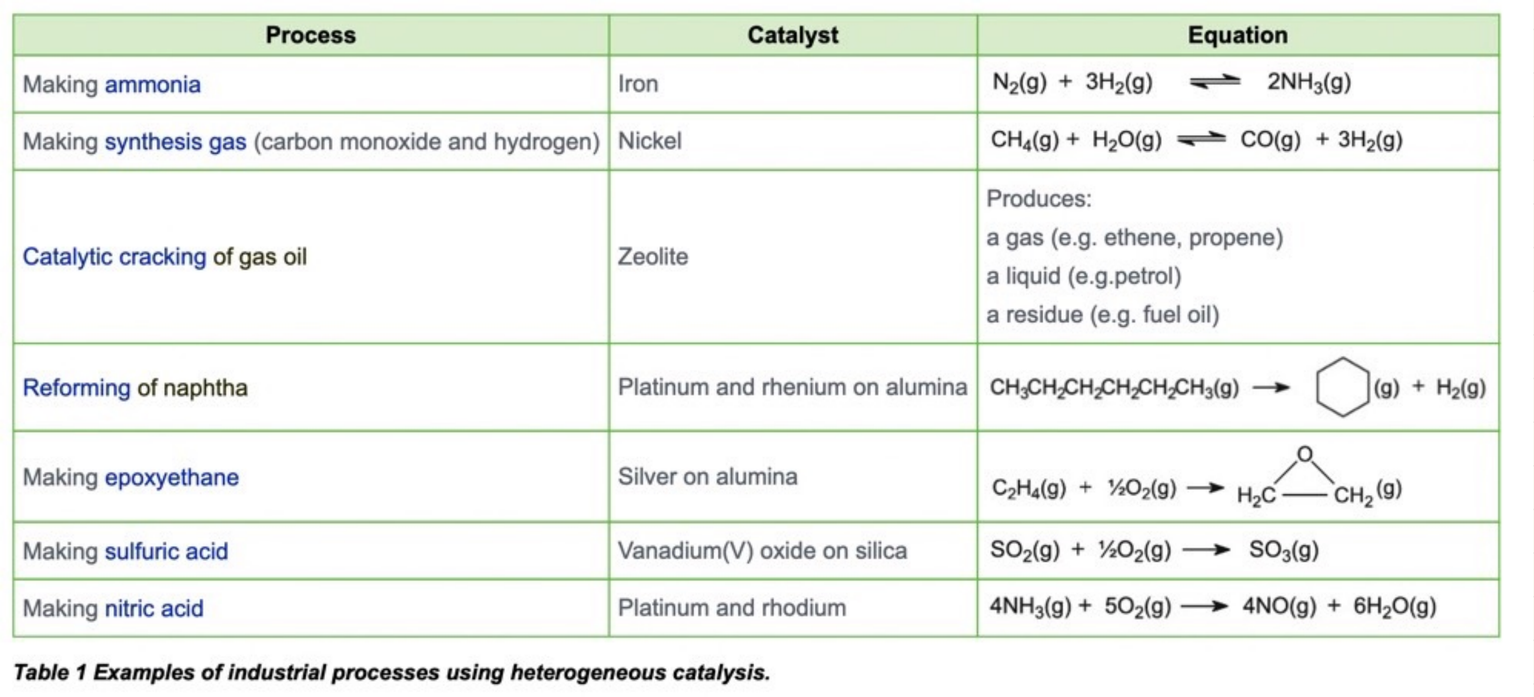
CBE 40445
9/14/20

HETEROGENEOUS CATALYSIS

ONE OF THE "GLORY" FIELDS OF CHEMICAL ENGINEERING

ALMOST ALL REACTIONS DONE FOR MONEY REQUIRE A CATALYST TO BE PROFITABLE (AND PRACTICAL)

A LARGE MAJORITY OF THESE INVOLVE A SOLID-PHASE CATALYST.

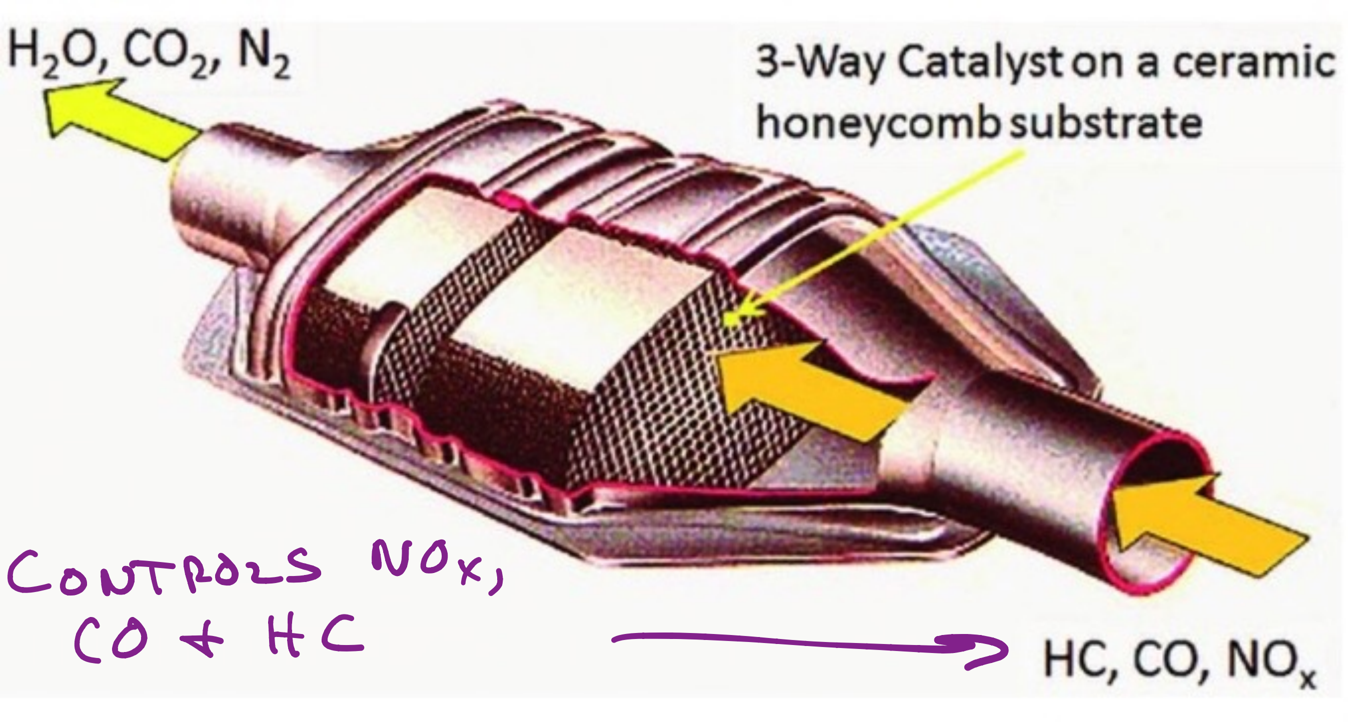


Process	Catalyst	Equation
Making ammonia	Iron	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Making synthesis gas (carbon monoxide and hydrogen)	Nickel	$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
Catalytic cracking of gas oil	Zeolite	Produces: a gas (e.g. ethene, propene) a liquid (e.g.petrol) a residue (e.g. fuel oil)
Reforming of naphtha	Platinum and rhenium on alumina	$CH_3CH_2CH_2CH_2CH_2CH_3(g) \rightarrow$ (g) + $H_2(g)$
Making epoxyethane	Silver on alumina	$C_2H_4(g) + ½O_2(g) \rightarrow \overset{O}{H_2C—CH_2}(g)$
Making sulfuric acid	Vanadium(V) oxide on silica	$SO_2(g) + ½O_2(g) \rightarrow SO_3(g)$
Making nitric acid	Platinum and rhodium	$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Table 1 Examples of industrial processes using heterogeneous catalysis.

https://www.essentialchemicalindustry.org/processes/catalysis-in-industry.html

ANOTHER HIGH VOLUME CATALYTIC DEVICE:



CONTROLS NO_x, CO & HC

FOR IT TO WORK, NEED RATHER PRECISE AIR-FUEL MIX

NEED SOME HC (RICH) TO HELP WITH NO_x REACTION
ULTIMATELY NEED O_2 (LEAN) TO OXIDIZE CO & HC'S

CHECK ENGINE

NO_x REACTIONS

$2CO + 2NO \rightarrow 2CO_2 + N_2$

$HC + NO \rightarrow CO_2 + H_2O + N_2$

$2H_2 + 2NO \rightarrow 2H_2O + N_2$

CO OXIDATION

$2CO + O_2 \rightarrow 2CO_2$

HC OXIDATION

$HC + O_2 \rightarrow H_2O + CO_2$

THE WORLD HAS TRADEOFFS!!

RECALL: ~ MARCH 2019

EFFICIENCY OF "OTTO CYCLE"

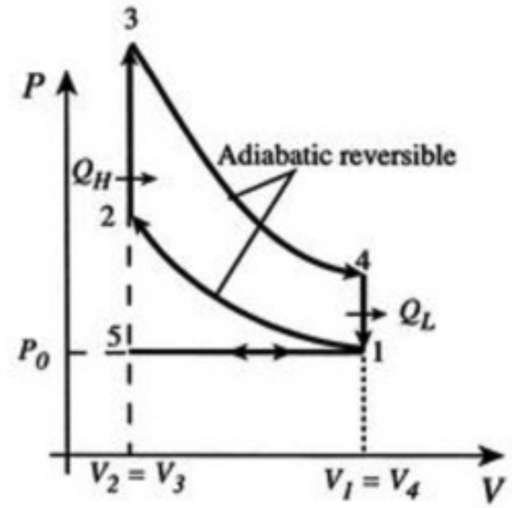


Figure 3.8: The ideal Otto cycle

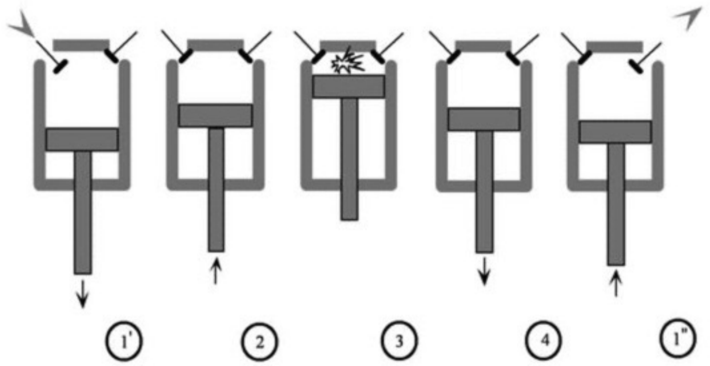


Figure 3.10: Piston and valves in a four-stroke internal combustion engine

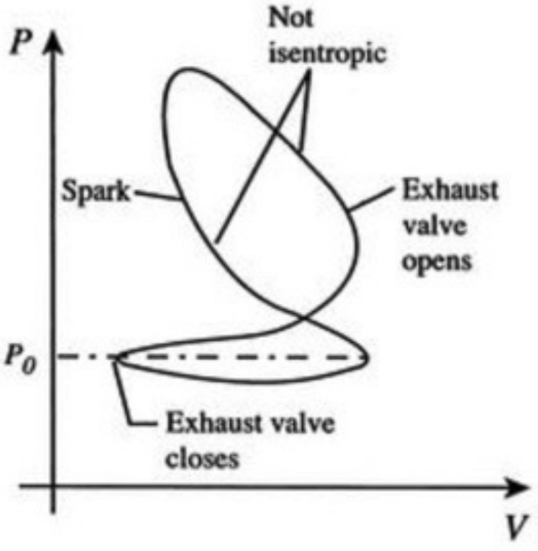


Figure 3.9: Sketch of an actual Otto cycle

$$\eta = \frac{\text{work}}{\text{heat input}} = \frac{Q_H + Q_L}{Q_H} = 1 + \frac{Q_L}{Q_H}.$$

$$\eta_{\text{Otto}} = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}} = 1 - \frac{1}{r^{\gamma-1}}.$$

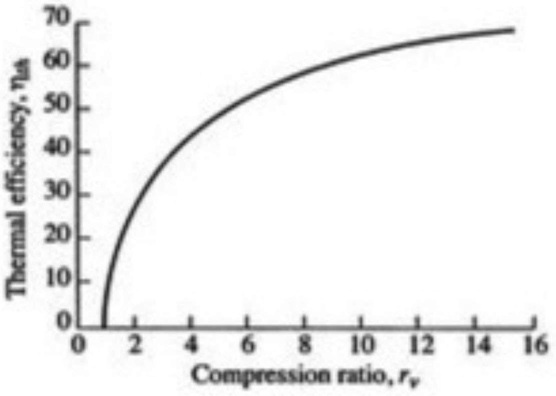


Figure 3.11: Ideal Otto cycle thermal efficiency

HIGHER COMPRESSION RATIO :
HIGHER TEMPERATURE

T IN GENERAL RUNNING LEAN GIVES
MORE COMPLETE COMBUSTION,
HENCE MORE EFFICIENT USE
OF GASOLINE BUT

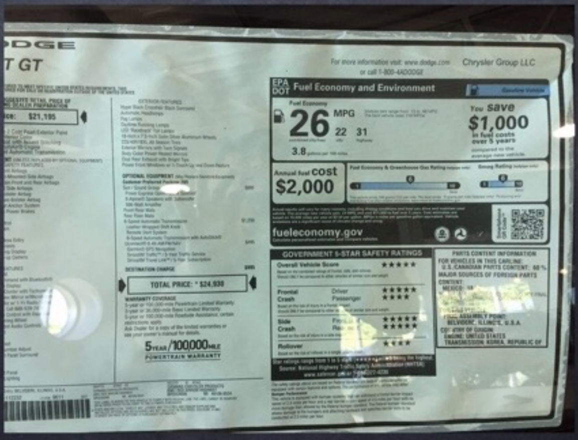
THIS FAVORS NO_x

http://ndcbechair.blogspot.com/

Significant Progress

- Gas mileage doubled since 1972

Actual successor to 1972 Plymouth



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Overall Vehicle Score ★★★★★

Frontial Crash Driver ★★★★★ Passenger ★★★★

Side Crash ★★★★★ ★★★★★

Rollover ★★★★

TOTAL PRICE: * \$24,930

5YEAR/100,000MILE POWERTRAIN WARRANTY

PARTS CONTENT INFORMATION

FOR VEHICLES IN THIS CARLINE:

U.S./CANADIAN PARTS CONTENT: 68 %

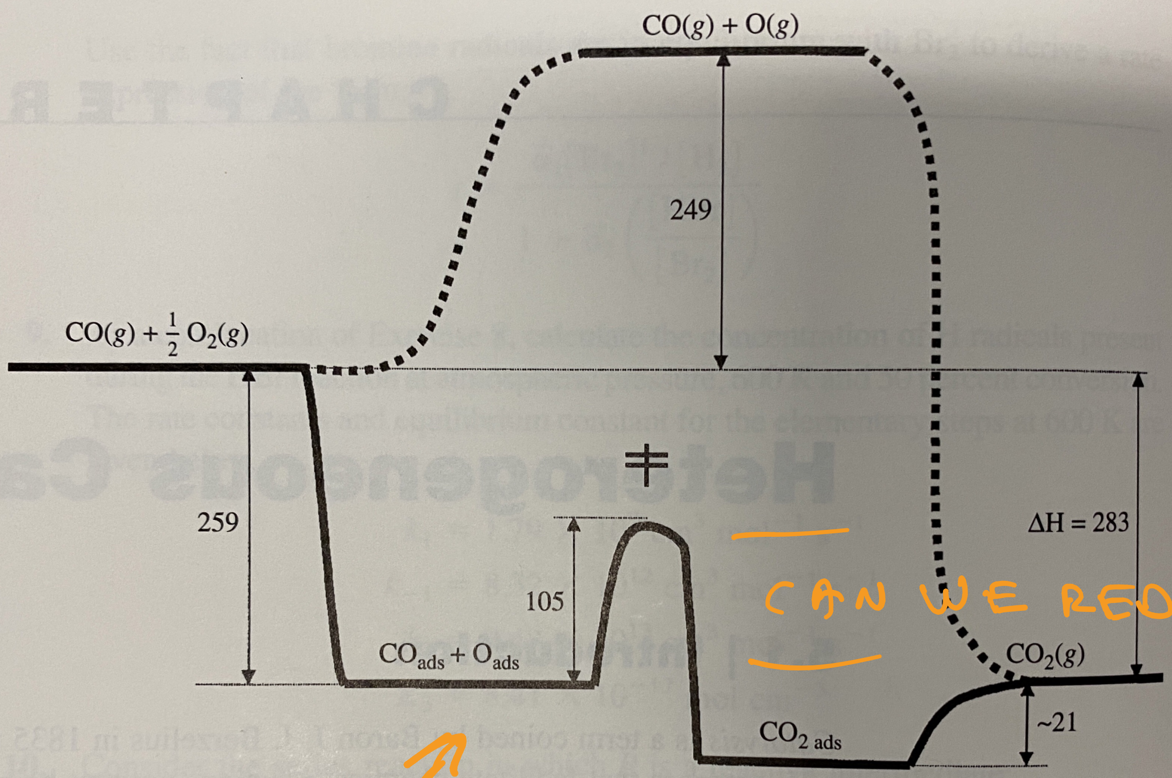
MAJOR SOURCES OF FOREIGN PARTS CONTENT

FINAL ASSEMBLY POINT: BELVIDERE, ILLINOIS, U.S.A.

COUNTRY OF ORIGIN:

ENGINE: UNITED STATES

TRANSMISSION: KOREA, REPUBLIC OF



CAN WE REDUCE THIS?

Figure 5.1.1 | Schematic energy diagram for the oxidation of CO and a Pt catalyst. (From data presented by G. Ertl in *Catalysis: Science and Technology,* J. R. Anderson and M. Boudart, Eds., vol. 4, Springer-Verlag, Berlin, 1983, p. 245.) All energies are given in kJ mol^{-1}. For comparison, the heavy dashed lines show a noncatalytic route.

"WHERE" EXACTLY DO CO + O ADSORB?

SURFACES OF CATALYSTS HAVE BEEN STUDIED IN GREAT DETAIL !!

CONTEXT:

- NEED TO MAXIMIZE SURFACE AREA FOR FIXED AMOUNT OF METAL CATALYST
- VARIOUS TECHNIQUES ARE KNOW FOR GETTING ~ nm SIZED PARTICLES
- AS PARTICLES GET SMALLER SURFACE STRUCTURE, CHEMISTRY CHANGES

- DIFFERENT CRYSTAL PLANES HAVE DIFFERENT CHEMISTRY

- ADVANCES IN "SPECTROSCOPY" HAVE BEEN EXPLOITED TO STUDY REACTIONS ON SPECIFIC SURFACE PLANES.

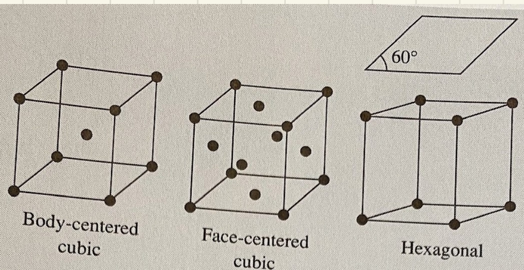


Figure 5.1.2 | Crystal structures of catalytically relevant transition metals.

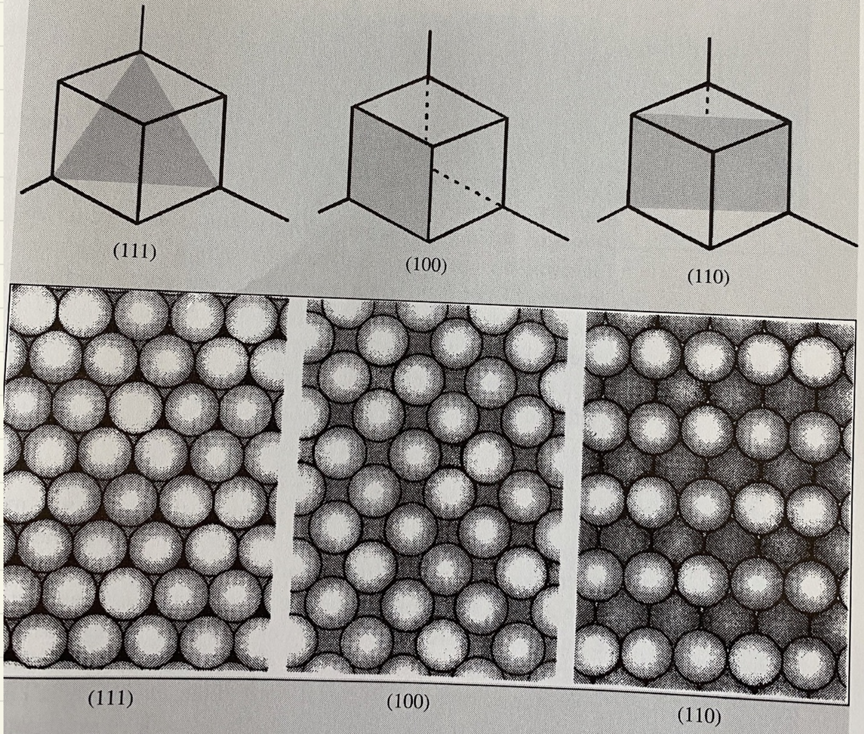


Figure 5.1.3 | Atomic arrangements of the low-index surface planes of an FCC crystal. (Adapted from R. Masel, *Principles of Adsorption and Reaction on Solid Surfaces,* Wiley, New York, copyright © 1996, p. 38, by permission of John Wiley & Sons, Inc.)

Single crystal surfaces are associated with planes in the unit

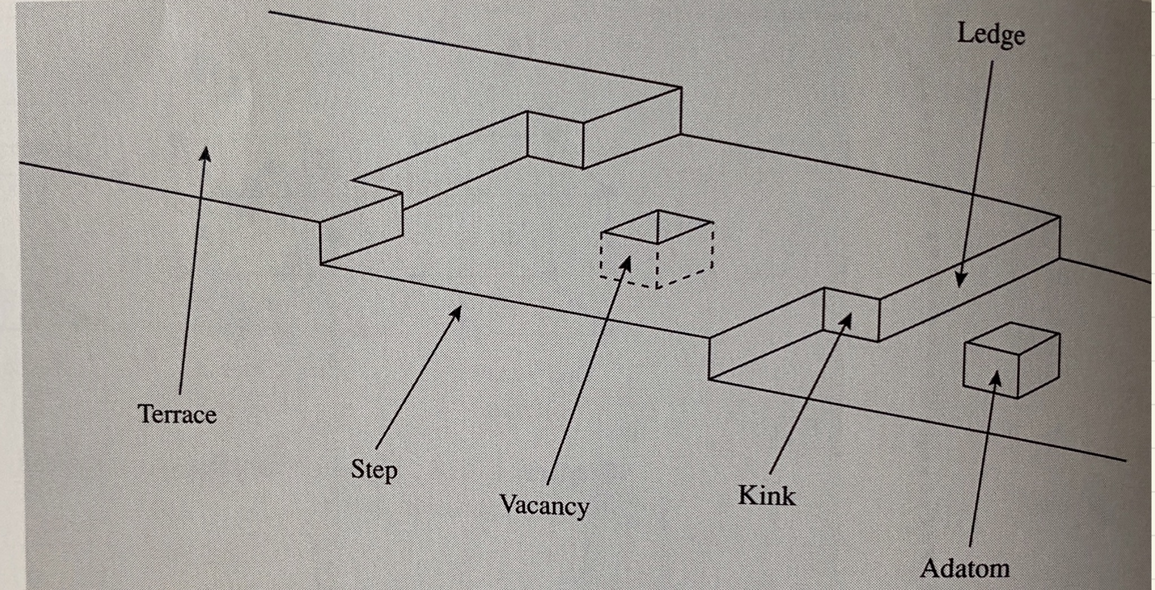


Figure 5.1.4 | Schematic representation of a single crystal surface.

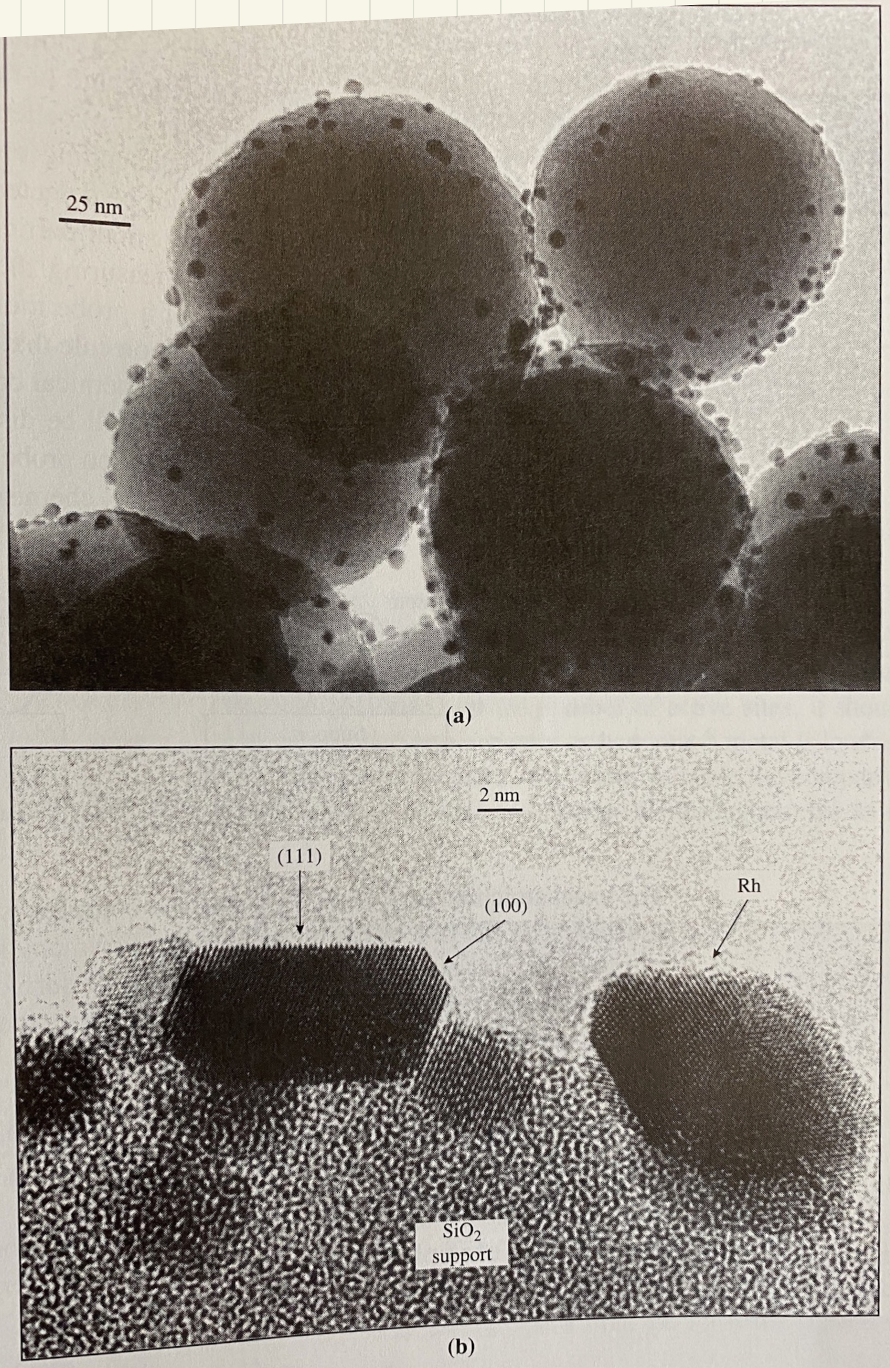


Figure 5.1.5 |
(a) Rhodium metal particles supported on silica carrier. (b) High-resolution electron micrograph shows how small supported Rh crystallites expose low-index faces. (Top photo courtesy of A. K. Datye. Bottom photo from "Modeling of heterogeneous catalysts using

IF WE CAN STUDY REACTIONS AT THIS SCALE, THE RATE CAN BE GIVEN AS

$$r_t = \frac{1}{S}\frac{dn}{dt}$$

NUMBER OF ACTIVE SITES.

TURNOVER FREQUENCY

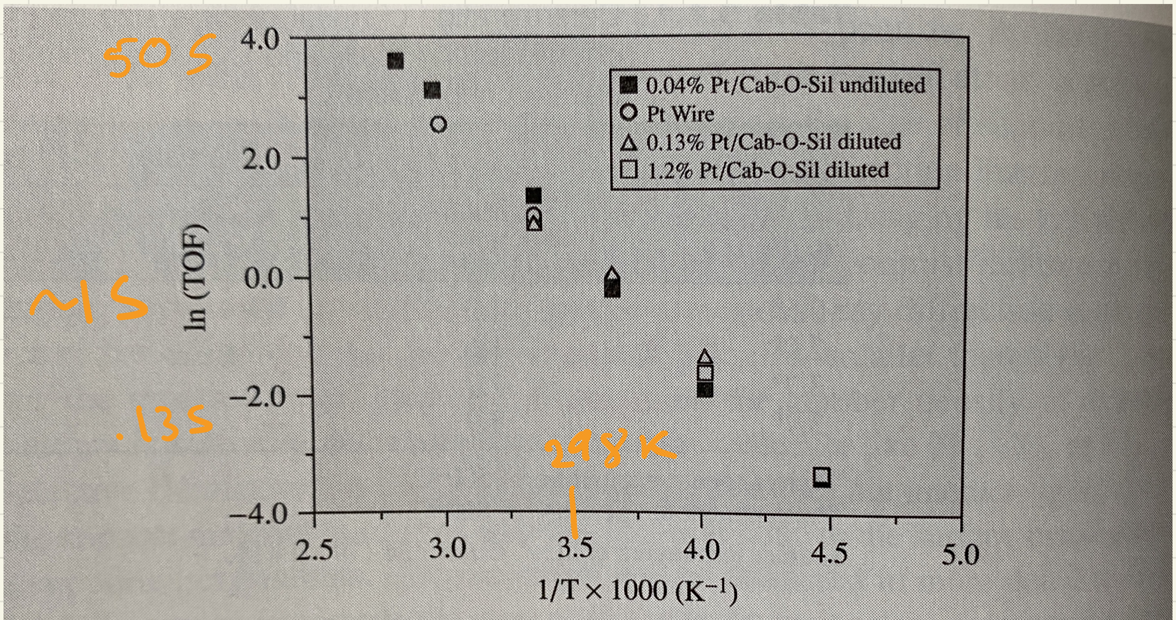


Figure 5.1.6 | Arrhenius-type plot of the turnover frequency for ethylene hydrogenation on bulk and supported Pt catalysts. (Figure from "Kinetic Study of Ethylene Hydrogenation" by R. D. Cortright, S. A. Goddard, J. E. Rekoske, and J. A. Dumesic, in *Journal of* Volume 127:342, copyright © 1991 by

THE CATALYST IS A SOLID SURFACE

THE REACTANT IS OFTEN A GAS, COULD BE A LIQUID IN A SOLVENT, BUT IN EITHER CASE A NECESSARY STEP IS ADSORPTION ONTO THE SURFACE

THE ADSORPTION PROBABLY HAS TO BE TO A SPECIFIC "SITE"

HENCE WE NEED NOTATION

" * " ACTIVE SITE

$$A + * \underset{k_{DES}}{\overset{k_{ADS}}{\rightleftharpoons}} A*$$

ADSORPTION OF A GAS ONTO A SURFACE CAN BE

A) PHYSICAL ~ CONDENSATON

~ "PHYSISORPTION" $\uparrow$ ΔH

OCCURS "ANYWHERE" ON SOLID

B) CHEMICAL ~ ΔH_{RXN}

"CHEMISORPTION"

OCCURS AT SPECIFIC SITES

SIMPLEST MODEL FOR ADSORPTION

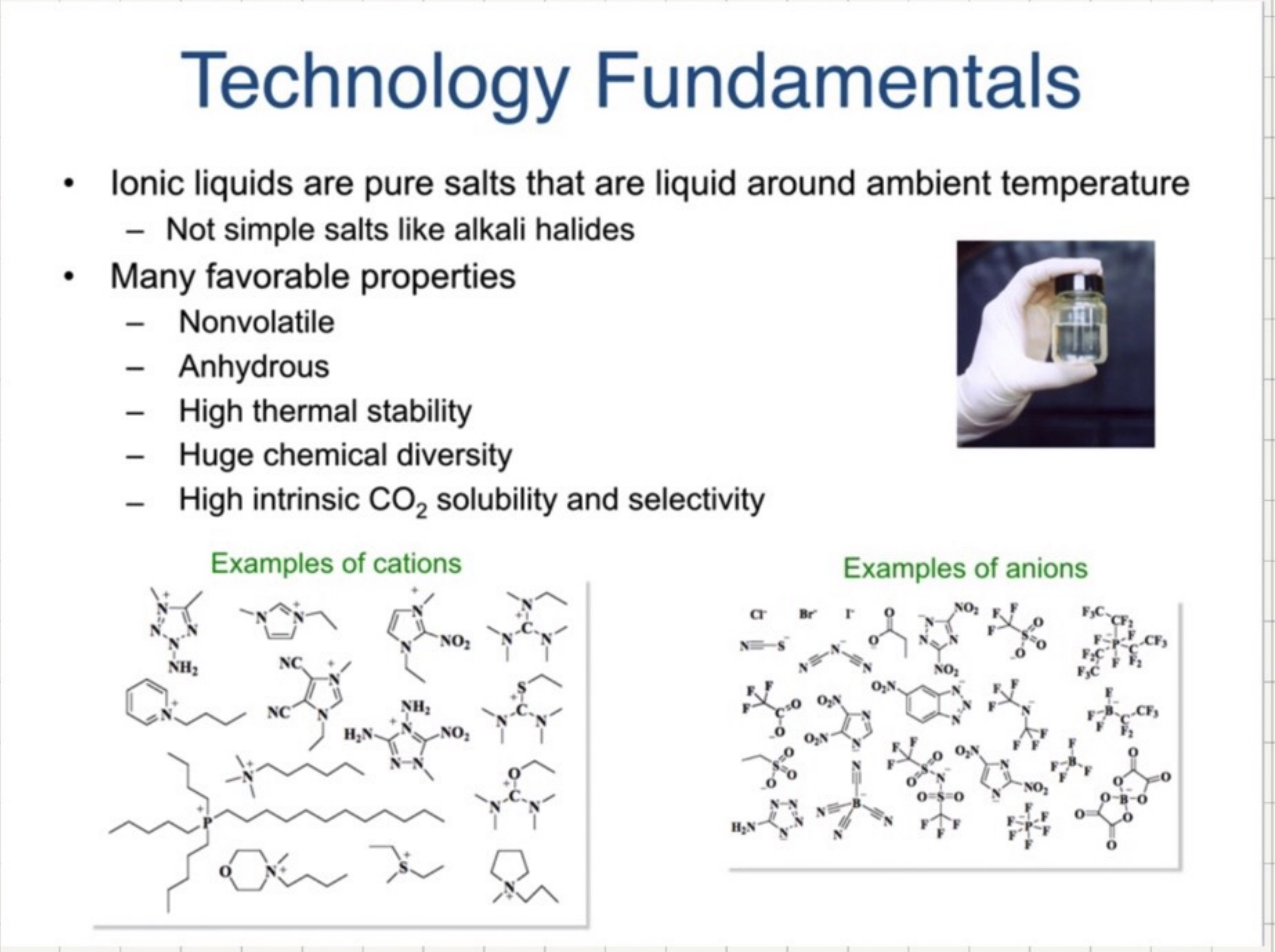
"LANGMUIR"

- PHYSICAL ADSORPTION OF
- 1 LAYER COVERAGE
- IDENTICAL SITES THAT DON'T INTERACT
- EQUILIBRIUM BETWEEN GAS PHASE AN CONDENSED COMPONENT ON SURFACE
- SHOWS HOW TEMPERATURE AFFECTS ADSORBED AMOUNT
- OFTEN WORKS WHEN YOU MIGHT NOT EXPECT....

BUT!!

- PERILS IN STRETCHING TOO FAR!!

WE HAVE FOUND THAT CHEMICAL COMPLEXATION OF GASEOUS CO_2 WITH 'DESIGNER' IONIC LIQUIDS FOLLOWS LANGMUIR

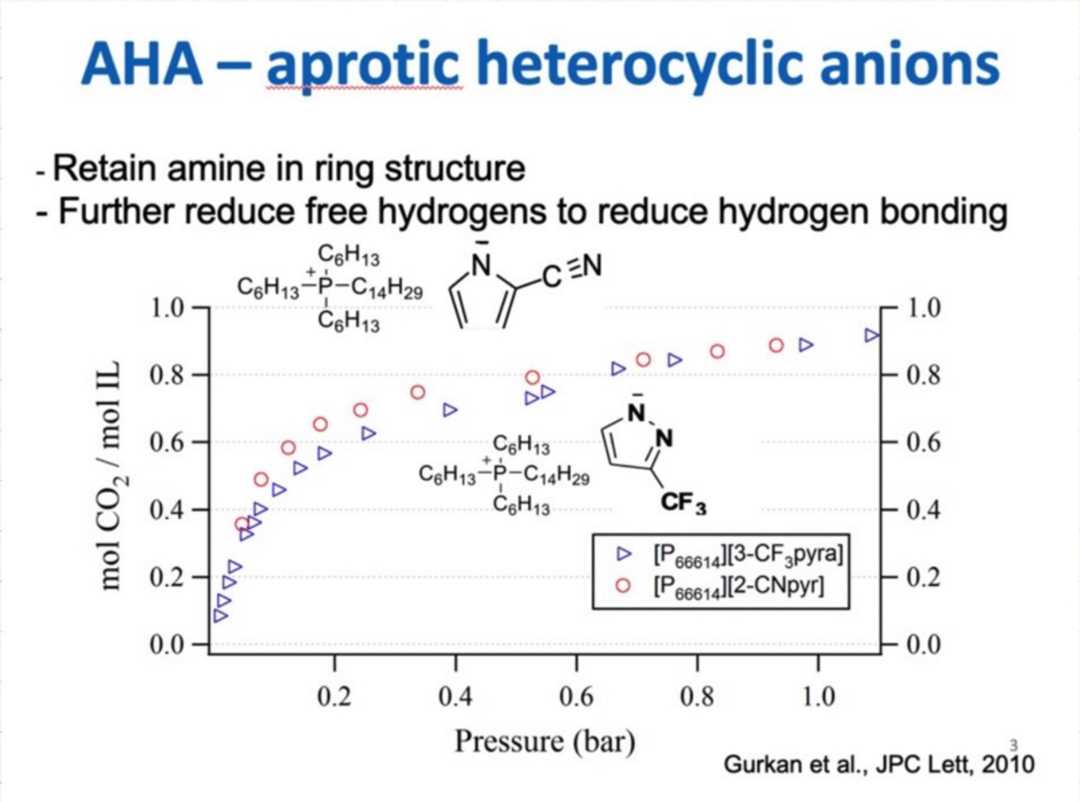


Technology Fundamentals

- Ionic liquids are pure salts that are liquid around ambient temperature
  - Not simple salts like alkali halides
- Many favorable properties
  - Nonvolatile
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity
  - High intrinsic CO_2 solubility and selectivity

Examples of cations

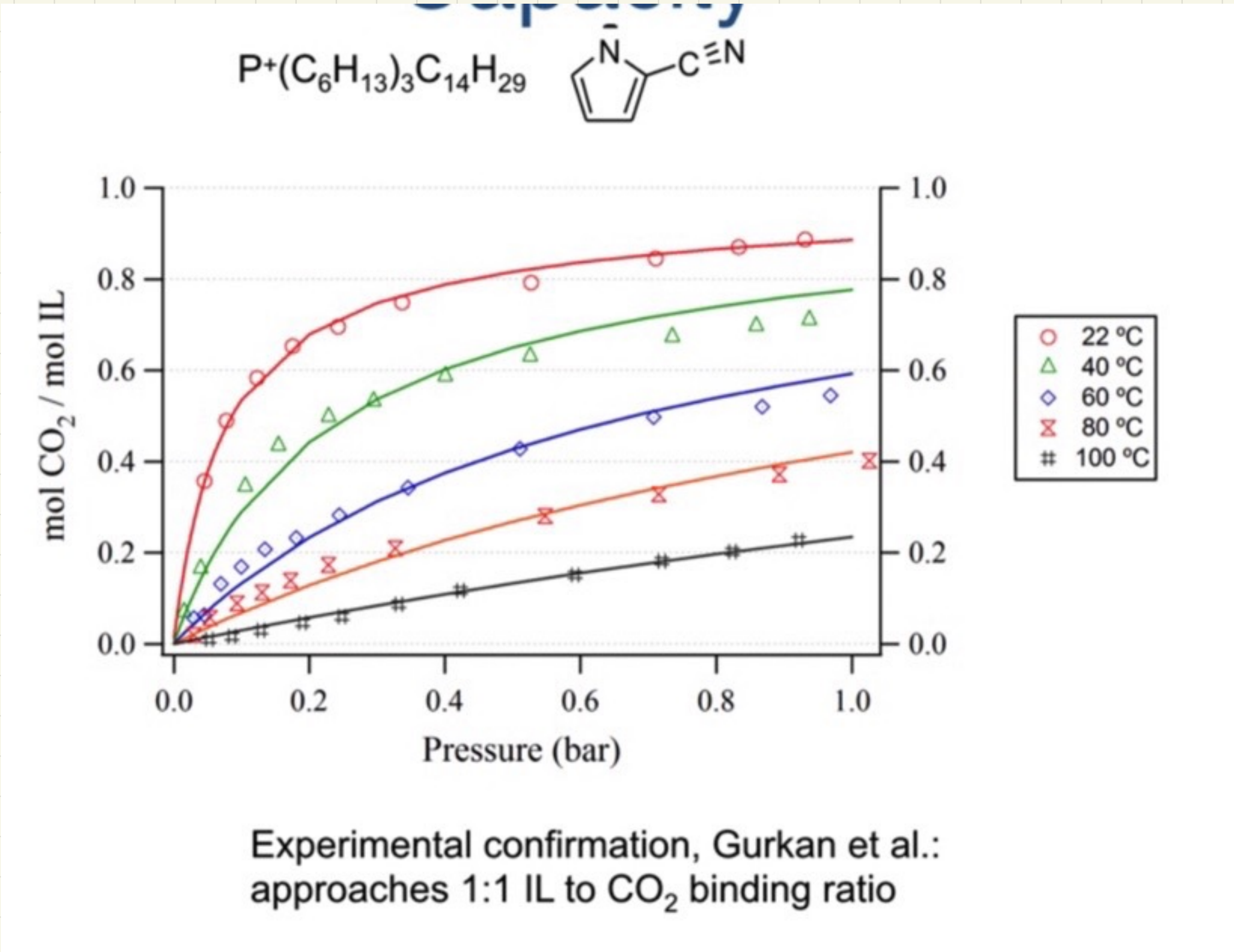
Examples of anions



AHA – aprotic heterocyclic anions

- Retain amine in ring structure
- Further reduce free hydrogens to reduce hydrogen bonding

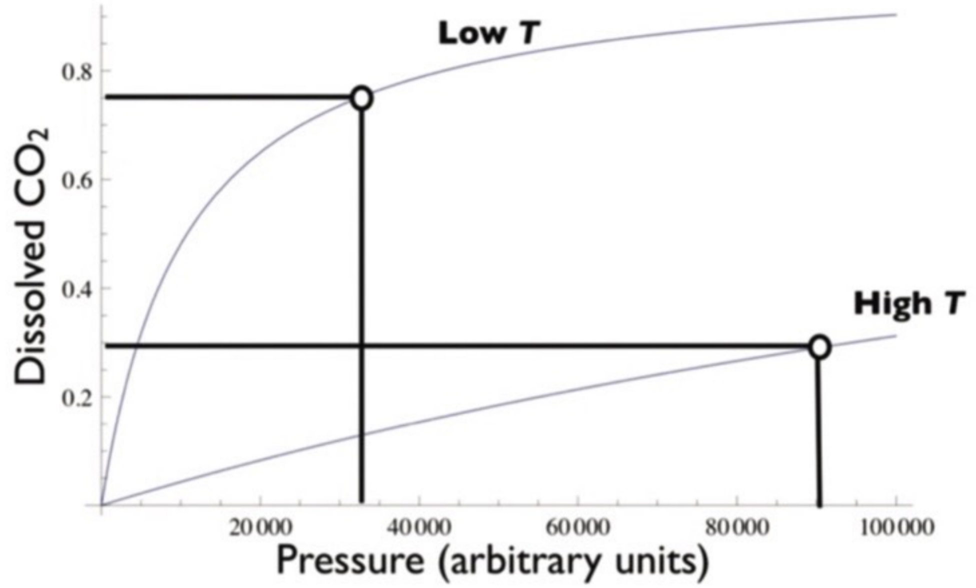
Gurkan et al., JPC Lett, 2010

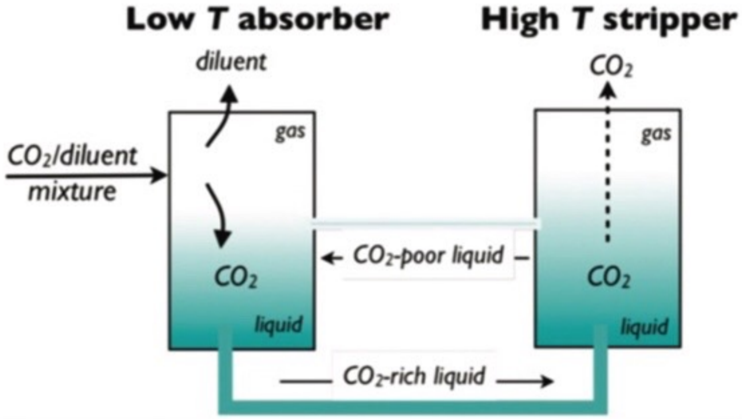


$P^+(C_6H_{13})_3C_{14}H_{29}$

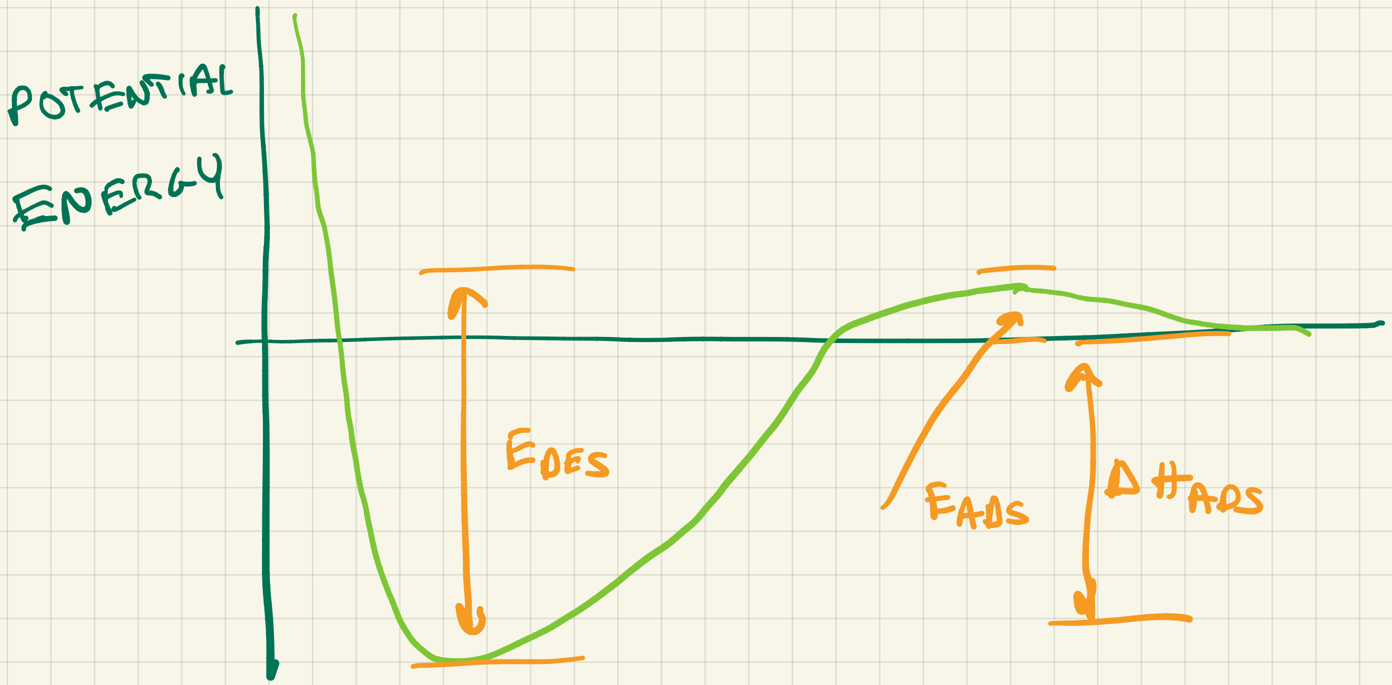
Experimental confirmation, Gurkan et al.: approaches 1:1 IL to CO_2 binding ratio

THE JOURNAL OF PHYSICAL CHEMISTRY
Letters





ENERGY DIAGRAM FOR ADSORPTION



THIS IS AN EQUILIBRIUM PROCESS BUT DERIVATION IS SIMPLEST IN TERMS OF RATES,

GAS PRESSURE

$$\Lambda_{AD} = k_{AD} P_A [S]$$

CONCENTRATION OF SURFACE SITES

$$\Lambda_D = k_D [A_{AD}]$$

$$k_{AD} P_A [S] = k_D [A_{AD}]$$

$$\frac{[A_{AD}]}{P_A [S]} = \frac{k_{AD}}{k_D} = K^A_{EQ}$$

$$[S_0] = \frac{S_0}{a}$$

TOTAL SITES

AREA

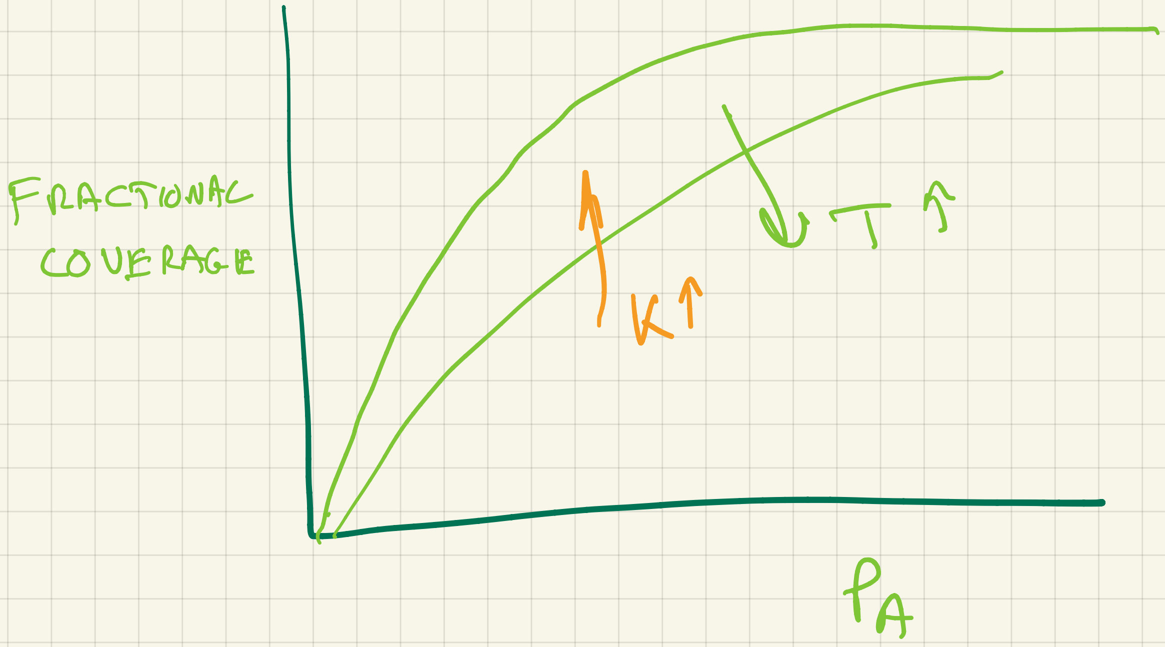
$$[S_0] = [S] + [A_{AD}]$$

$$[S_0] = \frac{[A_{AD}]}{K^A_{EQ} P_A} + [A_{AD}] = \frac{1 + K^A_{EQ} P_A}{K^A_{EQ} P_A} [A_{AD}]$$

$$\Theta_A = \frac{[A_{AD}]}{[S_0]}$$

FRACTIONAL COVERAGE

$$\Theta_A = \frac{K^A_{EQ} P_A}{1 + K^A_{EQ} P_A}$$



$$\Delta G = \Delta H - T\Delta S$$

↑ NEGATIVE

↑ MOST LIKELY NEGATIVE