한 물질의 전자 구름, 흡착열 - 물리흡착과 화학흡착에 따라 다름.

물리흡착과 화학흡착

◆ 이 기준은 절대적이 아님.

종류	세기	흡착열 ($\text{kJ}\cdot\text{mol}^{-1}$)	흡착량	속도	가역성	특수성
물리흡착 (physisorption)	약	< 20	다중 흡착도 가능함	빠름	있음	없음
화학흡착 (chemisorption)	강	> 80	단분자층 흡착만	느림 (빠를 수도 있음)	없음 (있을 수도)	있음

※ 물리흡착: 남자와 남자 또는 여자와 여자 사이 친구 되기

화학흡착: 남자와 여자의 결혼

주요 용어 II

◆ Surface coverage(표면덮임률, θ)

- 표면이 흡착하는 물질로 덮여 있는 정도를 나타내며, 흡착량을 단분자층 흡착량으로 나눈 값임.
- 흡착과 관련된 수식에서 흡착량을 나타내는 데 많이 사용함.
- 단분자층(monolayer) 흡착 상태: 모든 흡착점마다 한 분자씩 흡착한 상태를 일컬음.
- 다분자층(multilayer) 흡착 상태: 표면이 여러 층의 흡착한 분자로 덮여 있는 상태를 일컬음.

Monolayer $\theta = 1$; multilayer $\theta > 1$

◆ Associative adsorption

- 그대로흡착, 회합흡착
- 기체분자가 분자의 구조를 그대로 유지하면서 표면에 흡착함.
- 모든 경우에 흡착열이 발생함.

◆ Dissociative adsorption

- 나뉘어흡착, 해리흡착, 분리흡착
- 기체분자가 원자로 나누어져서(대칭적 또는 비대칭적) 표면에 흡착함.
- 엔트로피가 증가하여 흡열흡착도 가능함.

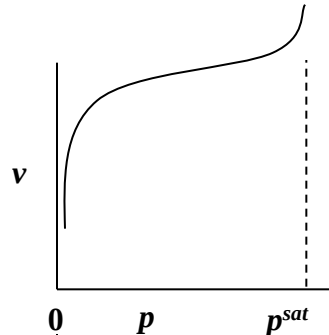
흡착의 정량적 표현 방법

◆ 흡착을 정량적으로 표현하려면 온도, 압력, 흡착량 세 변수가 필요함.

$$f(T, P, v) = 0$$

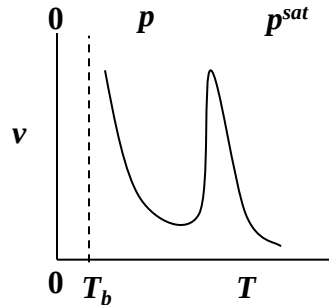
◆ 평면에 흡착 현상을 나타내려면 세 변수 중 하나를 고정해야 함.

- 흡착 등온선 (온도 고정) :
일정 온도에서 압력에 따른
흡착량의 변화



- 1) 흡착 현상의 개략적 묘사 용이
- 2) 일정 온도 압력에서
흡착량 계산 용이

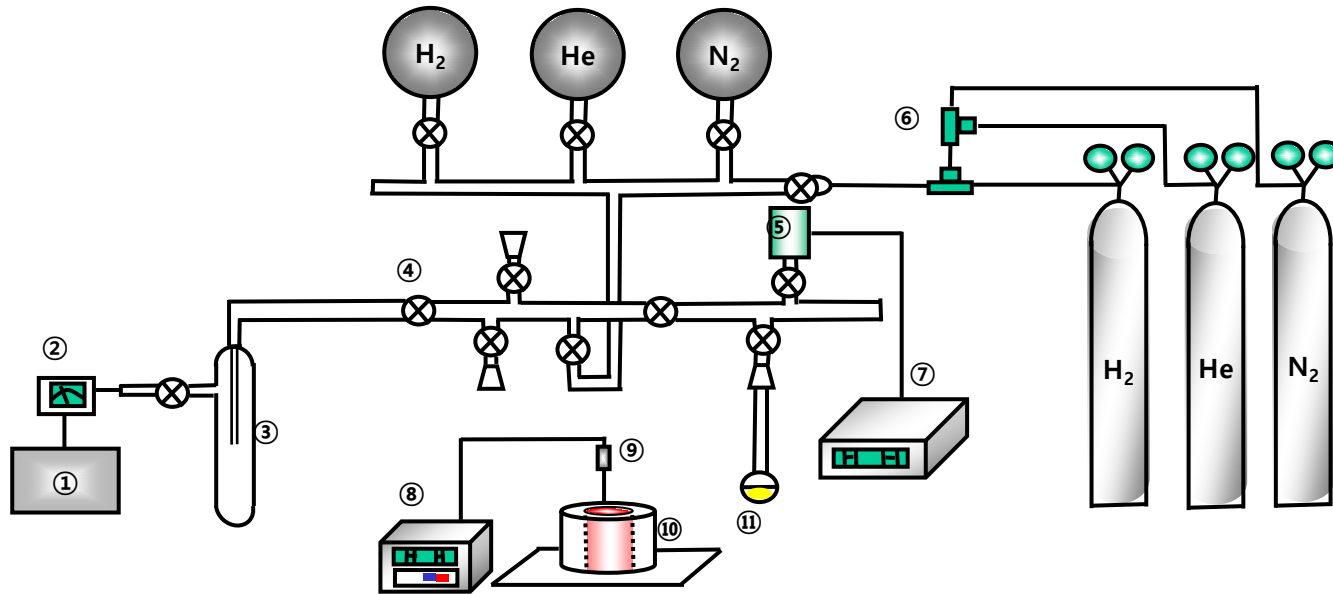
- 흡착 등압선 (압력 고정) :
일정 압력에서 온도에 따른
흡착량의 변화



에너지 측면에서 흡착 형태 판별 용이

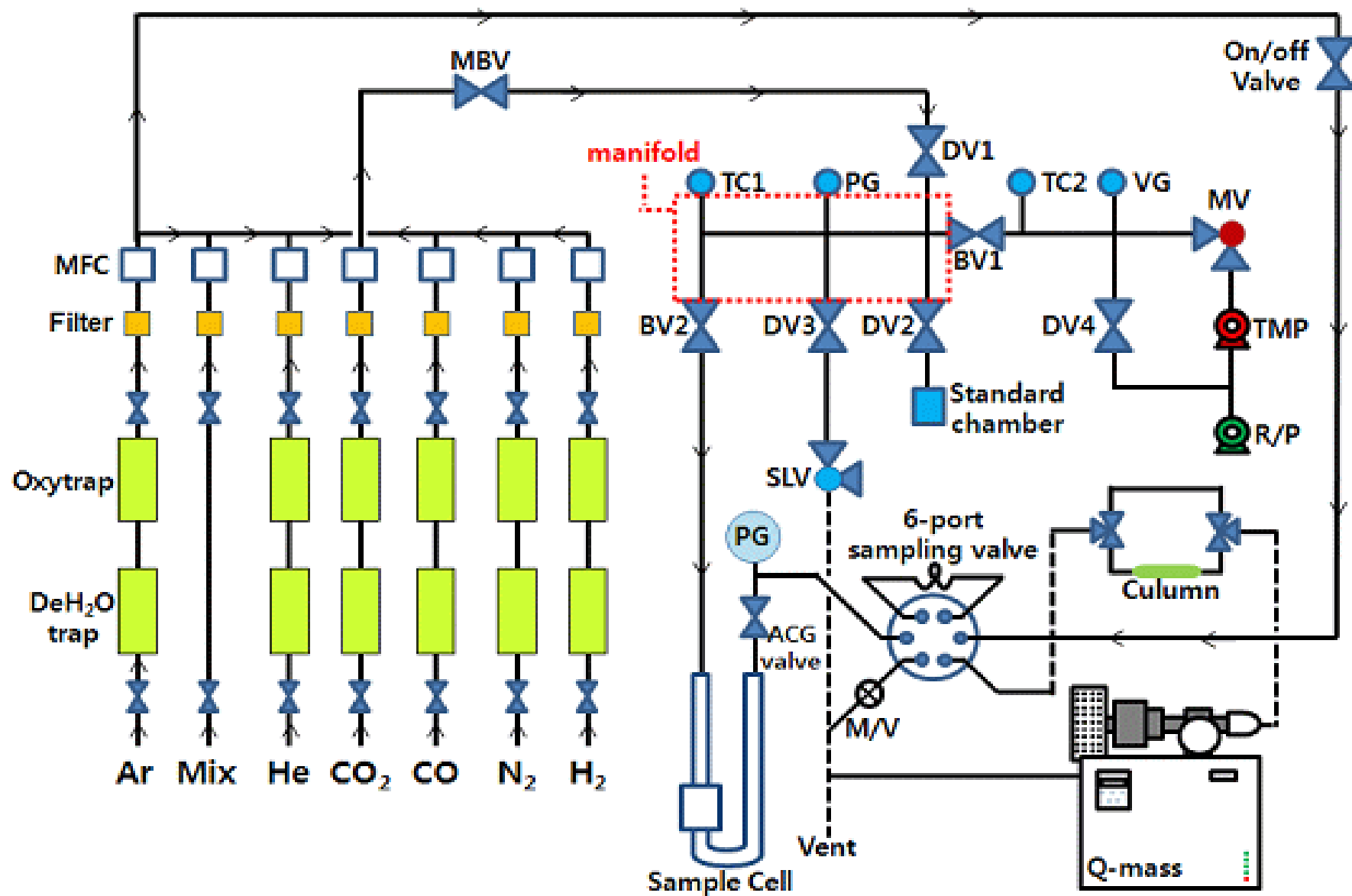
- 흡착 등량선

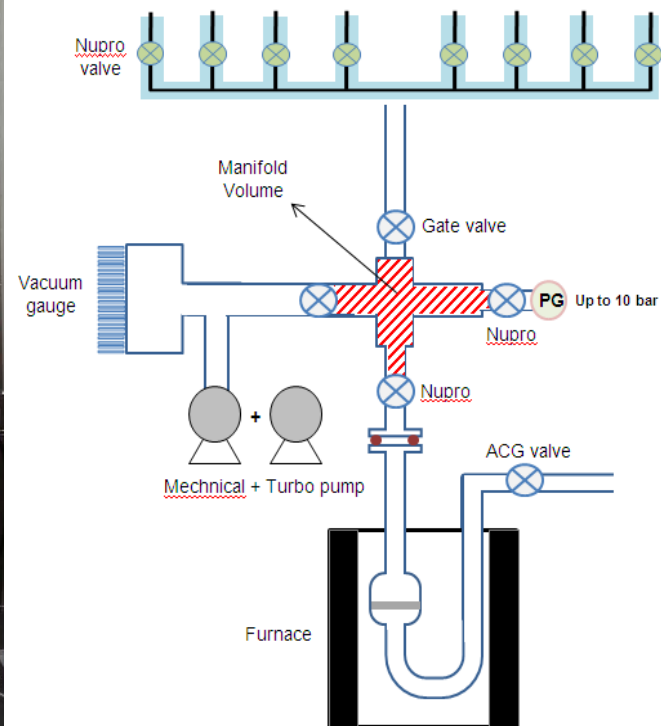
흡착량 측정 - 부피흡착법



- | | | | |
|------------------|-------------------|-----------------|------------------|
| ① Vacuum pump | ② Vacuum gauge | ③ Trap | ④ Valve |
| ⑤ Pressure gauge | ⑥ Three way valve | ⑦ DC volt meter | ⑧ PID controller |
| ⑨ Thermocouple | ⑩ Heater | ⑪ Sample tube | |

- ◆ 일정 온도에서 부피 변화로부터 고체시료에 따른 흡착량 결정
- ◆ 부피 흡착법은 흡착량 결정에 널리 사용되고 있음





Automated Adsorption System

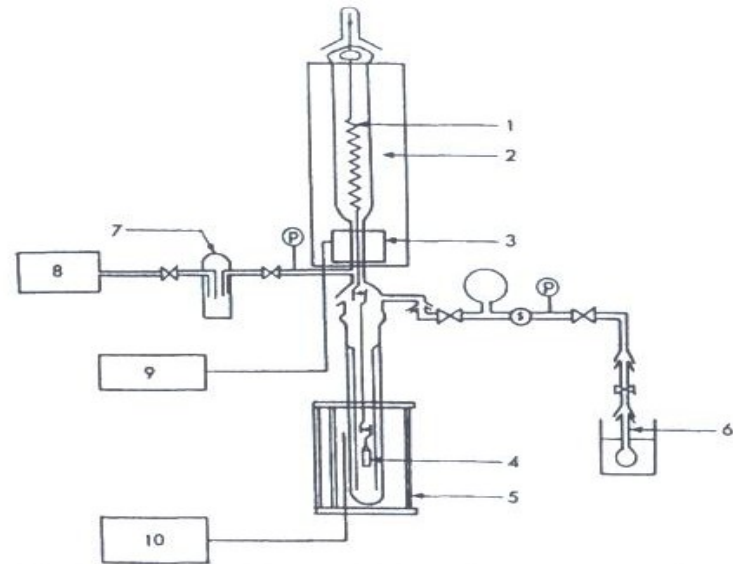


흡착량 측정 - 중량 흡착법



* 전자 마이크로 저울
(Cahn balance)

* 석영 스프링 저울

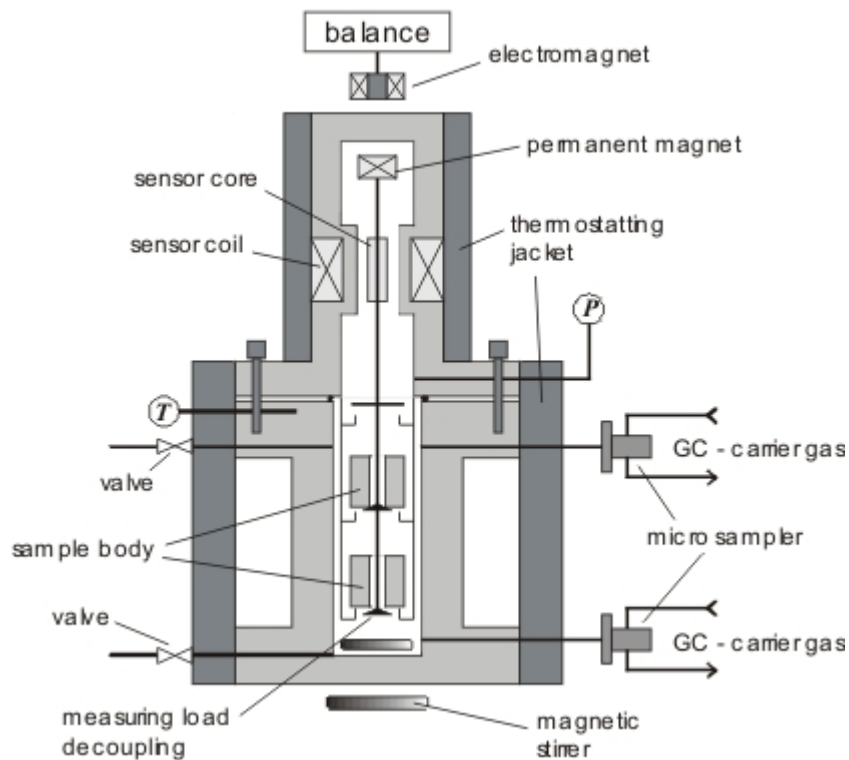


1. Quartz spring
2. Constant temperature chamber
3. Displacement meter
4. Sample
5. Heater or Liq. N₂ dewar

6. Solvent
7. Liq. N₂ trap
8. Vacuum system
9. Recorder
10. Temperature control unit

- ◆ 중량법으로는 유리나 구리스에 흡착하는 물질의 흡착량도 결정할 수 있음.
- ◆ 흡착과정(uptake curve)에서 흡착하는 물질의 확산 현상을 조사할 수 있음.
(예: HZSM-5 제올라이트에 *o*-자일렌을 흡착)

흡착량 측정 - 자석 저울



◆ 측정부와 시료가 완전히 분리되어 부식성 기체의 흡착량도 측정할 수 있음.

◆ 가장 최신 장치?

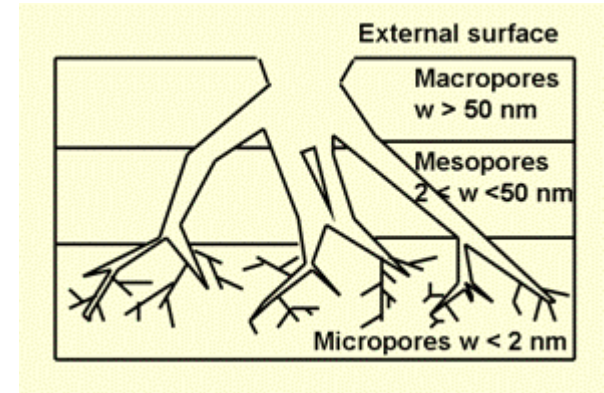
세공의 분류

◆ IUPAC 기준

미세세공: $< 2 \text{ nm}$

중간 또는 메조세공: $2 \text{ nm} < \text{mesopore} < 50 \text{ nm}$

큰 세공: $> 50 \text{ nm}$



◆ 질소 흡착에 대한 해석 방법에 기반 (?)

◆ 다중 세공 물질 (Hierarchical material):

물질전달의 제한을 줄이는 효과적인 세공 구조

- 접촉 분해반응, 특히 RFCC 반응에 효과적
- 피셔-트롭슈 합성반응

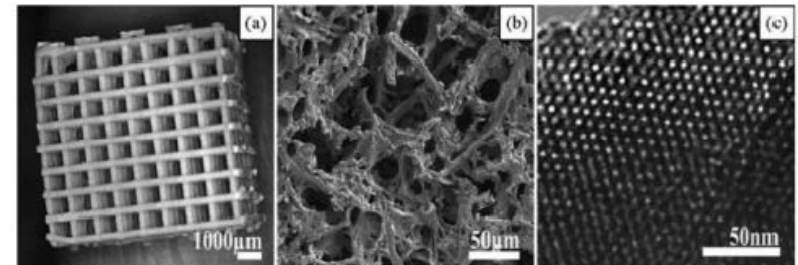
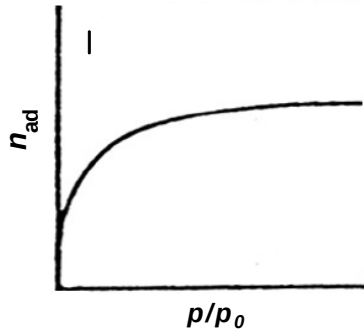


Fig. 4 (a) SEM of hierarchically giant, visible macropores on glass scaffold; (b) SEM of smaller macropores; (c) TEM of mesopores. Reprinted from ref. 66, with permission from Elsevier.

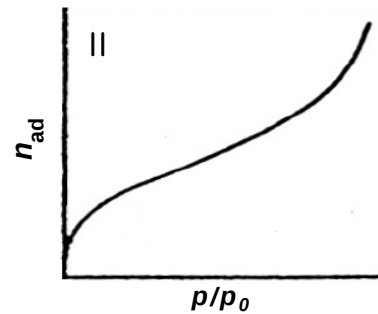
[C.M.R. Parlett, K. Wilson, and A.F. Lee, Chem. Soc. Rev., 42 (2013) 3876-3893.]

흡착 등온선 - I

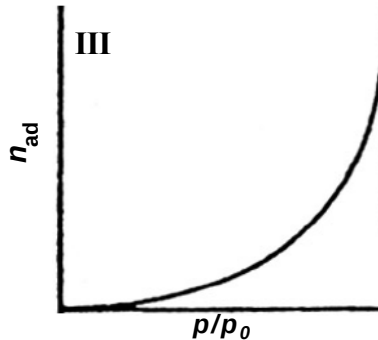
◆ 물리흡착



I 형: 외표면이 적고 미세세공이 발달한 고체
- 제올라이트, 활성탄



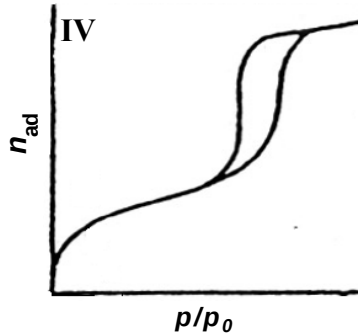
II형: 세공이 없거나 큰 세공만 있는 고체
- 세공의 제한이 없음
- 단분자층 흡착에서
다분자층 흡착으로 전이



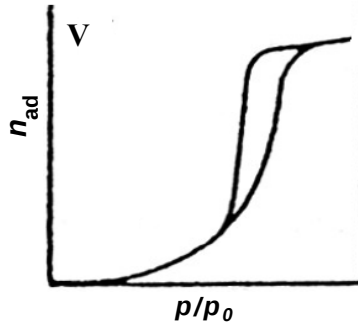
III형: 흡착물과 흡착제의 상호작용이 중요한 흡착제
(카본 블랙에 대한 물의 흡착)

흡착 등온선 - II

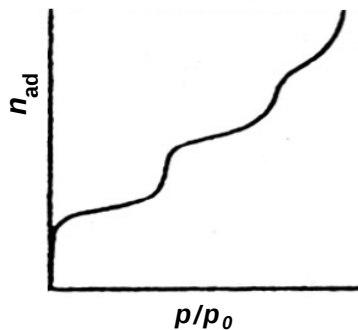
◆ 히스테리시스 - 흡착과 탈착 등온선의 불일치



IV형: 중간세공에서 모세관 응축이 히스테리시스
고리로 나타남
- 중간세공 물질



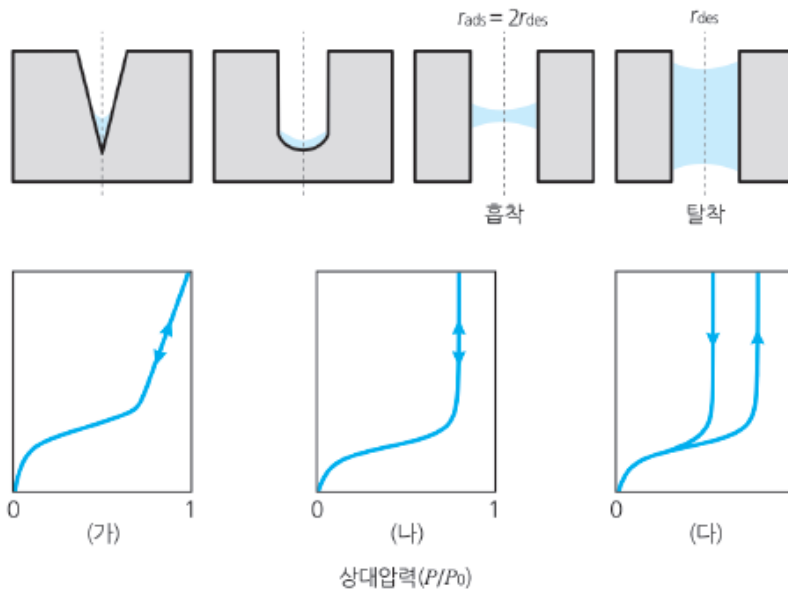
V형: 혼하지 않음
- 흡착물과 흡착제의 상호작용이 약한 계에서 나타남.



VI형: 계단형 다층 흡착
- 흑연과 카본블랙에 대한 액체질소 온도에서
알곤이나 크립톤의 흡착

히스테리시스 현상

- ◆ 흡착은 열역학적 현상 – 흡착과 탈착 등온선이 일치해야 함.
- ◆ 그러나 세공이 있으면 흡착과 탈착 등온선이 일치하지 않을 수 있음.
- ◆ 히스테리시스가 나타나는 압력과 모양 – 세공 모양과 크기에 의해 결정됨.



* 켈빈 식

$$\ln \frac{P_s}{P_0} = - \frac{2\gamma V_m}{r_s R T}$$

(Cohan equation)

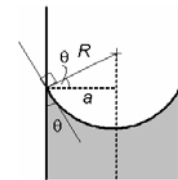
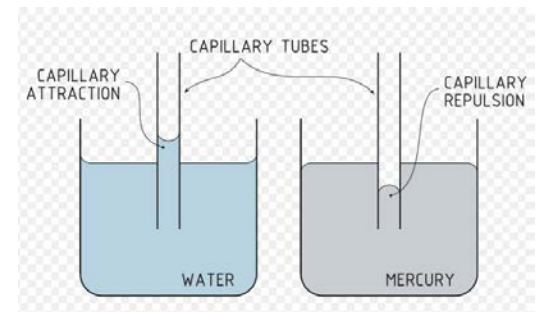
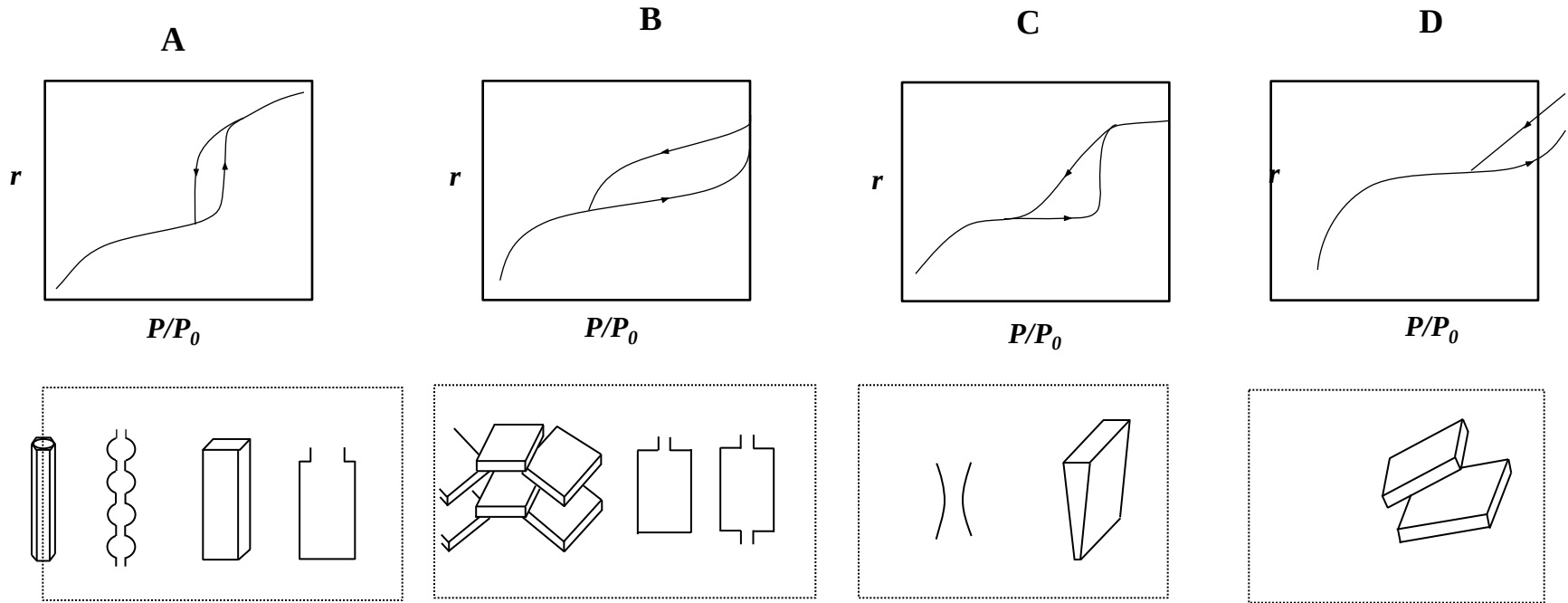


그림 2-8 흡착제의 세공구조와 흡착·탈착 과정의 흡착등온선 r_{ads} : 양끝이 열린 세공에서 흡착할 때 형성되는 원통형 메니스커스의 반지름. r_{des} : 탈착 과정에서 형성되는 구형 메니스커스의 반지름.

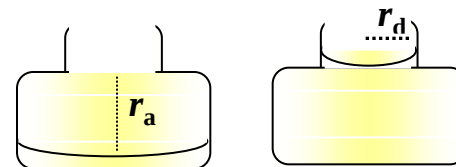
히스테리시스와 세공구조 - I



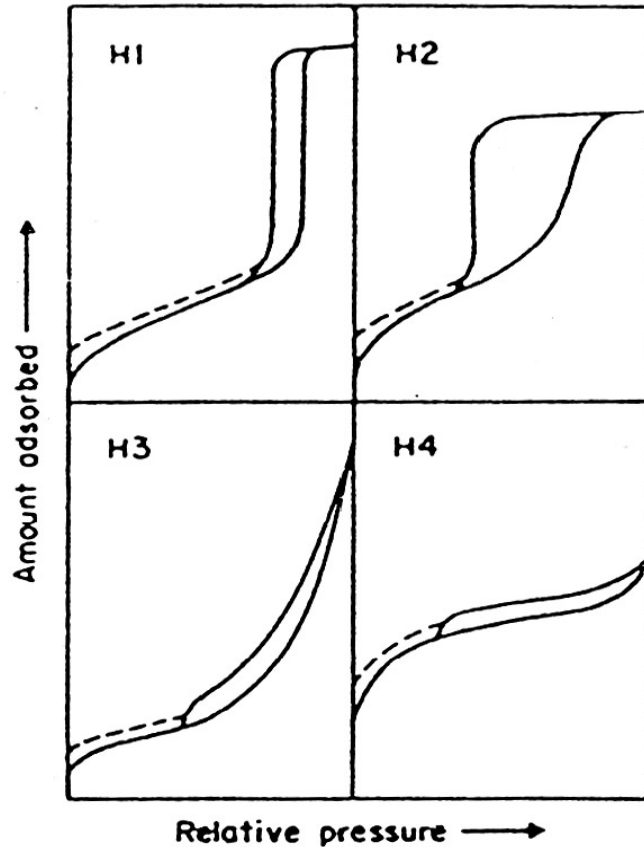
[J.M. Thomas and W.J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis", Academic Press, London (1967)]

◆ 흡착과 탈착 과정에서 세공의 크기가 달라짐

※ 잉크병 이론



히스테리시스와 세공구조 - II



H1: 실린더형 세공

H2: 실린더형 또는 구형 세공

H3: 불규칙적인 층 사이 세공과
틈새(slit이나 wedge) 형태 세공

H4: 미세와 중간세공이 같이 있는 경우

Adsorption Isotherms

1. One-Parameter Model

☐ Henry's Isotherm $q_e = K_{HE} C_e$

2. Two-Parameter Models

- ☐ Hill-Deboer Model
- ☐ Fowler-Guggenheim Model

☐ Langmuir Isotherm

$\rightarrow \log q_e = \log K_F + \frac{1}{n} \log C_e$

☐ Freundlich Isotherm

☐ Dubinin-Radushkevich Isotherm

☐ Temkin Isotherm

$\rightarrow q_e = \frac{Rt}{b} \ln K_T + \frac{RT}{b} \ln C_e$

- ☐ Flory-Huggins isotherm
- ☐ Hill isotherm
- ☐ Halsey Isotherm
- ☐ Harkin-Jura Isotherm
- ☐ Jovanovic Isotherm
- ☐ Elovich Isotherm
- ☐ Kiselev Isotherm

(Continued)

3. Three-Parameter Models

☐ Redlich-Peterson Isotherm

☐ Sips isotherm

$$\rightarrow q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$$

☐ Toth isotherm

$$\rightarrow \frac{q_e}{q_m} = \theta = \frac{K_e C_e}{[1 + (K_L C_e)^n]^{1/n}}$$

☐ Koble-Carrigan isotherm

☐ Kahn isotherm

☐ Radke-Prausnitz isotherm

☐ Langmuir-Freundlich isotherm

☐ Jossens isotherm

4. Four-Parameter Models

☐ Fritz-Schlunder Isotherm

☐ Baudu Isotherm

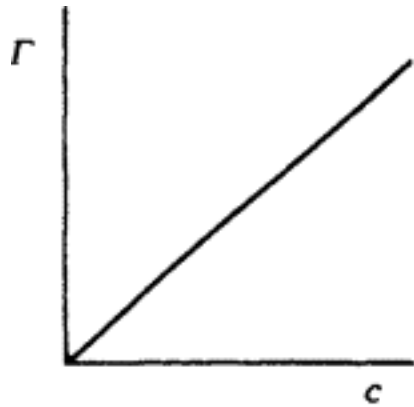
☐ Weber-Van Vliet Isotherm

☐ Marczewski-Jaroniec Isotherm

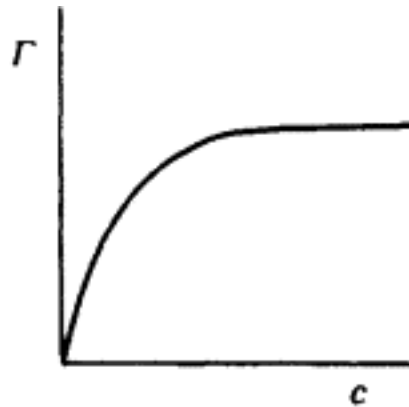
5. Five-Parameter Model

☐ Fritz-Schlunder Isotherm

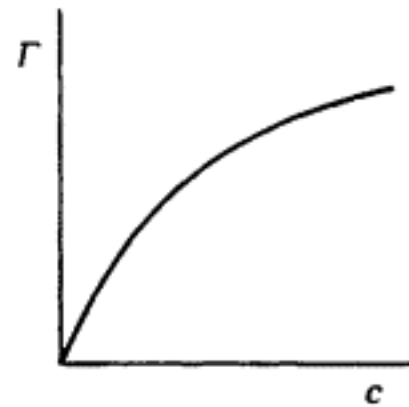
Isotherm Types



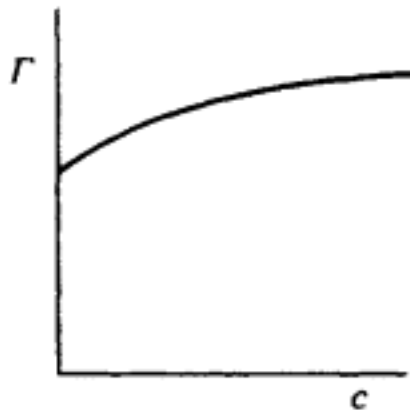
Linear



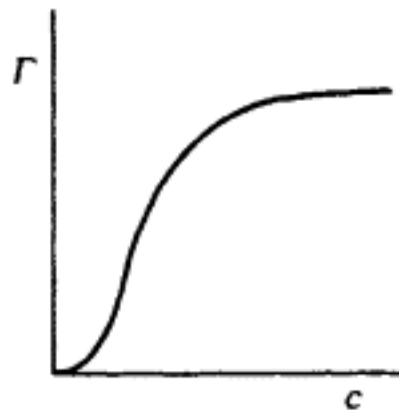
L-Langmuir



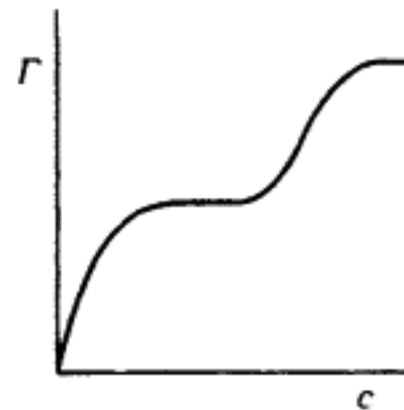
F-Freundlich



H-High Affinity



S-Sigmoid



Step Isotherm

Adsorption Theory by Langmuir (1916)

-1st quantitative theory-

I. Langmuir, "The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids", J. Am. Chem. Soc. 38 (1916) 2221.

CONSTITUTION OF SOLIDS AND LIQUIDS.

2221

Bismuth.—Oeschner de Coninck and Gérard,¹ by reduction of bismuth chloride to metal, found Bi = 208.50.

Molybdenum.—Müller,² by oxidation of the metal, found Mo = 96.035.

Neodymium.—Baxter, Whitcomb, Stewart, and Chapin,³ by analyses of the chloride, find Nd = 144.27.

Columbium.—Smith and Van Haagen,⁴ from the ratio between sodium columbate (NaCbO₃) and sodium chloride, find Cb = 93.13. The value 93.1 might be adopted in the table.

Argon.—Schultze⁵ has redetermined the density of argon. The corresponding atomic weight is A = 39.945.

Signed, F. W. CLARKE,
T. E. THORPE,
G. URBAIN.

NOTE.—Because of the European war the Committee has had much difficulty in the way of correspondence. The German member, Professor Ostwald, has not been heard from in connection with this report. Possibly the censorship of letters, either in Germany or *en route*, has led to a miscarriage.

F. W. CLARKE, *Chairman*.

[CONTRIBUTION FROM RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY, SCHENECTADY, N. Y.]

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.

PART I. SOLIDS.

By IRVING LANGMUIR.

Received September 5, 1916.

The importance of the work of W. H. Bragg and W. L. Bragg in its bearing on chemistry has not, as yet, been generally recognized. In hearing two of W. H. Bragg's lectures in this country a few years ago, the writer was impressed with the very great significance of this work in the field of chemistry. The structure of crystals as found by the Braggs leads to new and more definite conceptions as to the nature of chemical forces.

The writer has constantly endeavored to apply this new conception in his work on heterogeneous reactions and particularly in connection with a study of the phenomena of adsorption and surface tension. In this way he has gradually been led to form more or less definite theories of the mechanism of evaporation, condensation, liquefaction, adsorption, and capillary phenomena. According to this theory, both solids and liquids

¹ *Compt. rend.*, 162, 252 (1916).

² *THIS JOURNAL*, 37, 2046 (1915).

³ *Ibid.*, 38, 302 (1916).

⁴ *Ibid.*, 38, 1783 (1916).

⁵ *Ann. Physik*, [iv] 48, 269 (1915).

(Continued)

layer will be negligible.¹ When a gas molecule strikes a portion of the surface already covered, it thus evaporates so quickly that in effect it is equivalent to a reflection. Therefore, the rate of condensation of the gas on the crystal surface is $\alpha\theta\mu$ where θ represents the fraction of the surface which is bare. Similarly the rate of evaporation of the molecules from the surface is equal to $\nu_1\theta_1$ where ν_1 is the rate at which the gas would evaporate if the surface were completely covered and θ_1 is the fraction actually covered by the adsorbed molecules. When a gas is in equilibrium with a solid surface these two rates must be equal so we have

$$\alpha\theta\mu = \nu_1\theta_1. \quad (14)$$

Furthermore

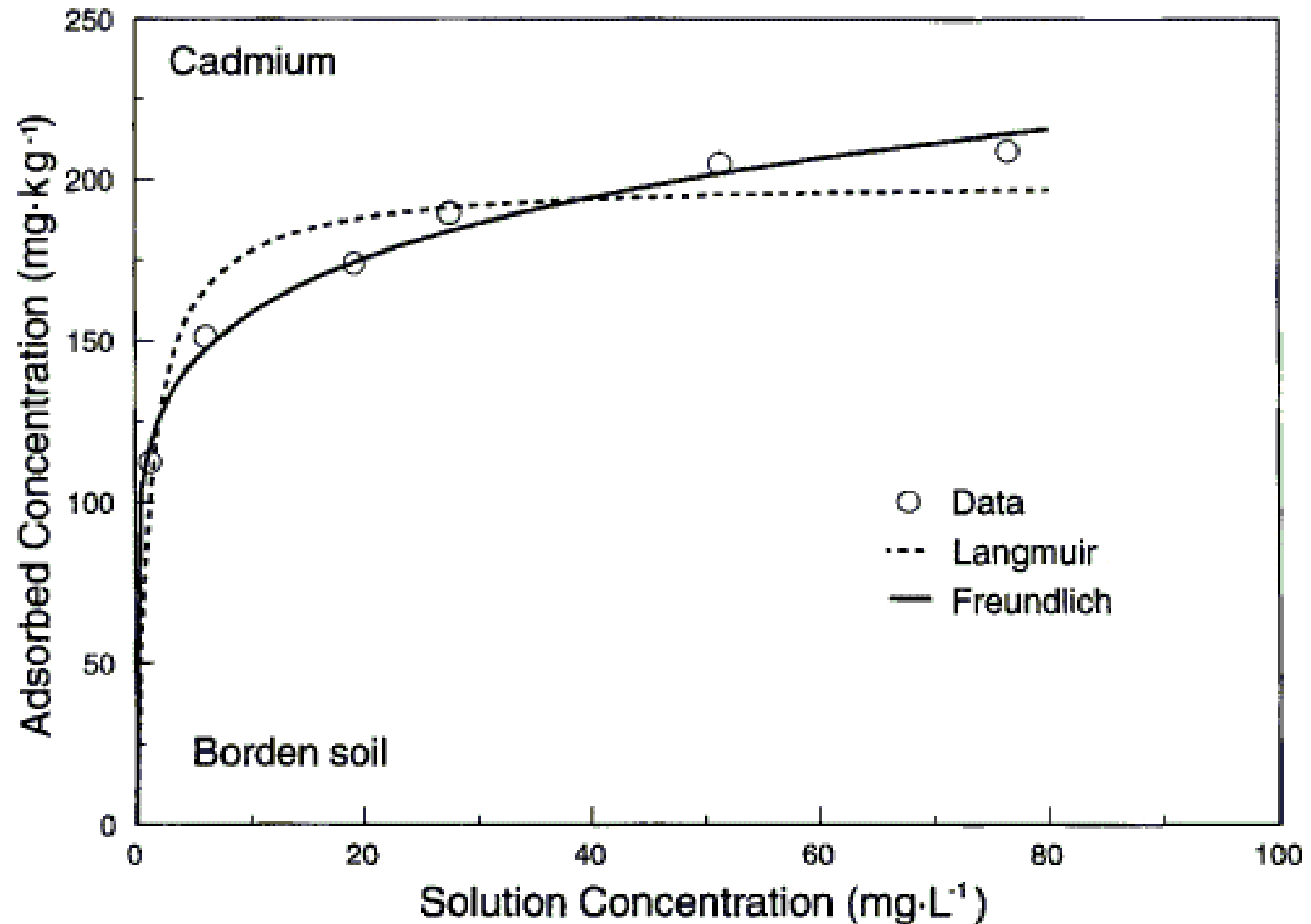
$$\theta + \theta_1 = 1. \quad (15)$$

Whence

$$\theta_1 = \frac{\alpha\mu}{\nu_1 + \alpha\mu}. \quad (16)$$

The quantity θ_1 is a measure of the amount of gas adsorbed. It should be noted that for low gas pressures the amount of adsorbed gas is proportional to the pressure, but as the pressure increases θ_1 increases more slowly and finally the surface becomes saturated ($\theta_1 = 1$). These relations are in good qualitative agreement with known facts.²

What is the correct model?



Langmuir 흡착 등온선

◆ 예:

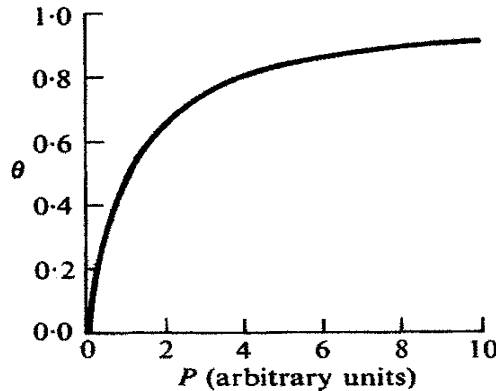


FIG. 2.3. The Langmuir adsorption isotherm.

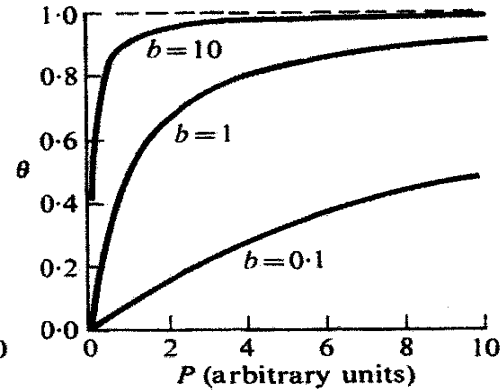


FIG. 2.4. Langmuir adsorption isotherms with various values of b .

[G.C.Bond, "Heterogeneous Catalysis", 2nd Ed., Oxford Science Publications (1987)]

◆ 가정: - 모든 흡착점은 **균일**

- 흡착한 분자는 흡착점에 **고정**

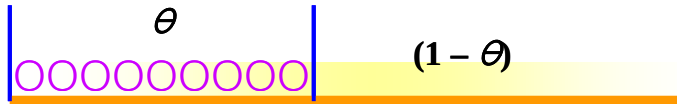
- **단분자층** 흡착

- **인접 분자간**(latenal) **상호작용이 없음**.

- 기체는 **이상기체**로 가정함.

Langmuir 흡착 등온선의 이해

모형



V : adsorbed volume

V_m : monolayer volume

$$\theta = \frac{V}{V_m} \quad : \text{surface coverage}$$

단성분계에서 흡착등온선 유도

$$r_a = k(1 - \theta)P$$

$$r_d = k'\theta$$

평형에서

$$r_a = r_d \quad k(1 - \theta)P = k'\theta$$

b : adsorption parameter

$$\theta = \frac{\frac{k}{k'}P}{1 + \frac{k}{k'}P} = \frac{bP}{1 + bP}$$

충돌 빈도를 고려하면 :

$$\frac{1}{b} = \frac{v}{S'} (2\pi mkT)^{1/2} \exp\left(\frac{\Delta H}{RT}\right)$$

저압 $\theta = bP$

고압 $\theta = 1.0$

Langmuir 흡착 등온선의 활용

◆ 이성분계에 적용

$$\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B}$$

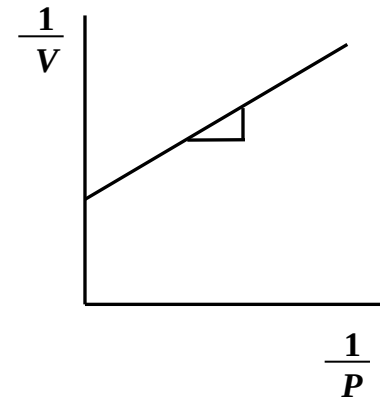
◆ 해리흡착에 적용

$$\theta = \frac{(bP)^{1/2}}{1 + (bP)^{1/2}}$$

◆ 흡착 매개변수의 결정 - 선형화

$$\frac{V}{V_m} = \frac{bp}{1 + bp} \Rightarrow \frac{1}{V} = \frac{1}{V_m bp} + \frac{1}{V_m}$$

$$[\text{or } \frac{p}{V} = \frac{p}{V_m} + \frac{1}{V_m b}]$$



$$\text{slope: } \frac{1}{V_m b}$$

$$\text{intercept: } \frac{1}{V_m}$$

활용

: 화학흡착에 적절

물리흡착은 흡착량이 적을 때에만 적용 가능
촉매반응의 속도식 유도에 적절함.

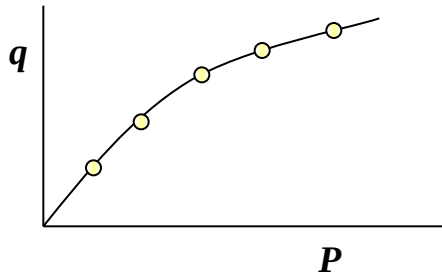
Freundlich 흡착 등온선

◆ 등온선: $\theta = kP^{1/n}$, $q = mP^{1/n}$

q : 흡착량

◆ Shape:

m, n : 흡착 매개 변수



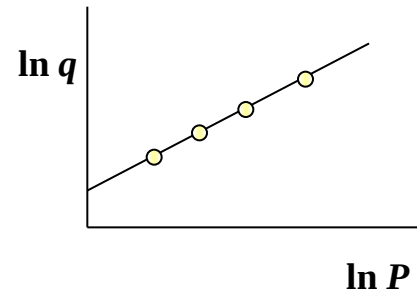
※ 압력이 높아져도 θ 가 1에 도달하지 않음.

– Langmuir 흡착 등온선과 다른 점임.

※ m 은 흡착량 증가와, n 은 흡착세기와 관련됨.

◆ 흡착 매개변수의 결정:

$$\ln q = \ln m + 1/n \ln P$$



◆ 활용: 흡착열이 불균일한 고체에 대한 흡착

– 실제 상황에 근사

◆ 흡착열의 불균일성: 극장 좌석의 실제 가치(관람표) – 명목 요금, 선택 가능한 상황에서 가격
균일 또는 불균일?

Brunauer–Emmett–Teller (BET) Theory

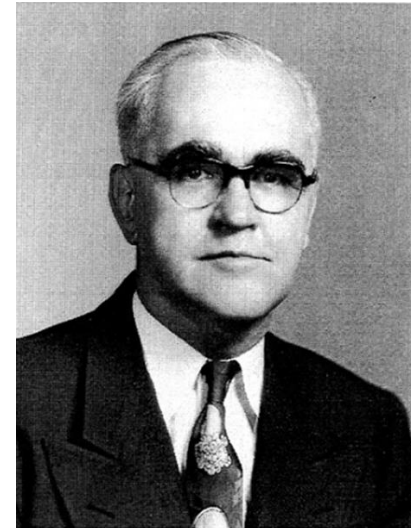
Stephen Brunauer (1903–1986)

- born in Budapest, Hungary
- worked at the chemistry department at Clarkson University (1965)



Paul Hugh Emmett (1900–1985)

- born in Portland, Oregon
- received PhD at Caltech
- close friend of Linus Pauling
- worked at the Chemical Engineering Department at The Johns Hopkins University (1937)



Edward Teller (1908–2003)

- born in Hungary
- the Jahn Teller effect
- the precursor of density functional theory
- “the father of the hydrogen bomb”



(Continued)

Stephen Brunauer, P.H. Emmett, Edward Teller, Adsorption of Gases in Multimolecular Layers, *J. Am. Chem. Soc.* 60 (1938) 309-319.

Feb., 1938

ADSORPTION OF GASES IN MULTIMOLECULAR LAYERS

309

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS AND GEORGE WASHINGTON UNIVERSITY]

Adsorption of Gases in Multimolecular Layers

By STEPHEN BRUNAUER, P. H. EMMETT AND EDWARD TELLER

Introduction

The adsorption isotherms of gases at temperatures not far removed from their condensation points show two regions for most adsorbents: at low pressures the isotherms are concave, at higher pressures convex toward the pressure axis. The higher pressure convex portion has been variously interpreted. By some it has been attributed to condensation in the capillaries of the adsorbent on the assumption that in capillaries of molecular dimensions condensation can occur at pressures far below the vapor pressure of the liquid. By others such isotherms are believed to indicate the formation of multimolecular adsorbed layers. DeBoer and Zwicker¹ explained the adsorption of non-polar molecules on ionic adsorbents by assuming that the uppermost layer of the adsorbent induces dipoles in the first layer of adsorbed molecules, which in turn induce dipoles in the next layer and so on until several layers are built up. The isotherm equation which they, and later Bradley,² derived on the basis of this polarization theory is practically the only quantitative expression that has been so far proposed to account for multimolecular adsorption. However, as we shall show in the first part of this paper, the polarization of the second layer of adsorbed gas by the first layer is already much too small to constitute the major portion of the binding energy between the two adsorbed layers, at least in those instances in which the gas molecules do not possess considerable permanent dipole moments.

It seems to us that the same forces that produce condensation are chiefly responsible for the binding energy of multimolecular adsorption. On this assumption, in the second part of this paper we shall carry out a derivation of the isotherm equation for multimolecular adsorption by a method that is a generalization of Langmuir's treatment of the unimolecular layer. In the third part of the paper we shall then apply the isotherm equation to a variety of experimental isotherms obtained by others and by us on a number of catalysts, catalyst supports and other adsorbents.

I. The Polarization Theory of DeBoer and Zwicker

According to DeBoer and Zwicker, the induced dipole in the i th layer polarizes the $i + 1$ st layer, thus giving rise to induced dipole moments and binding energies that decrease exponentially with the number of layers. If we call the dipole moment of a molecule in the i -th layer μ_i , it follows that

$$\mu_i = c_i C^i \quad (1)$$

where c_i and C are appropriate constants, C actually being equal³ to μ_i/μ_{i-1} . The corresponding binding energy is proportional to the square of the dipole moment

$$\phi_i = c_i C^{2i} \quad (2)$$

where c_2 is another constant. The equilibrium pressure of the n th layer (top layer), p_n , according to Boltzmann's law varies exponentially with the binding energy of that layer and, if the only binding energy were that due to polarization, would be given by the equation

$$p_n = c_2 e^{-\phi_n/RT} \quad (3)$$

It follows, therefore, that

$$\ln \frac{p_n}{c_2} = -\frac{\phi_n}{RT} C^{2n} \quad (4)$$

which is identical with DeBoer and Zwicker's equation

$$\ln \frac{p_n}{K_2 p_0} = K_2 K_1^n \quad (4a)$$

if c_2 be replaced by $K_2 p_0$, $-c_2/RT$ by K_2 , and C^2 by K_1 .

One can substitute $n = v/v_m$, where v is the volume of gas adsorbed at pressure p_n , and v_m is the volume adsorbed in one complete unimolecular layer. DeBoer and Zwicker,¹ and subsequently

(3) According to DeBoer and Zwicker the μ_i values for all layers, except the first and the top layer, satisfy the equations

$$\mu_i = k(\mu_{i-1} + \mu_{i+1}) \quad (1a)$$

Equation (1) is a solution of (1a) if

$$C = \frac{1 - \sqrt{1 - 4k^2}}{2k} \quad (1b)$$

DeBoer and Zwicker give the approximate expression

$$C = k/(1 - k^2) \quad (1c)$$

which for $k \ll 1$ is a good approximation for (1b). It should be noted, however, that when $k \ll 1$ only a few layers are usually adsorbed and, since equation (1a) is not valid for the top layer, in this case all of the equations are to be considered approximate. Bradley, using equation (1c), derived the values of 0.6075 and 0.615 for k for copper sulfate and aluminum sulfate, respectively, even though the upper limit of k according to (1b) is 0.5.

Substituting into (26) we obtain the isotherm equation

$$v = \frac{v_m c p}{(p_0 - p) \{1 + (c - 1)(p/p_0)\}} \quad (28)$$

The following considerations show that equa-

For the purpose of testing, equation (28) can be put in the form

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_0} \quad (A)$$

Equation (A) is in a convenient form, since a plot of $p/v(p_0 - p)$ against p/p_0 should give a straight line, whose intercept is $1/v_m c$ and whose slope is $(c - 1)/v_m c$. Thus from the slope and intercept the two constants v_m and c can be evaluated, the former being the volume of gas required to form a complete unimolecular adsorbed layer, the latter, as we shall see later, being

(1) DeBoer and Zwicker, *Z. physik. Chem.*, **B8**, 407 (1929).

(2) Bradley, *J. Chem. Soc.*, 1467 (1936).

(Continued)

$$\frac{1}{v[(p_0/p) - 1]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0} \right) + \frac{1}{v_m c}$$

v = adsorbed gas quantity

p_0 = saturation pressure of adsorbate

p = equilibrium pressure of adsorbate

c = BET constant = $\exp \left(\frac{E_1 - E_L}{RT} \right)$

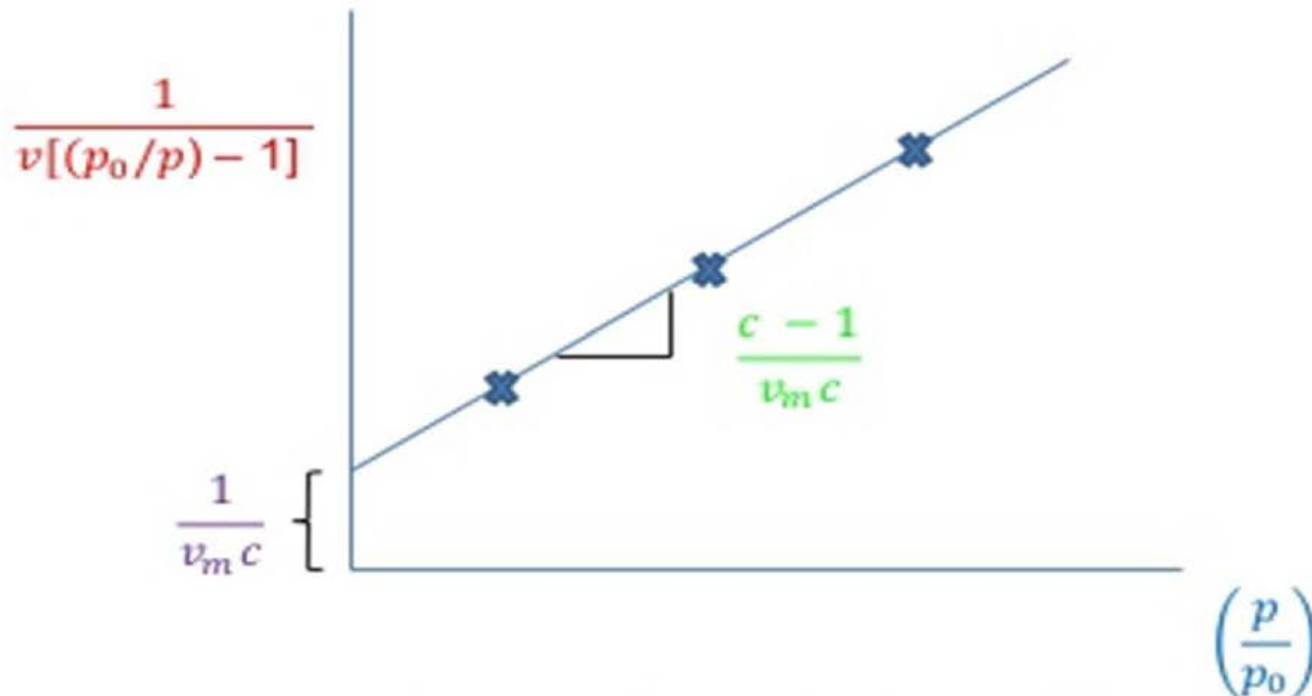
E_1 = heat of adsorption for the first layer

E_L = heat of vaporization

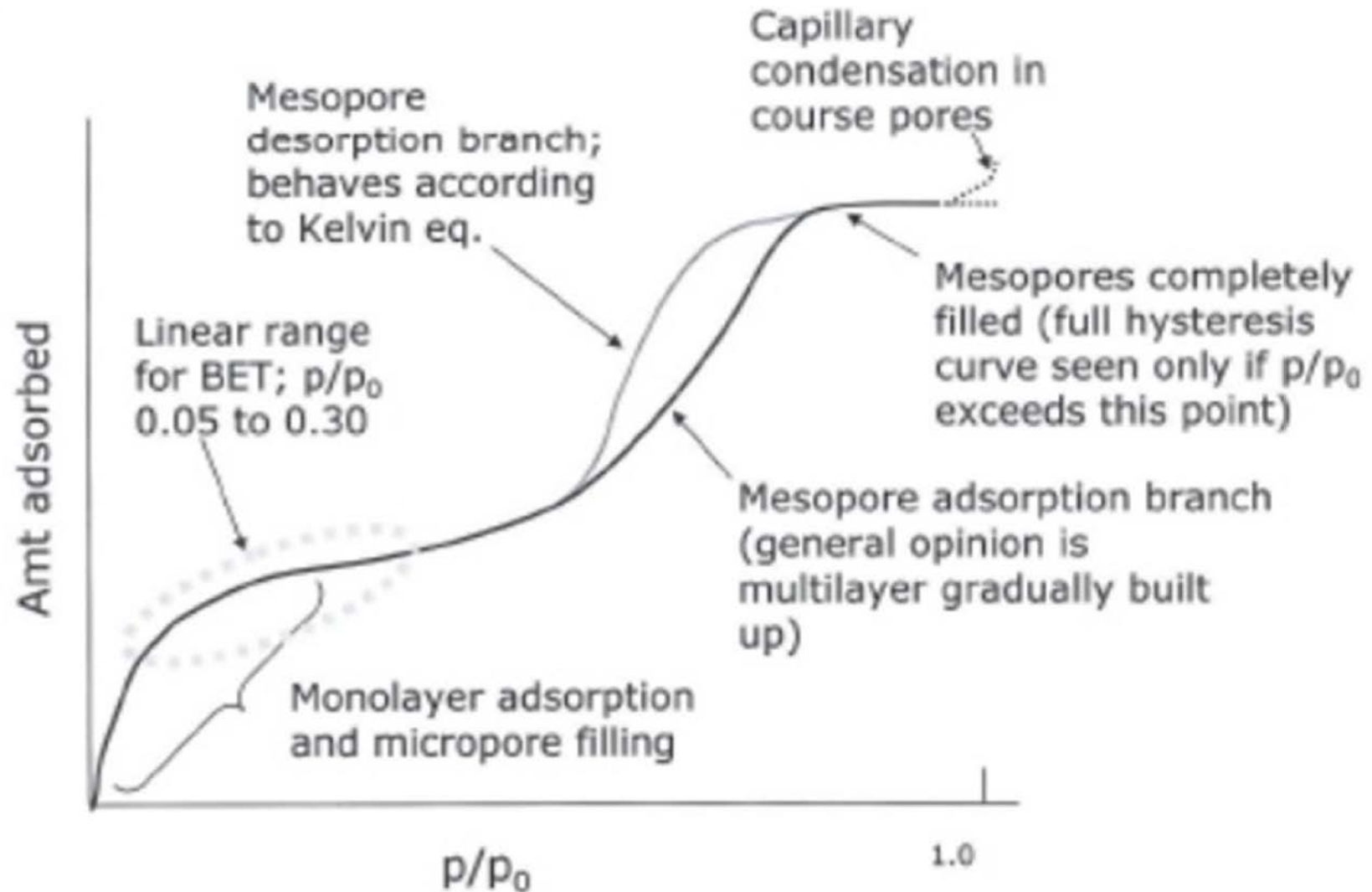
(Continued)

$$\frac{1}{v[(p_0/p) - 1]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0} \right) + \frac{1}{v_m c}$$

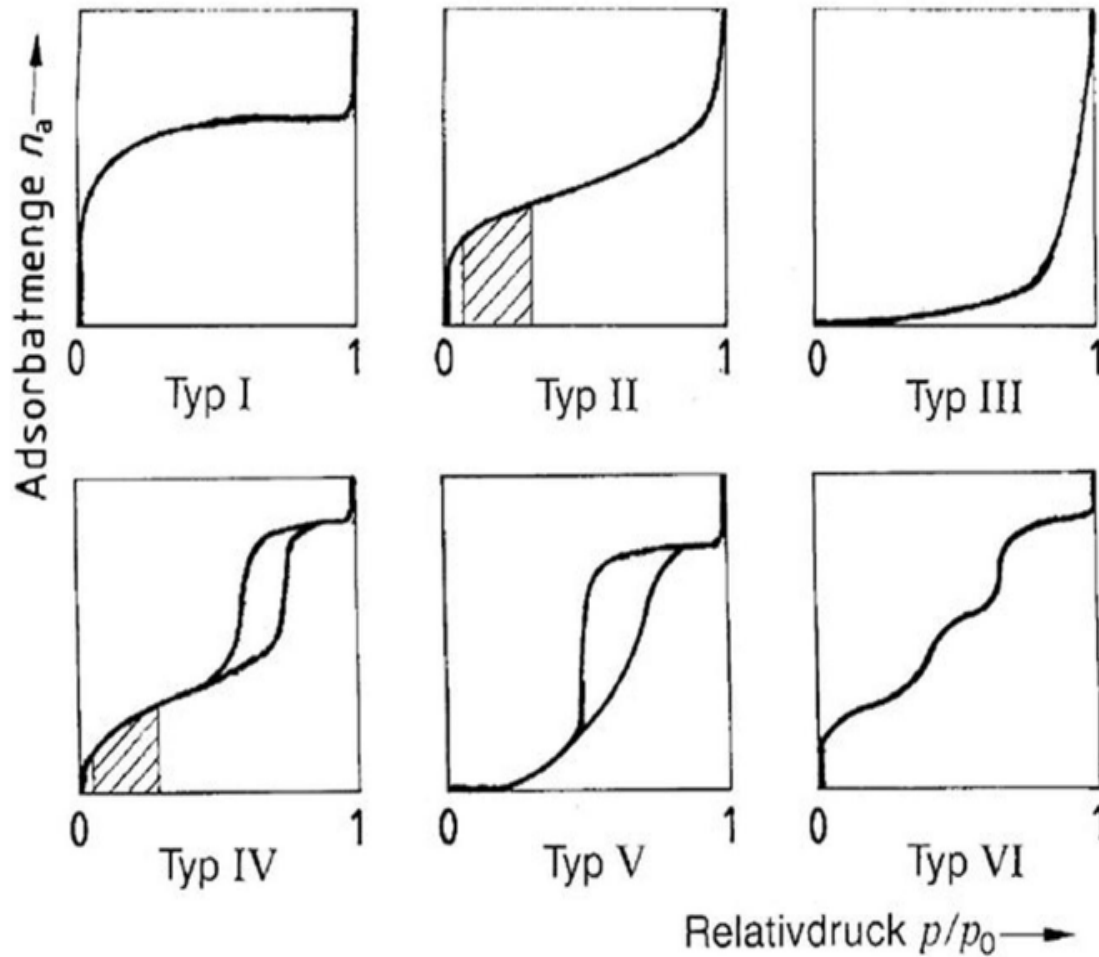
$$y = mx + b$$



BET Isotherm Interpretation



(Continued)



How to do?

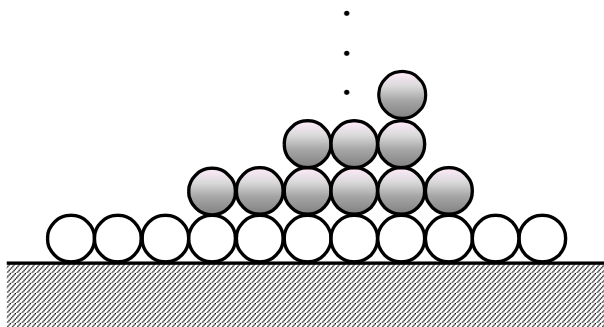
Fit with the BET equation in
the range of
 $p/p_0 = 0.05 \dots 0.3$

Sometimes even at lower
upper limit

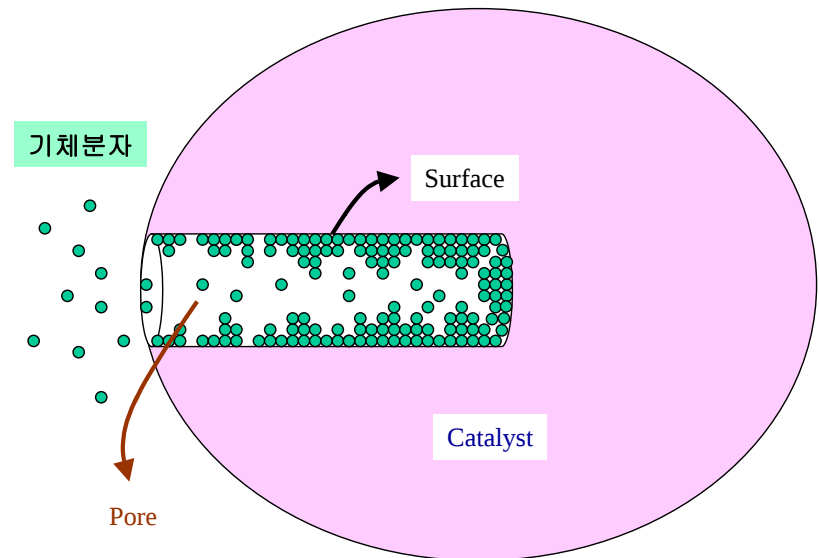
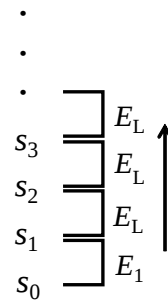
Theoretical Derivation

◆ 가정:

- 1) 흡착한 분자 위에 다시 흡착할 수 있음. – 다분자층 흡착
- 2) 제1층 흡착열은 E_{ads} 이나 제2층부터 흡착열은 액화열(ΔH_{liq})과 같음.



다분자층 흡착 모형



$$a_1 P s_0 = b_1 s_1 \exp(-E_1/RT)$$

$$a_2 P s_1 = b_2 s_2 \exp(-E_L/RT)$$

$$\vdots$$

$$a_i P s_{i-1} = b_i s_i \exp(-E_L/RT)$$

$$x = (a_2/b_2) P \exp(E_L/RT)$$

$$s_1 = y s_0$$

$$s_2 = x s_1$$

$$s_3 = x s_2$$

$$s_i = x s_{i-1}$$

$$s_i = x s_{i-1} = x^2 s_{i-2} = x^{i-1} s_1 = y x^{i-1} s_0 = c x^i s_0$$

$$A = \sum_{i=0}^{\infty} s_i \quad v = v_0 \sum_{i=0}^{\infty} i s_i \quad \longrightarrow \quad \theta = \frac{v}{A v_0} = \frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i} = \frac{c s_0 \sum_{i=0}^{\infty} i x^i}{s_0 \{1 + c \sum_{i=0}^{\infty} x^i\}}$$

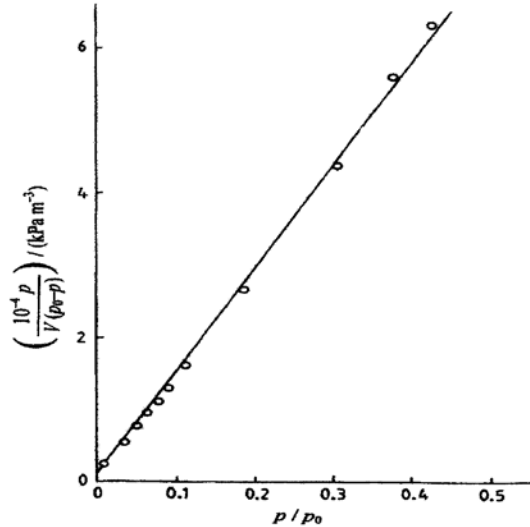
※ Equation:
$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{c - 1}{V_m c} \frac{P}{P_0}$$

V_m : 단분자층 흡착량 (monolayer volume)

P_0 : 포화 증기압 (saturation pressure)

c : 흡착 매개변수 (adsorption parameter)

BET equation의 활용



◆ 표면적 계산: 기울기(α)와 절편(β) 이용

$$(\alpha + \beta)^{-1} = V_m$$

Figure 4.4 Linearized BET plot to determine surface area.

◆ 표면적 결정

$$S_s = \frac{V_m (\text{cm}^3 \text{g}^{-1})}{22,400 (\text{cm}^3 \text{mol}^{-1})} \times N_A (6.023 \times 10^{23} \text{mol}^{-1}) \times \sigma_{\text{N}_2} (0.162 \times 10^{-18} \text{m}^2) = 4.36 \times V_m (\text{m}^2/\text{g})$$

◆ BET 방법

- 표준 방법 – 대표적이고 편리한 방법
- BET 표면적의 의미 – 세공 발달 정도

V : 몰부피 (molar volume)

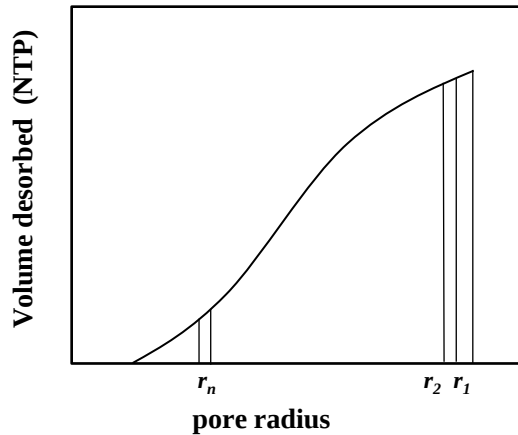
S_s : 비표면적 (specific surface area)

N_A : 아보가드로 수 (Avogadro number)

σ : 단분자 점유면적

세공크기 분포 결정

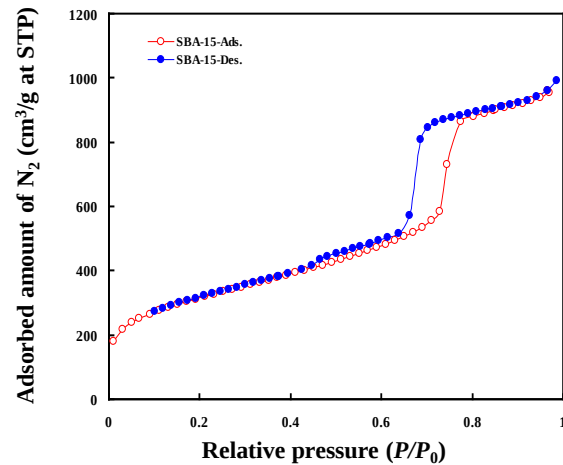
◆ $P/P_0 \rightarrow$ Kelvin 식 - 세공크기



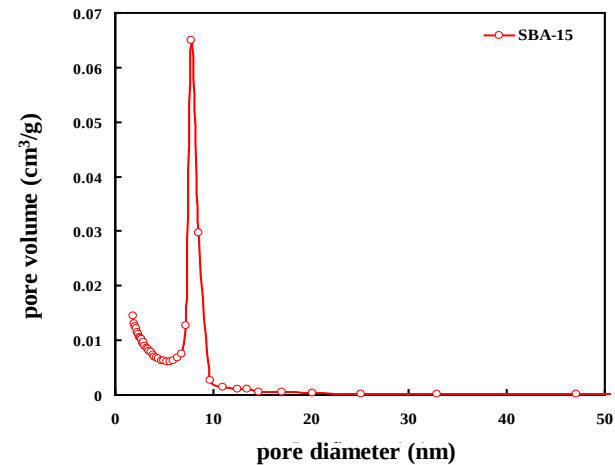
※ 질소의 흡착량 증가

= 표면에 흡착 + 비어있는 세공을 채우는 흡착

① 흡착 - 탈착 등온선



② 세공 크기 분포



질소 흡착 등온선의 예

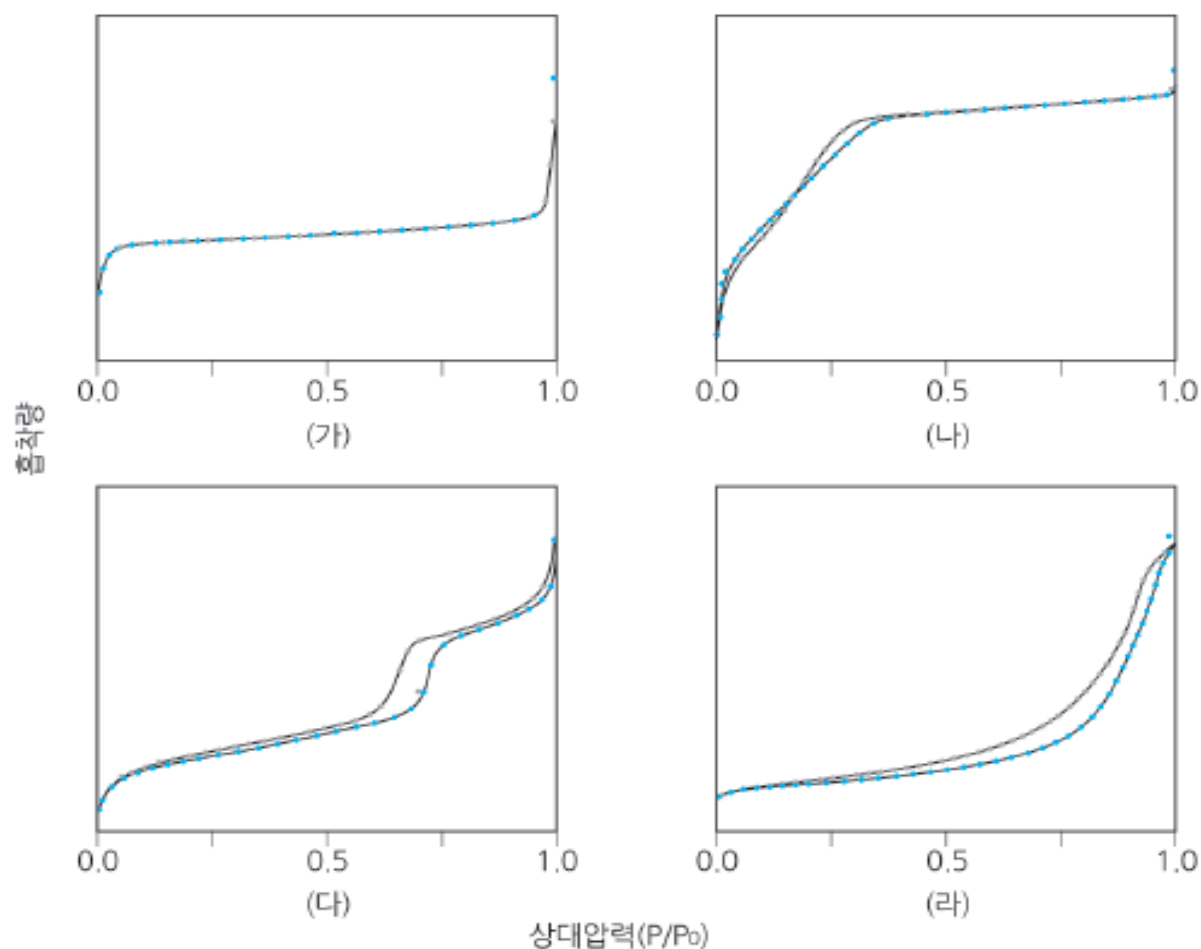


그림 2-10 다공성물질의 여러 가지 흡착등온선 (가) MOR 제올라이트 (나) MCM-41 중간세공물질 (다) SBA-15 중간세공물질 (라) 실리카-알루미나

BET Plot의 예

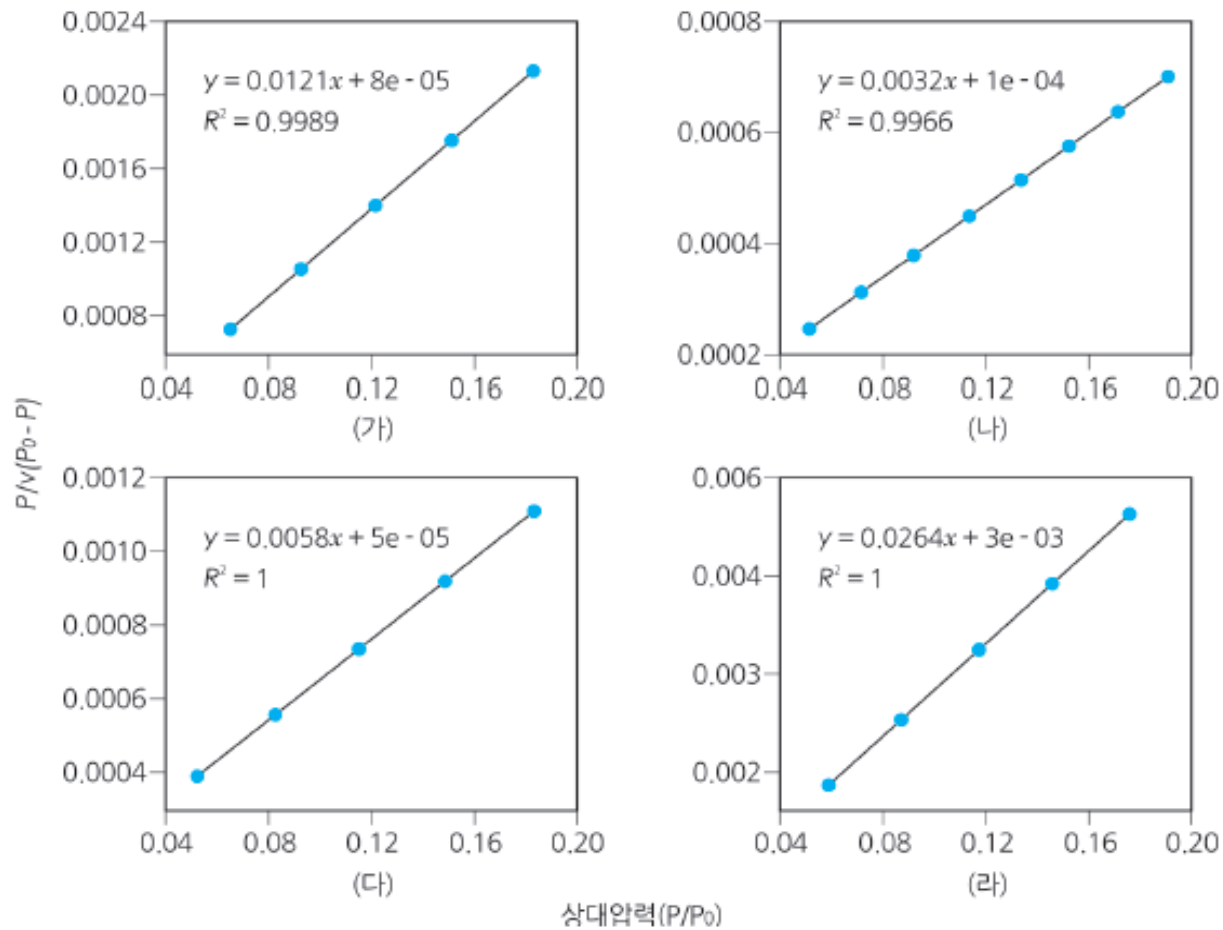


그림 2-13 여러 다공성물질의 질소 흡착등온선에서 구한 BET 그림 (가) MOR 제올라이트 (나) MCM-41 중간세공 물질 (다) SBA-15 중간세공물질 (라) 실리카-알루미나

세공 크기 분포의 예

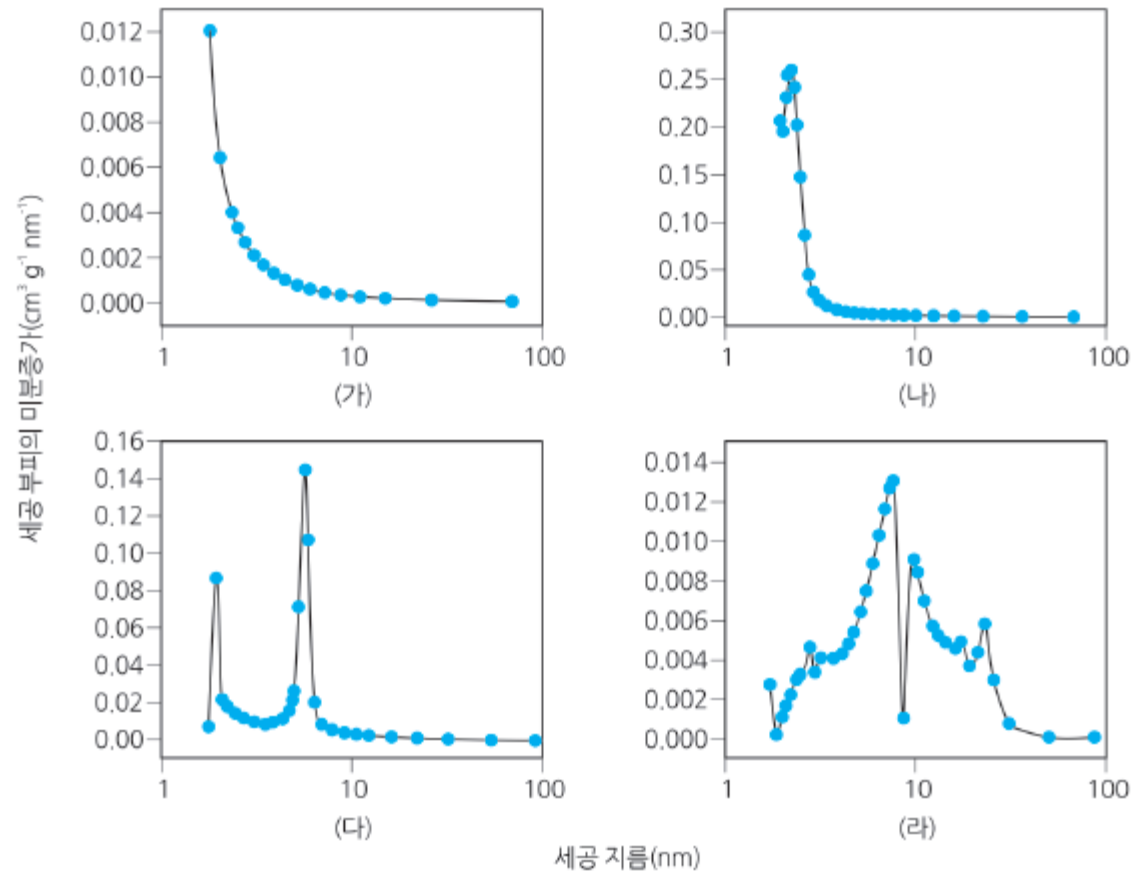


그림 2-14 여러 다공성물질의 세공크기 분포도 (가) MOR 제올라이트 (나) MCM-41 중간세공물질 (다) SBA-15 중
간세공물질 (라) 실리카-알루미나

퍼텐셜 이론

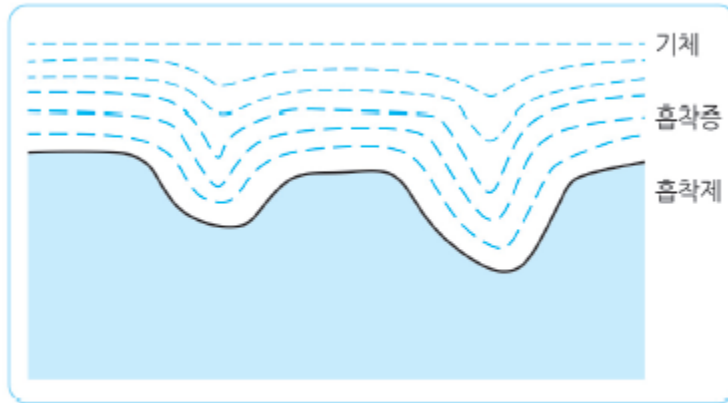


그림 2-1 고체 표면에서 흡착층의 단면도 점선의 굵기는 흡착한 물질의 농도를 나

$$\varepsilon = \int_{P_g}^{P_s} V dP$$

$$v = \sum \int_0^x (\rho_x - \rho_g) dx$$

$$W = W_0 \exp[-(a_D \varepsilon^2)]$$

$$\varepsilon = RT \ln \frac{f}{f_g} = RT \ln \frac{P}{P_g}$$

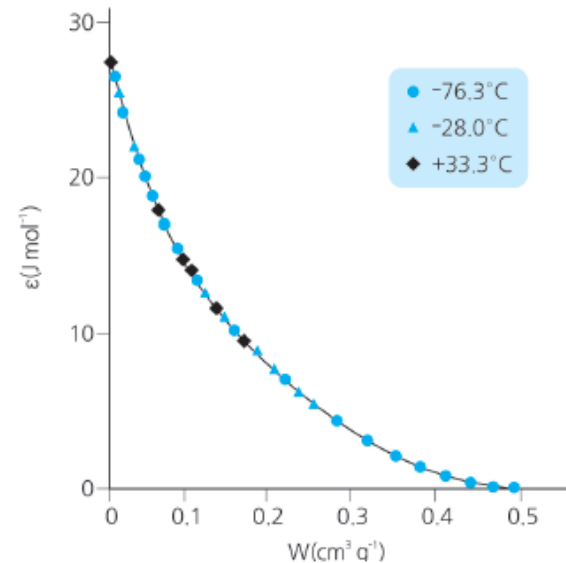
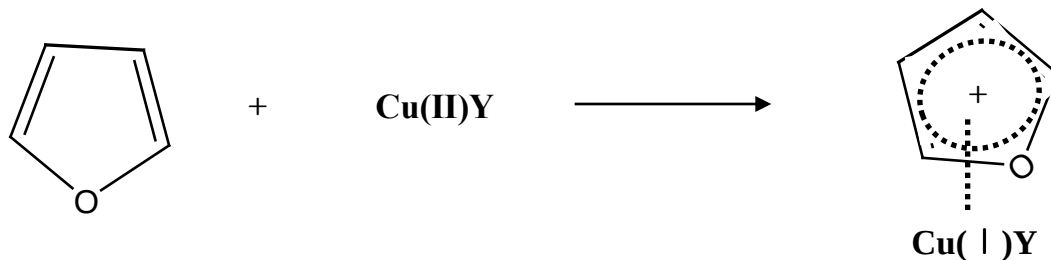
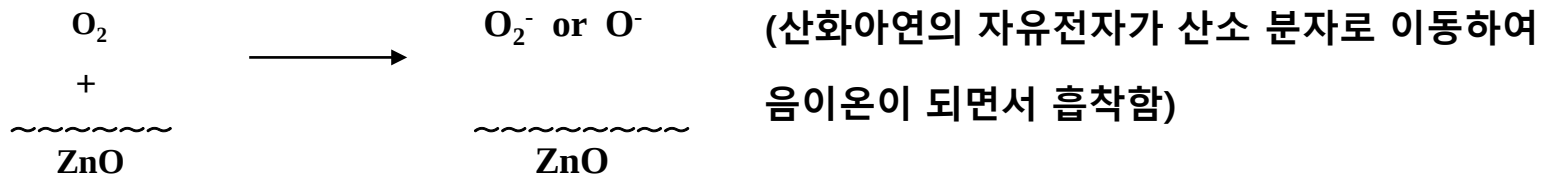


그림 2-17 활성탄에 대한 테트라플루오로에틸렌의 흡착특성곡선[16]

화학흡착 - I

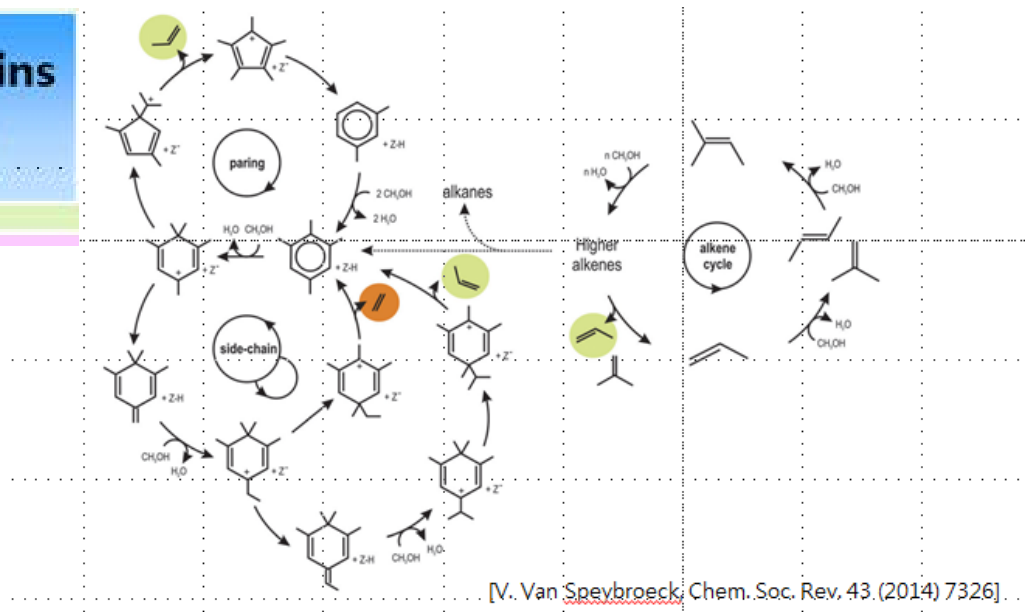
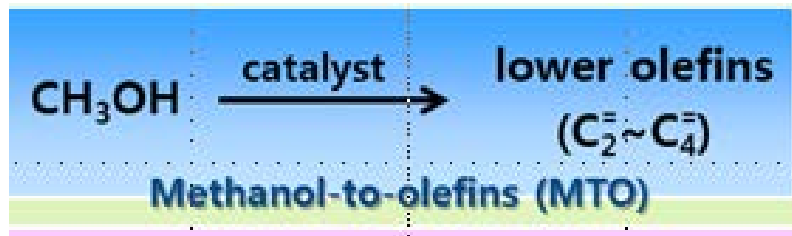
- ◆ 정의: 흡착하는 분자와 표면 원자 사이에 화학결합이 이루어지면서 일어나는 흡착
 - 표면과 흡착하는 분자 사이에 전자가 이동함.

◆ 이온결합

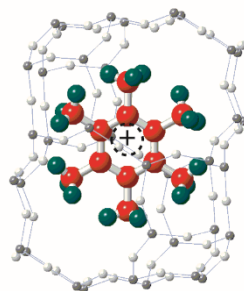
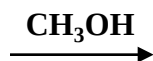
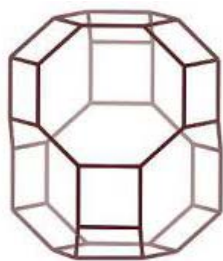


- ※ Cu(I) 이온은 EPR에서 신호가 나타나지 않으나 Cu(II) 이온에서는 EPR 스펙트럼이 나타남
 - Cu(II)Y 에 퓨란이 흡착하면서 전자가 이동하여 EPR 스펙트럼이 달라짐.

화학흡착 - II



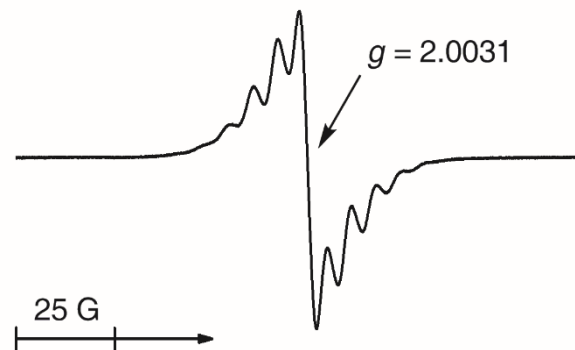
◆ SAPO-34 등지에 생성된 hexamethyl-benzenium cation radical



MeOH

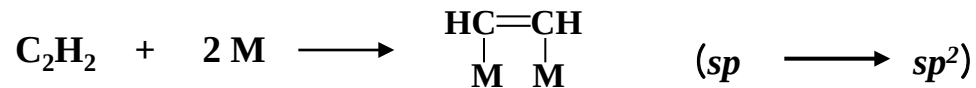
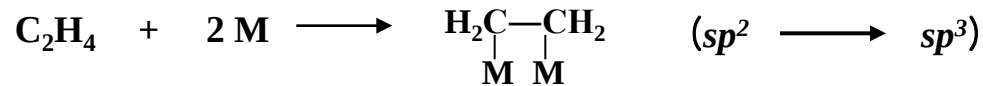
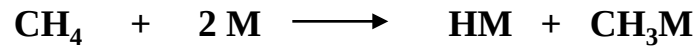


Light
olefins

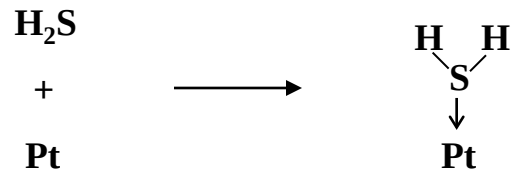


화학흡착 - III

◆ 공유 결합



◆ 배위 결합



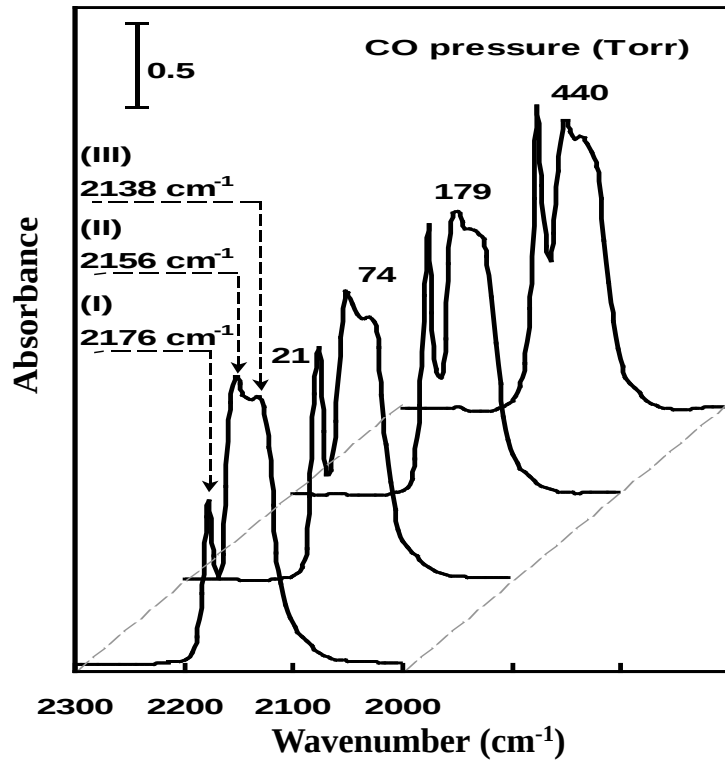
화학흡착 - IV

표 2-2 담지 금속 촉매에 대한 일산화탄소의 흡착[20]

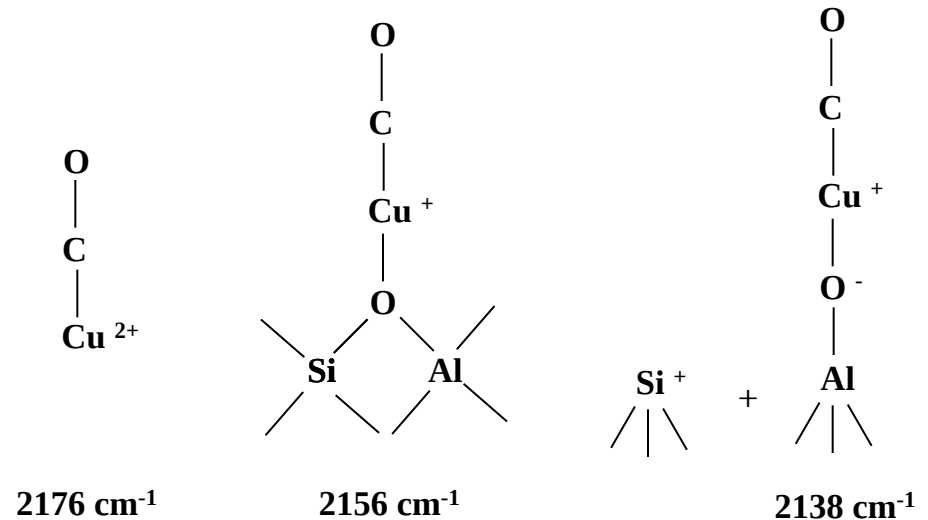
금속	지지체	흡수띠 파수(cm^{-1})	세기	흡착 형태
Fe	SiO_2	1,960	s	$\text{Fe}-\text{C}\equiv\text{O}$
Pt	SiO_2	2,070	s	$\text{Pt}-\text{C}\equiv\text{O}$
Ni	SiO_2	2,030	w	$\text{Ni}-\text{C}\equiv\text{O}$
		1,905	s	$\begin{array}{c} \text{Ni} \\ \\ \text{C}=\text{O} \\ \\ \text{Ni} \end{array}$
Pd	SiO_2	2,050	w	$\text{Pd}-\text{C}\equiv\text{O}$
		1,920	s	$\begin{array}{c} \text{Pd} \\ \\ \text{C}=\text{O} \\ \\ \text{Pd} \end{array}$
		1,827	sh	
Rh	$\alpha\text{-Al}_2\text{O}_3$	2,100	s	$\begin{array}{c} \text{C}\equiv\text{O} \\ / \\ \text{Rh} \\ \backslash \\ \text{C}\equiv\text{O} \end{array}$
		2,030		
		2,000	s	$\text{Rh}-\text{C}\equiv\text{O}$
		1,850		
		$\sim 1,900$	m	$\begin{array}{c} \text{Rh} \\ \\ \text{C}=\text{O} \\ \\ \text{Rh} \end{array}$
Rh	제올라이트	2,116		
		2,044	s	$\begin{array}{c} \text{C}\equiv\text{O} \\ / \\ \text{Rh} \\ \backslash \\ \text{C}\equiv\text{O} \end{array}$
		2,103		
		2,106	s	$\begin{array}{c} \text{C}\equiv\text{O} \\ / \\ \text{Rh} \\ \backslash \\ \text{C}\equiv\text{O} \end{array}$

* s: 강함, m: 중간, w: 약함, sh: 어깨봉우리

화학흡착 - V



Adsorbed state:



◆ CuY에 흡착한 CO의 IR 스펙트럼

◆ 기체 CO의 흡수를 배제하기 위해 25 °C 에서 배기한 후 스펙트럼을 그림.

화학흡착과 촉매작용 - I

◆ 화학흡착은 촉매반응에서 반응물을 활성화시킴

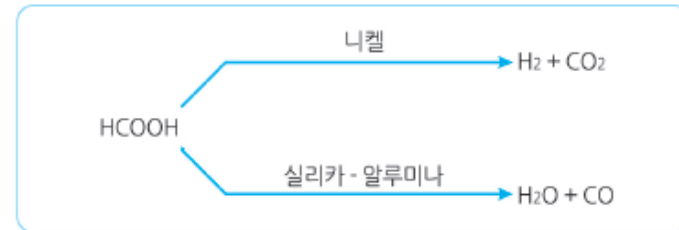


그림 2-5 개미산의 분해반응에서 촉매와 생성물의 관계

* 촉매 활성과 화학흡착 세기

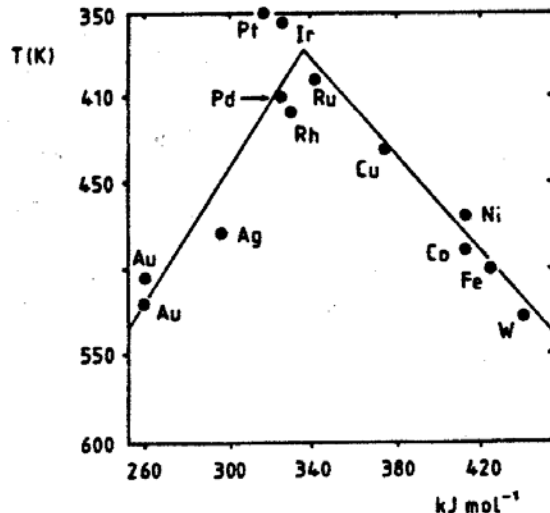


Figure 1.13 A typical volcano plot of the kind discussed by Balandin. The ordinate gives the temperature for a specified conversion of the reactant (formic acid) on a metal catalyst, and the abscissa gives the enthalpy of formation of the metal formate. With permission from J. Fahrenfort, L. L. van Reijen, W. M. H. Sachtler, *The Mechanism of Heterogeneous Catalysis* (Ed. J. H. de Boer). Elsevier, Amsterdam 1960.

◆ 화산형 그림 (Volcano plot):

- 반응물의 화학흡착이 촉매반응에 필수적이거나 너무 강하면 촉매 활성이 낮아짐.
- 아주 강한 화학흡착은 촉매 독!

화학흡착과 촉매작용 - II

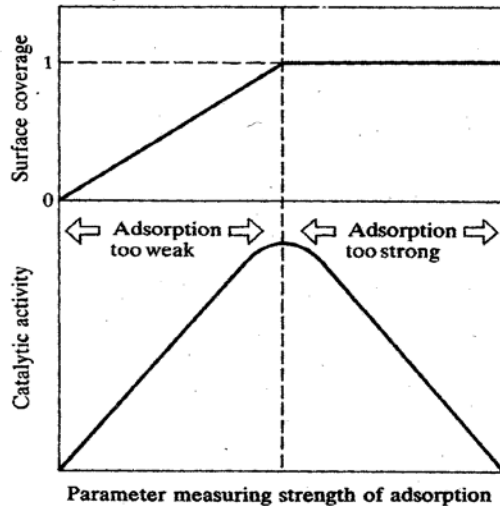


FIG. 6.1. The volcano curve: dependence of catalytic activity upon strength of reactant adsorption (lower part) and the corresponding variation in surface coverage (upper part).

[G.C.Bond, "Heterogeneous Catalysis", 2nd Ed., Oxford Science Publications (1987) 63.]

◆ 속도식이 $r = k\theta_A\theta_B$ 인 $A + B \rightarrow C$ 화학반응의 속도에서 화산형 그림이 나타남.

- 흡착세기, 반응온도, 반응물 농도에 대한 촉매 활성의 의존성에서도 최고값이 있는 화산형 그림이 나타남.

화학흡착과 촉매작용 - III

	O ₂	C ₂ H ₂	C ₂ H ₄	CO	H ₂	CO ₂	N ₂
Ti, Cr, Mo, Fe	+	+	+	+	+	+	+
Ni, Co	+	+	+	+	+	+	-
Pd, Pt	+	+	+	+	+	-	-
Mn, Cu	+	+	+	+	±	-	-
Al, Au	+	+	+	-	-	-	-
Li, Na, K	+	+	-	-	-	-	-
Mg, Ag, Zn, Pb	+	-	-	-	-	-	-

* +, Strong chemisorption; ±, chemisorption; -, no chemisorption.

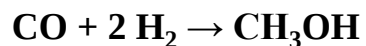
◆ 화학흡착 세기

acetylene > alkene > alkane

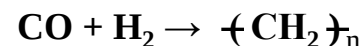
O₂ > C₂H₂ > C₂H₄ > CO > H₂ > CO₂ > N₂

◆ 촉매 반응에 적절한 금속 선정

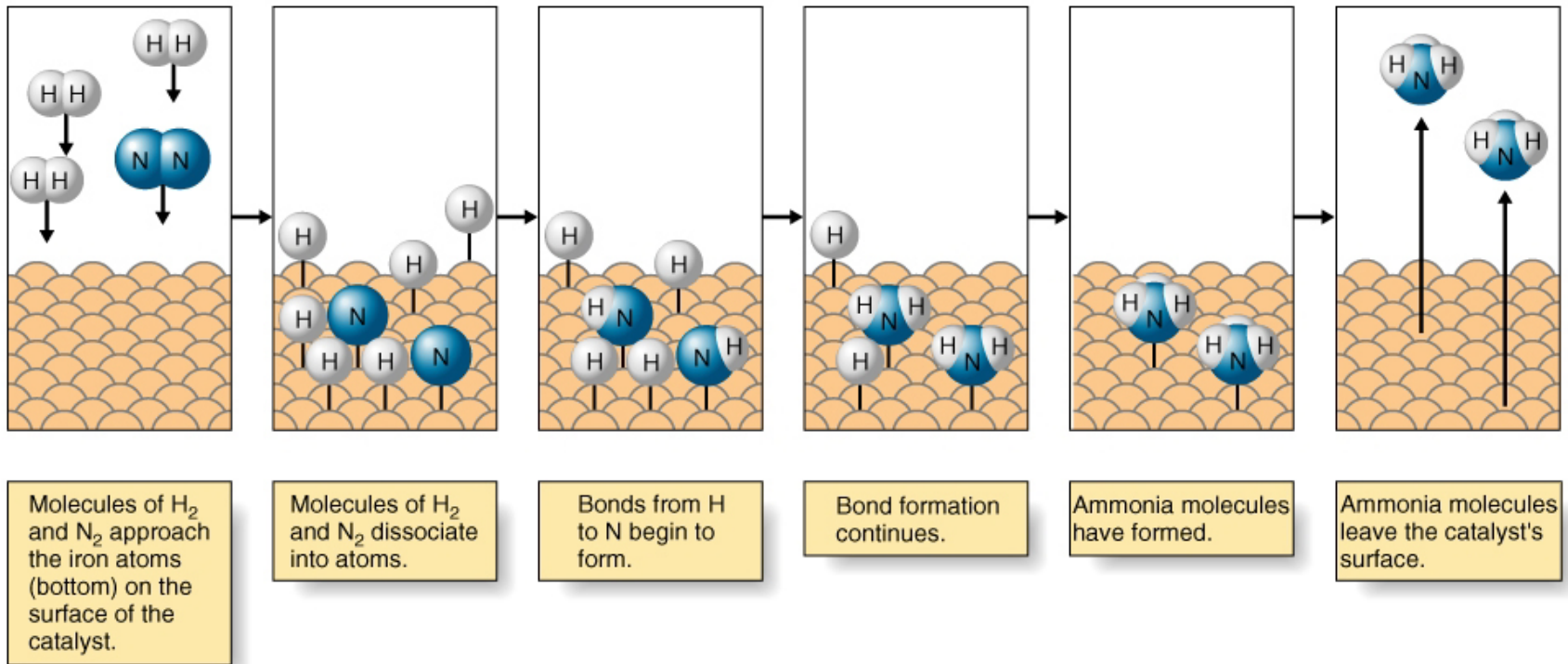
* 메탄올 합성



* 피셔 - 트롭슈 합성



Haber-Bosch 공정



◆ N_2 와 H_2 의 해리

◆ 적절한 흡착세기 고려

⇒ Fe, Ru

흡착을 이용한 촉매와 촉매작용 조사

◆ 물리흡착

- 표면 구조와 조성에 대해 선택성이 없음.
- 표면적, 세공크기 분포, 세공부피 등 결정

◆ 화학흡착

- 표면 구조와 조성에 따라 선택성이 달라짐.
- 촉매의 화학적 성질 조사
 - 흡착열로부터 흡착점의 에너지 상태
 - 검시 기체(예: 수소)의 흡착량에서 활성물질의 분산 상태
 - 흡착 상태와 흡착열에서 반응물의 활성화 상태
- 반응 경로
 - 반응물과 중간체의 흡착 상태에서 반응경로 추론
- 흡착한 반응물의 표면 농도
 - 흡착등온선에서 구한 반응물의 표면 농도로부터 반응속도 계산

요 약

- 흡착의 기본 개념
 - 정의, 원동력, 분류
- 물리흡착과 화학흡착, 분자흡착과 해리흡착
- 흡착 등온선(등온 흡착선)과 Hysteresis phenomena
 - Langmuir isotherm
 - Freundlich isotherm
 - BET isotherm
 - ※ Mesoporous substances give a hysteresis loop.
- 화학흡착과 촉매작용
- 흡착 방법을 이용한 촉매와 촉매 작용 조사