

# ORIGINS OF SELECTIVITY. PART I

## EQUILIBRIUM SELECTIVITY

- SELECTIVITY BY SPECIES - E.G. PROTON; OXYGEN, ETC.
- SELECTIVITY BY GROUP- E.G. VOLATILE HYDROCARBONS:  
ENZYME INHIBITORS, ETC
- SELECTIVITY BY FUNCTION- E.G. POISONS; EXPLOSIVES; HERBICIDES....

**EQUILIBRIUM SELECTIVITY DOES NOT APPLY TO  
THERMAL SENSORS!**

# INTERACTION ENERGIES

Type of Interaction	Distance Relationship [nm]	Order of Magnitude (KJ / mole)
covalent bond	0.08 – 0.2	50 - 200
hydrogen bond	0.1 – 0.3	20 - 150
donor-acceptor	0.1 – 0.3	50 - 150
Hydrophobic bond		
CH <sub>3</sub> - CH <sub>3</sub>	< 0.1	(1.2) *
Φ <sup>+</sup> - Φ <sup>-</sup>	< 0.1	(5) *
ion-ion	$E \propto \frac{z_1 z_2}{Dr}$	90
Ion - dipole	$E \propto \frac{z_1 \mu_2 \cos \Theta}{Dr^2}$	15
Dipole – dipole (stationary)	$E \propto \frac{\mu_1 \mu_2}{Dr^3}$	+2 —
Dipole - induced dipole	$E \propto \frac{z_1 \alpha_2}{Dr^4}$	2
Dispersion	$E \propto \frac{\alpha_1 \alpha_2}{r^6} \frac{I_1 I_2}{I_1 + I_2}$	2-4

# CHARACTERISTICS OF SENSING INTERACTIONS

- WEAK 1 - 100 KJ/MOL
- SHORT RANGE (0.1 - 10 nm)
- MULTIPLE
- DEPENDENT ON ENVIRONMENT (I.E. WATER, TEMPERATURE, IONIC STRENGTH, ETC.)
- BOTH ENTHALPY AND ENTROPY DRIVEN
- SHAPE SENSITIVE

# SHAPE RECOGNITION

①

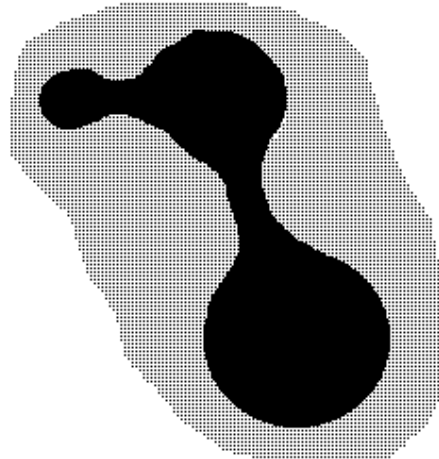
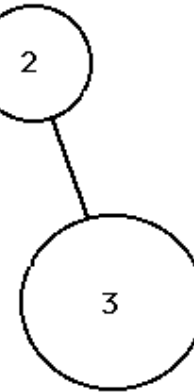
$A = 1$

①—②

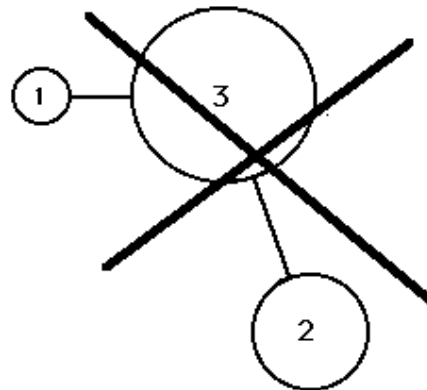
$A = 3$

①—②

$A = 12$



BINDING SITE



A MISFIT

# ENTROPIC INTERACTION

## HYDROPHOBIC BOND

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

$$\Delta S = k \ln \Delta W$$

in vacuum

k - Boltzmann constant

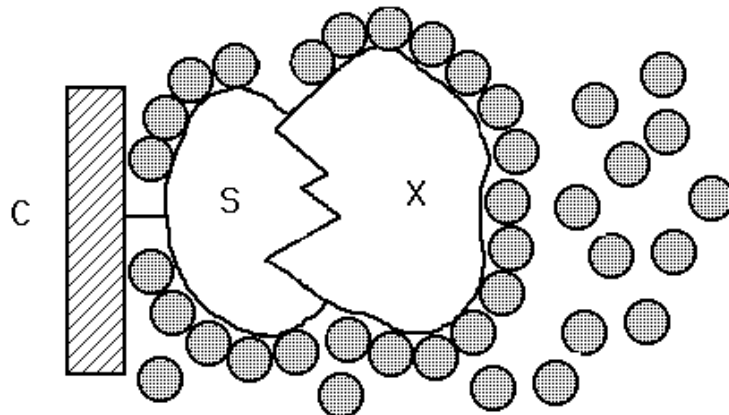
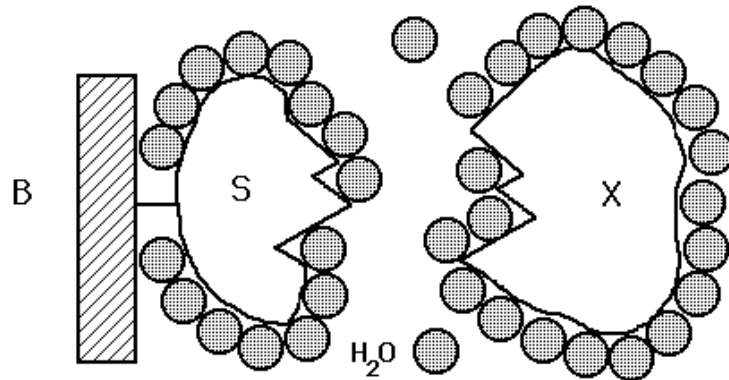
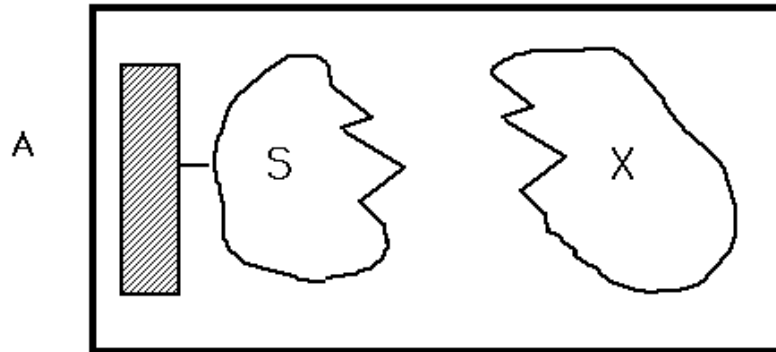
W - “randomness” (probability)

● water molecule

$W = 3 \times 3 = 9$  degrees of freedom

$W = 3 \times 14 = 42$  degrees of freedom

$\Delta W = 33$  - entropy increase



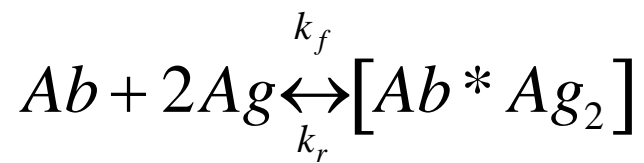
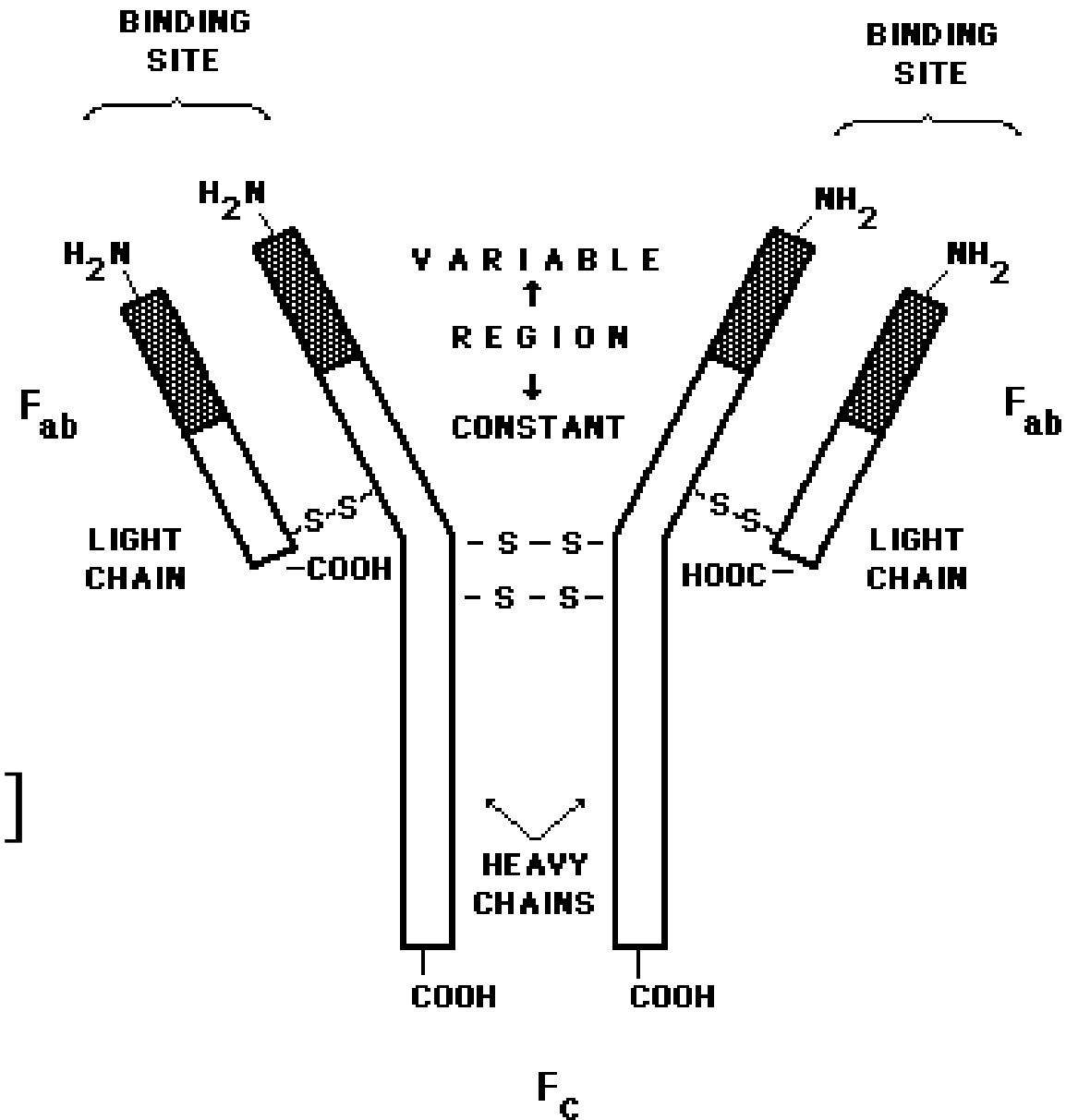
# BIOSELECTIVITY

## GENERAL ATTRIBUTES

- HYDROPHOBIC BOND IS DOMINATING (IgG, DNA)
- HYDROGEN BONDING (DNA;RNA)
- COULOMBIC INTERACTIONS ARE LESS IMPORTANT
- HIGHLY SHAPE-SELECTIVE
- BINDING CONSTANT IS USUALLY TOO STRONG FOR “REVERSIBLE” SENSING OPERATION

BIOLIGAND	USE
Antibodies/antigens	Immunoassays;
Oligonucleotides	DNA (RNA) bioassays
Aptamers	Bioassays
Enzymes	Enzyme sensors
Receptors	Bioassays
Cells & Tissues	Bioassays

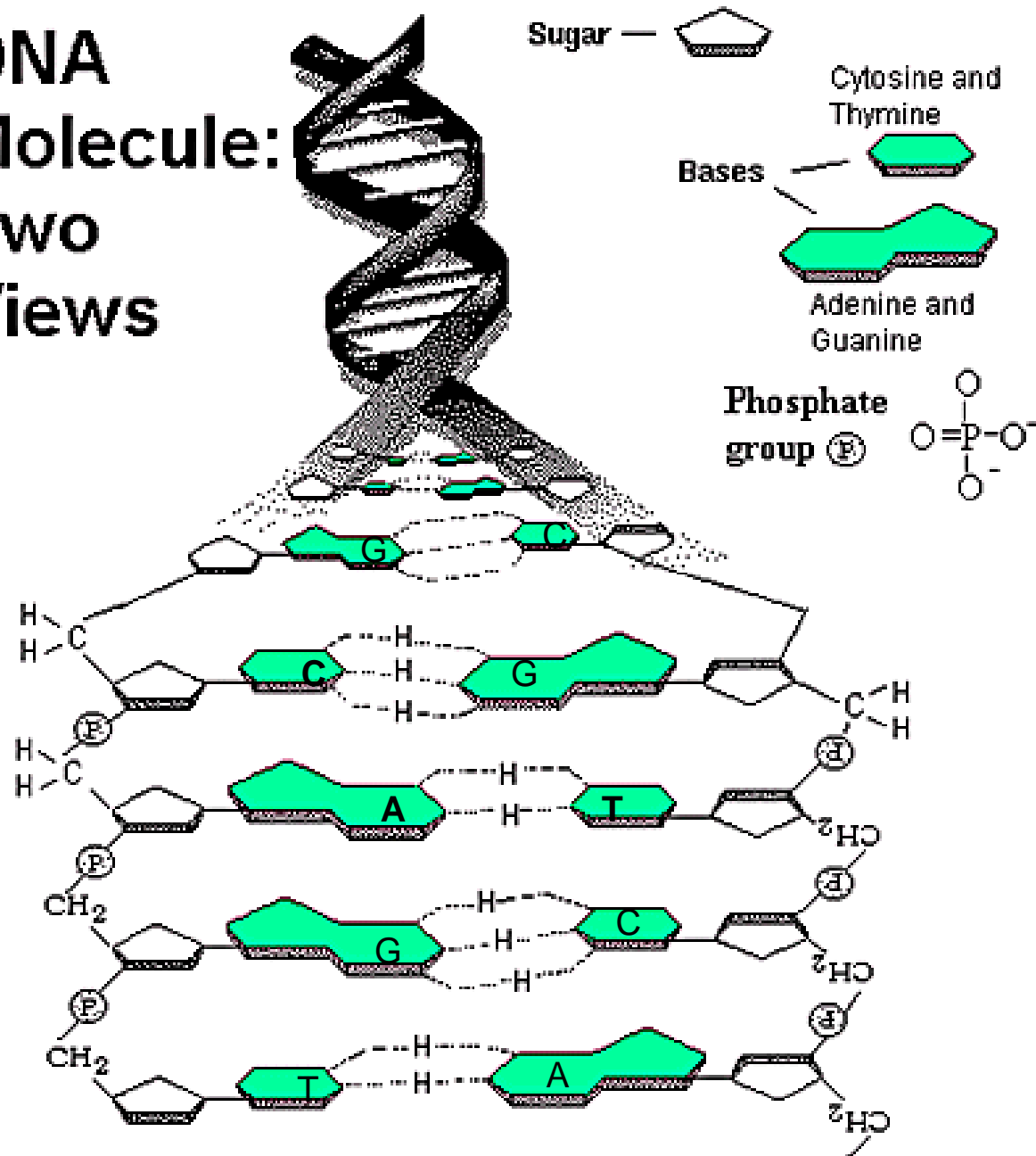
# IMMUNOGLOBULINS



$$K > 10^9 \text{ mol}^{-1}$$

# DNA/RNA

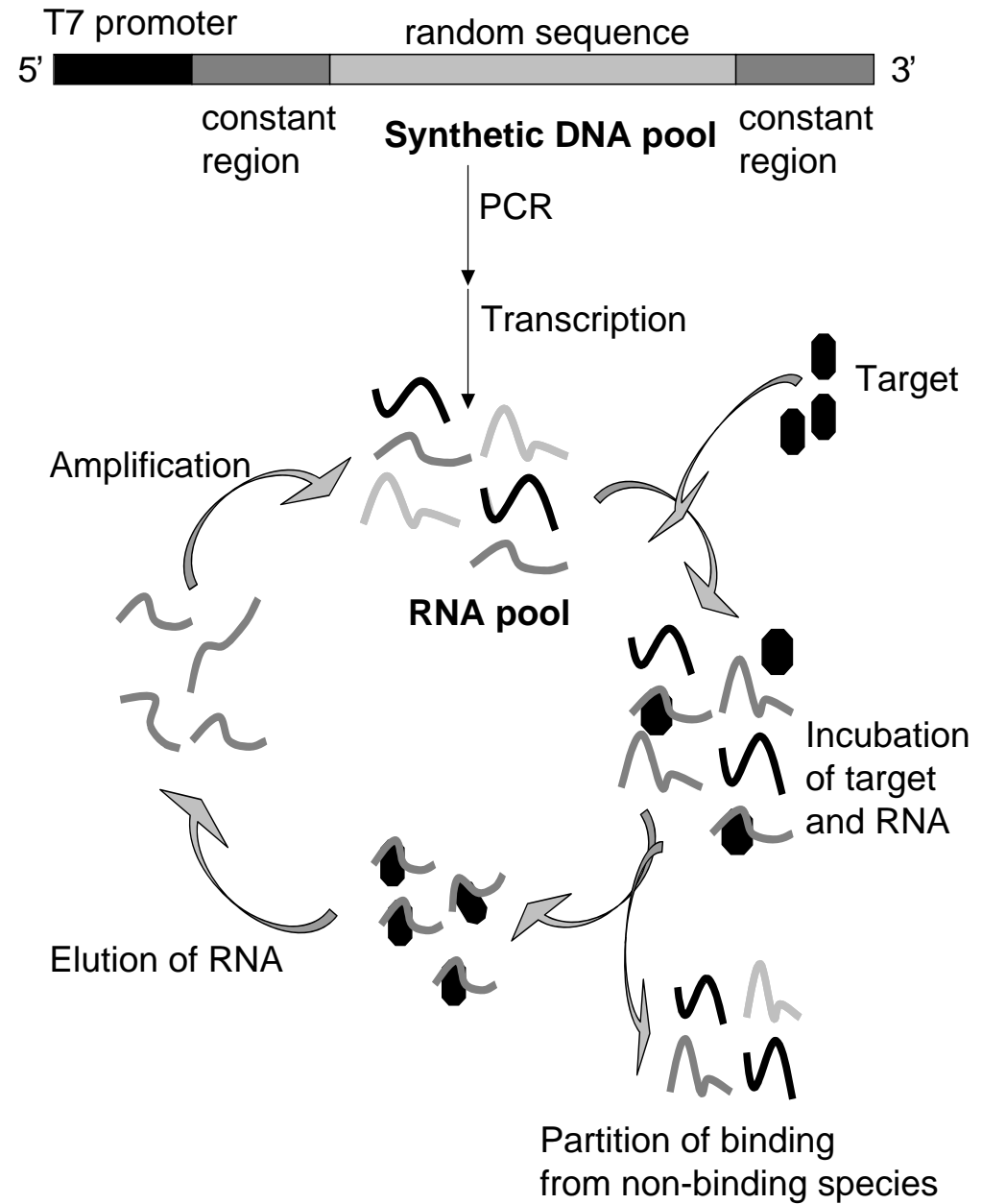
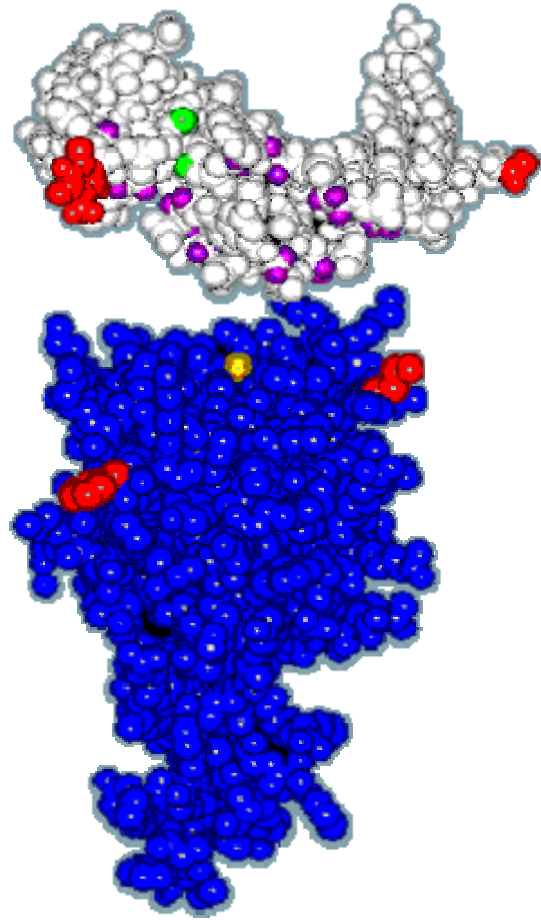
## DNA Molecule: Two Views



# DNA BINDING INTERACTIONS

QuickTime™ and a  
TIFF (LZW) decompressor  
are needed to see this picture.

# APTAMERS



# MOLECULAR IMPRINTING

## GENERAL

QuickTime™ and a  
TIFF (LZW) decompressor  
are needed to see this picture.

# MOLECULAR IMPRINTING

## COVALENT

QuickTime™ and a  
TIFF (LZW) decompressor  
are needed to see this picture.

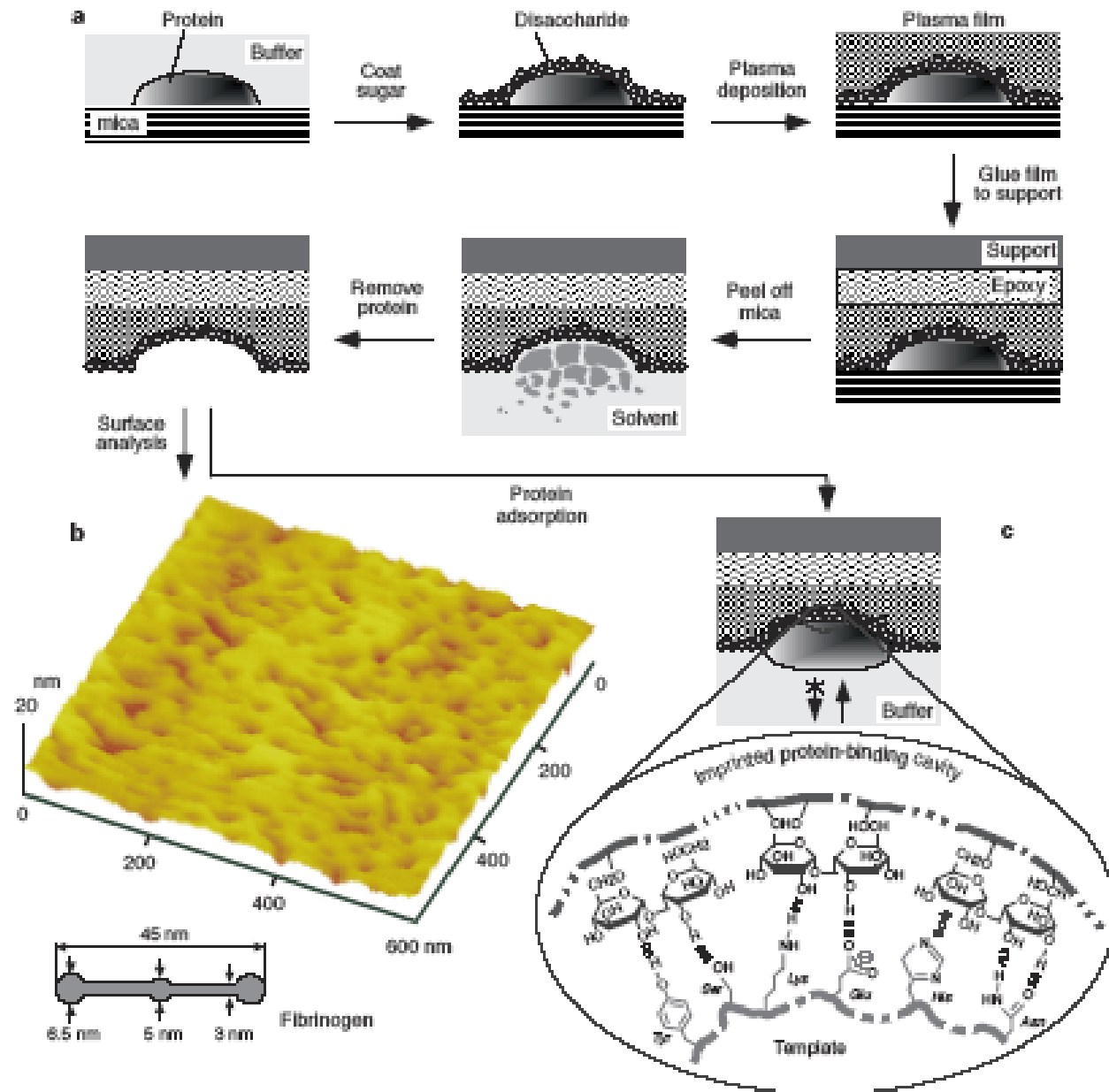
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## NON-COVALENT

QuickTime™ and a  
TIFF (LZW) decompressor  
are needed to see this picture.

# MOLECULAR IMPRINTING

## SURFACE



# SOLUBILITY BASED SELECTIVITY

LINEAR SOLVATION ENERGY RELATIONSHIP:

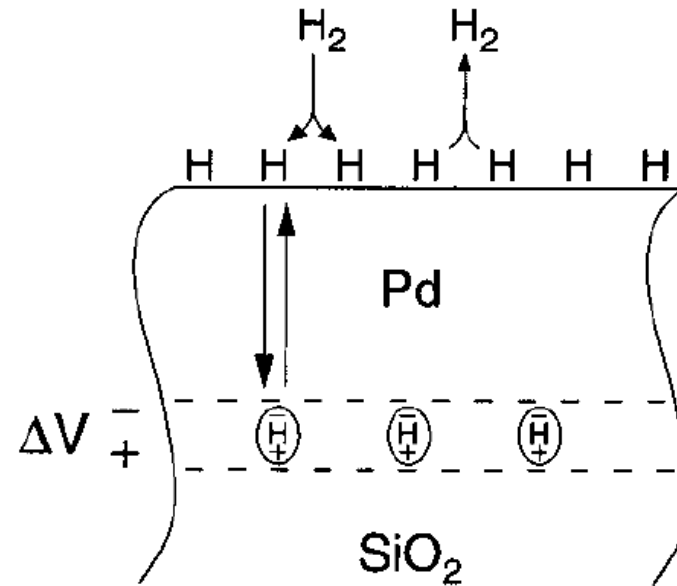
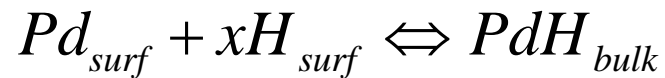
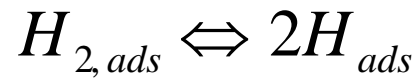
$$\Delta G_s^0 = -\mathfrak{R}T \ln K_s = c + rR_2 + s\pi_2 + a\sum\alpha_2^H + b\sum\beta_2^H + l\text{Log}L^{16}$$

partitioning  
coefficient (GC)      polarizability      polarity      hydrogen  
bonding  
acidic      hydrogen  
bonding  
basic      dispersion

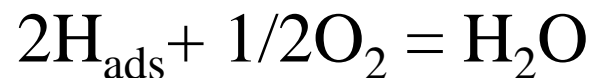
# CHARGE TRANSFER

## IN GAS - SOLID INTERACTIONS

- IN INORGANIC MATERIALS



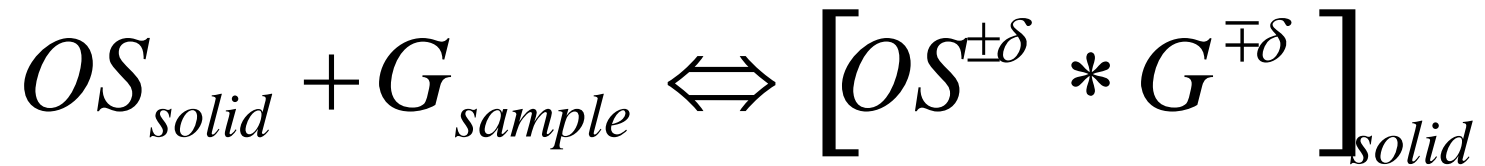
- INTERFERENCE



# CHARGE TRANSFER

## IN GAS - SOLID INTERACTIONS

- IN ORGANIC SEMICONDUCTORS



- EXAMPLE



Electron  
acceptor

Electron  
donor