CH.4 Intermolecular Forces, Corresponding States and Osmotic Systems

Forces of attraction and repulsion between molecules are responsible for the phase transition.

Attractive forces make gases condense to form liquids.

Repulsive forces make condensed matter resist to compression

Classification of intermolecular forces

Electrostatic forces

between charged particles and between permanent dipoles, quadrupoles, etc..

Induction forces

Between permanent dipole (or quadrupoles) and induced dipole

Dispersion (attraction) forces

Specific (chemical) forces

Formation of loose chemical bonds; hydrogen bonds, charge-transfer complexes

4.1 Potential-Energy Functions

Potential energy Γ as a function of intermolecular distance r

$$\boxed{F = -\frac{d\Gamma}{dr}} \qquad (4\text{-}1)$$

4.2 Electrostatic Forces

Coulomb’s law

$$F = \frac{q_i q_j}{4\pi\varepsilon_o r^2} \tag{4-3}$$

$\varepsilon_o = 8.85419\times10^{-12}\ \mathrm{C^2\ J^{-1}\ m^{-1}}$. dielectric permittivity of vacuum

$$\Gamma_{ij} = \frac{q_i q_j}{4\pi\varepsilon_o r}$$

Equivalently

$$\boxed{\Gamma_{ij} = \frac{z_i z_j e^2}{4\pi\varepsilon_o r}} \tag{4-5}$$

$e = 1.60218\times10^{-19}\ \mathrm{C}$ unit charge

For a medium other than vacuum

$$\Gamma_{ij} = \frac{z_i z_j e^2}{4\pi\varepsilon r} \tag{4-5a}$$

$\varepsilon = \varepsilon_o \varepsilon_r$

dielectric constant e.g.) water at 25°C, $\varepsilon_r = 78.41$

Coulomb energy between Cl^- and Na^+ in contact in vacuo

$$\Gamma_{ij} = \frac{(-1)(+1)(1.60218\times10^{-19})^2}{(4\pi)(8.8542\times10^{-12})(0.276\times10^{-9})} = -8.36\times10^{-19}\ \mathrm{J}$$

~ 200 kT

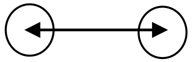
$$kT = (1.38\times10^{-23}\ \mathrm{J\ K^{-1}})\times(300\ \mathrm{K}) = 0.0414\times10^{-19}\ \mathrm{J}$$

is thermal energy (kinetic energy of molecules)

Coulomb energy between Cl^- and Na^+ in contact in water ~ 3kT

Dipole moment

$$\mu = e\,d \qquad (4\text{-}6)$$



$$1\ \mathrm{D} = 3.33569\times10^{-30}\ \mathrm{C\ m} = 10^{-18}\ \mathrm{esu} = 10^{-18}\ (\mathrm{erg\ cm^3})^{1/2}].$$

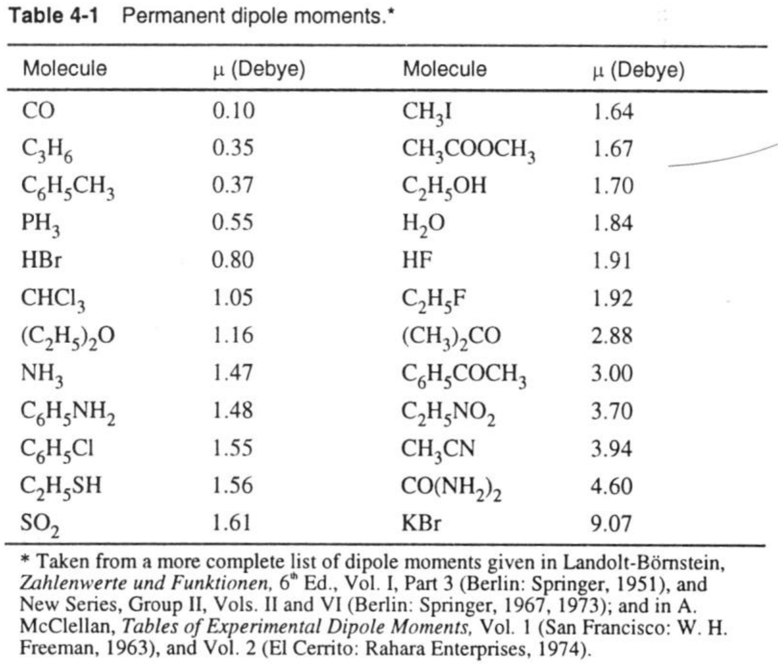


Table 4-1 Permanent dipole moments.*

Molecule	μ (Debye)	Molecule	μ (Debye)
CO	0.10	CH_3I	1.64
C_3H_6	0.35	CH_3COOCH_3	1.67
$C_6H_5CH_3$	0.37	C_2H_5OH	1.70
PH_3	0.55	H_2O	1.84
HBr	0.80	HF	1.91
$CHCl_3$	1.05	C_2H_5F	1.92
$(C_2H_5)_2O$	1.16	$(CH_3)_2CO$	2.88
NH_3	1.47	$C_6H_5COCH_3$	3.00
$C_6H_5NH_2$	1.48	$C_2H_5NO_2$	3.70
C_6H_5Cl	1.55	CH_3CN	3.94
C_2H_5SH	1.56	$CO(NH_2)_2$	4.60
SO_2	1.61	KBr	9.07

* Taken from a more complete list of dipole moments given in Landolt-Börnstein, *Zahlenwerte und Funktionen,* 6th Ed., Vol. I, Part 3 (Berlin: Springer, 1951), and New Series, Group II, Vols. II and VI (Berlin: Springer, 1967, 1973); and in A. McClellan, *Tables of Experimental Dipole Moments,* Vol. 1 (San Francisco: W. H. Freeman, 1963), and Vol. 2 (El Cerrito: Rahara Enterprises, 1974).

→ →

Potential energy of two permanent dipoles ($r >> d_i, r >> d_j$)

$$\Gamma_{ij} = -\frac{\mu_i \mu_j}{4\pi\varepsilon_0 r^3}[2\cos\theta_i \cos\theta_j - \sin\theta_i \sin\theta_j \cos(\phi_i - \phi_j)] \qquad (4\text{-}7)$$

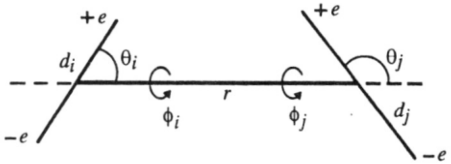


Figure 4-1 Orientation of two dipoles.

a maximum → ←

a minimum → →

Average potential energy by averaging over all orientation is

$$\boxed{\bar{\Gamma}_{ij} = -\frac{2}{3}\frac{\mu_i^2 \mu_j^2}{(4\pi\varepsilon_0)^2 kT r^6} + \cdots} \qquad (4\text{-}8)^{6}$$

attractive $\propto r^{-6}$

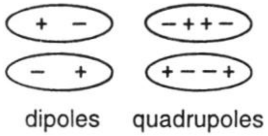
where average is taken with Boltzmann weight

$$\bar{\Gamma} = \frac{\int \Gamma[\exp(-\Gamma / kT)]\, d\Omega}{\int [\exp(-\Gamma / kT)]\, d\Omega}$$

and

$$d\Omega = \sin\theta_1 \sin\theta_2\, d\theta_1\, d\theta_2\, d\phi, \text{ where } \phi = \phi_1 - \phi_2$$

Quadrupole moment



For example, CO_2) has no dipole moment but has a quadrupole that is strong enough to affect cthermodynamic properties

$$Q = \sum_i e_i d_i^2 \tag{4-9}$$

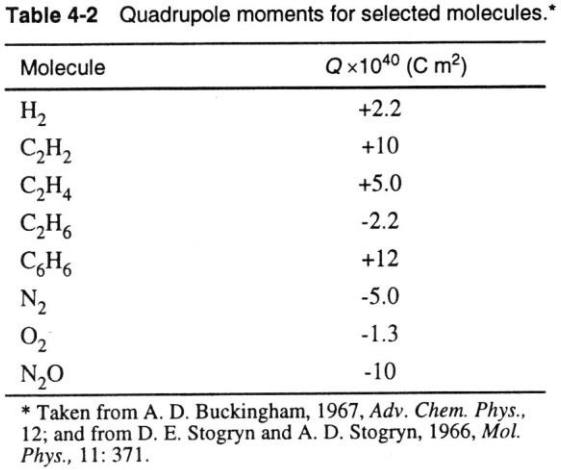


Table 4-2 Quadrupole moments for selected molecules.*

Molecule	$Q \times 10^{40}$ (C m^2)
H_2	+2.2
C_2H_2	+10
C_2H_4	+5.0
C_2H_6	-2.2
C_6H_6	+12
N_2	-5.0
O_2	-1.3
N_2O	-10

* Taken from A. D. Buckingham, 1967, *Adv. Chem. Phys.*, 12; and from D. E. Stogryn and A. D. Stogryn, 1966, *Mol. Phys.*, 11: 371.

Experimental determination of Q is difficult.

Average potential between **dipole i … quadrupole j**

$$\overline{\Gamma}_{ij} = -\frac{\mu_i^2 Q_j^2}{(4\pi\varepsilon_o)^2 kT r^8} + \cdots \qquad (4\text{-}10)$$

attractive $\propto r^{-8}$

Average potential between **quadrupole i … quadrupole j**

$$\overline{\Gamma}_{ij} = -\frac{7}{40}\frac{Q_i^2 Q_j^2}{(4\pi\varepsilon_o)^2 kT r^{10}} + \cdots \qquad (4\text{-}11)$$

attractive $\propto r^{-10}$

Higher order mutipoles have less effect on thermodynamic properties
as the resulting intermolecular potential decay faster with higher inverse power of *r*.

4.3 Polarizability and Induced Dipoles

When a nonpolar molecule such as argon or methane is subjected to an electric field, the electrons are displaced resulting in an induced dipole moment.

Induced dipole moment proportional to the electric field *E*

$$\mu^{i} = \alpha E \qquad (4\text{-}12)$$

α is the polarizability measuring how easily electrons can be displaced by an electric field

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_o}$$

polarizability volume [vol], ~ roughly the size of molecule

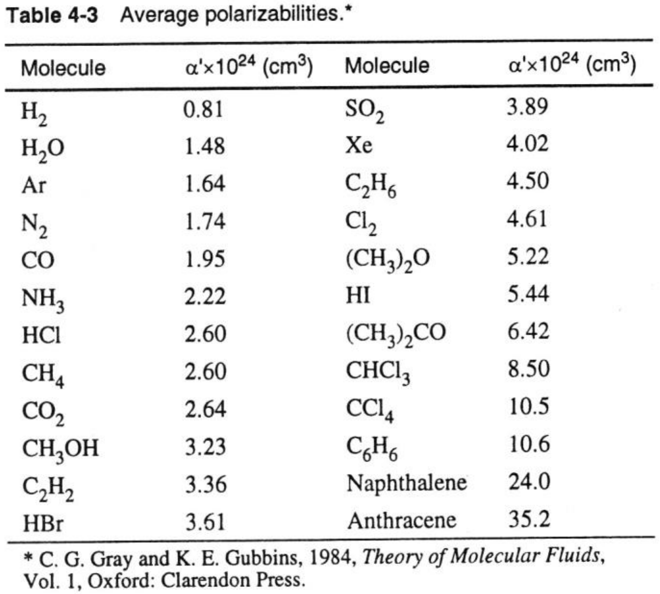


Table 4-3 Average polarizabilities.*

Molecule	$\alpha' \times 10^{24}$ (cm^3)	Molecule	$\alpha' \times 10^{24}$ (cm^3)
H_2	0.81	SO_2	3.89
H_2O	1.48	Xe	4.02
Ar	1.64	C_2H_6	4.50
N_2	1.74	Cl_2	4.61
CO	1.95	$(CH_3)_2O$	5.22
NH_3	2.22	HI	5.44
HCl	2.60	$(CH_3)_2CO$	6.42
CH_4	2.60	$CHCl_3$	8.50
CO_2	2.64	CCl_4	10.5
CH_3OH	3.23	C_6H_6	10.6
C_2H_2	3.36	Naphthalene	24.0
HBr	3.61	Anthracene	35.2

* C. G. Gray and K. E. Gubbins, 1984, *Theory of Molecular Fluids*, Vol. 1, Oxford: Clarendon Press.

Orientation averaged potential between between **induced dipole … permanent dipole**

$$\bar{\Gamma}_{ij} = -\frac{\alpha_i \mu_j^2}{(4\pi\varepsilon_0)^2 r^6} \qquad (4\text{-}13)$$

Debye

Potential energy due to induction between **two polar molecules**

$$\boxed{\bar{\Gamma}_{ij} = -\frac{(\alpha_i \mu_j^2 + \alpha_j \mu_i^2)}{(4\pi\varepsilon_0)^2 r^6}} \qquad (4\text{-}14)$$

attractive $\propto r^{-6}$

if two molecules have quadrupole moments

$$\boxed{\bar{\Gamma}_{ij} = -\frac{3}{2}\frac{(\alpha_i Q_j^2 + \alpha_j Q_i^2)}{(4\pi\varepsilon_0)^2 r^8}} \qquad (4\text{-}15)$$

attractive $\propto r^{-8}$

4.4 Intermolecular Forces between Nonpolar Molecules

In 1930, London (not city!) showed that nonpolar molecules are nonpolar only when viewed over a period of time.

The oscillations of the electrons about the nucleus cause a temporary dipole moment.

The resulting attractive force is called the *induced dipole- induced dipole force* (or *dispersion force*).

With some assumptions, London showed

$$\Gamma_{ij} = -\frac{3}{2}\frac{\alpha_i\alpha_j}{(4\pi\varepsilon_o)^2 r^6}\left(\frac{h\nu_{0i}\,h\nu_{0j}}{h\nu_{0i}+h\nu_{0j}}\right) \qquad (4\text{-}16)^{10}$$

h is Planck's constant, ν_0 is a characteristic electronic frequency.

Relation to the index of refraction n

$$n-1 = \frac{c}{\nu_0^2-\nu^2} \qquad (4\text{-}17)$$

$h\nu_0$ is nearly equal to the first ionization potential.

$$\boxed{\Gamma_{ij} = -\frac{3}{2}\frac{\alpha_i\alpha_j}{(4\pi\varepsilon_o)^2 r^6}\left(\frac{I_i I_j}{I_i+I_j}\right)} \qquad (4\text{-}18)$$

For the same species

$$\Gamma_{ii} = -\frac{3}{4}\frac{\alpha_i^2 I_i}{(4\pi\varepsilon_o)^2 r^6} \qquad (4\text{-}19)$$

attractive $\propto r^{-6}$

The dispersion potential energy is more sensitive to the polarizability that it is to the ionization potential.

I does not change much from one molecule to another.

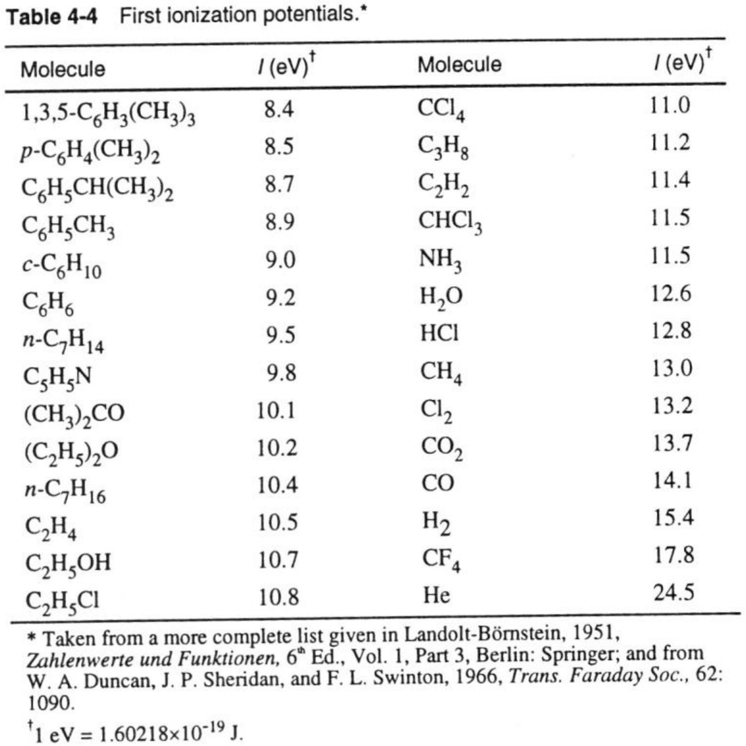


Table 4-4 First ionization potentials.*

Molecule	I (eV)[†]	Molecule	I (eV)[†]
1,3,5-$C_6H_3(CH_3)_3$	8.4	CCl_4	11.0
p-$C_6H_4(CH_3)_2$	8.5	C_3H_8	11.2
$C_6H_5CH(CH_3)_2$	8.7	C_2H_2	11.4
$C_6H_5CH_3$	8.9	$CHCl_3$	11.5
c-C_6H_{10}	9.0	NH_3	11.5
C_6H_6	9.2	H_2O	12.6
n-C_7H_{14}	9.5	HCl	12.8
C_5H_5N	9.8	CH_4	13.0
$(CH_3)_2CO$	10.1	Cl_2	13.2
$(C_2H_5)_2O$	10.2	CO_2	13.7
n-C_7H_{16}	10.4	CO	14.1
C_2H_4	10.5	H_2	15.4
C_2H_5OH	10.7	CF_4	17.8
C_2H_5Cl	10.8	He	24.5

* Taken from a more complete list given in Landolt-Börnstein, 1951, *Zahlenwerte und Funktionen,* 6th Ed., Vol. 1, Part 3, Berlin: Springer; and from W. A. Duncan, J. P. Sheridan, and F. L. Swinton, 1966, *Trans. Faraday Soc.,* 62: 1090.

[†] 1 eV = 1.60218×10^{-19} J.

(4-18) and (4-19) can be written as

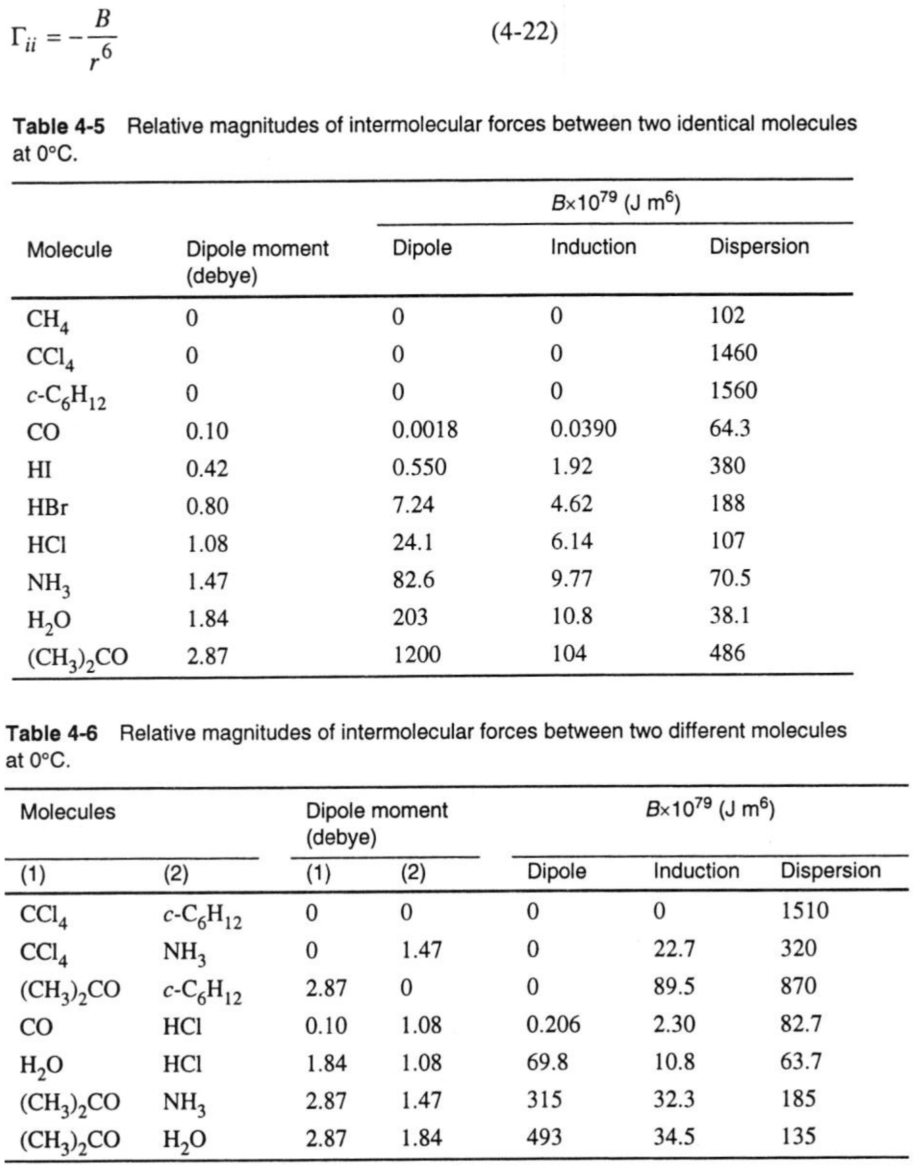
$$\Gamma_{ij} = k' \frac{\alpha_i \alpha_j}{r^6} \qquad \Gamma_{ii} = k' \frac{\alpha_i^2}{r^6} \qquad \Gamma_{jj} = k' \frac{\alpha_j^2}{r^6} \tag{4-20}$$

Thus

$$\Gamma_{ij} = (\Gamma_{ii}\,\Gamma_{jj})^{1/2} \tag{4-21}$$

A theoretical reason for the geometrical mean rule.

Relative magnitude of dipole, induction, and dispersion forces ($\propto r^{-6}$)



$$\Gamma_{ii} = -\frac{B}{r^6} \tag{4-22}$$

Table 4-5 Relative magnitudes of intermolecular forces between two identical molecules at 0°C.

Molecule	Dipole moment (debye)	$B \times 10^{79}$ (J m^6) Dipole	Induction	Dispersion
CH_4	0	0	0	102
CCl_4	0	0	0	1460
$c\text{-}C_6H_{12}$	0	0	0	1560
CO	0.10	0.0018	0.0390	64.3
HI	0.42	0.550	1.92	380
HBr	0.80	7.24	4.62	188
HCl	1.08	24.1	6.14	107
NH_3	1.47	82.6	9.77	70.5
H_2O	1.84	203	10.8	38.1
$(CH_3)_2CO$	2.87	1200	104	486

Table 4-6 Relative magnitudes of intermolecular forces between two different molecules at 0°C.

Molecules		Dipole moment (debye)		$B \times 10^{79}$ (J m^6)		
(1)	(2)	(1)	(2)	Dipole	Induction	Dispersion
CCl_4	$c\text{-}C_6H_{12}$	0	0	0	0	1510
CCl_4	NH_3	0	1.47	0	22.7	320
$(CH_3)_2CO$	$c\text{-}C_6H_{12}$	2.87	0	0	89.5	870
CO	HCl	0.10	1.08	0.206	2.30	82.7
H_2O	HCl	1.84	1.08	69.8	10.8	63.7
$(CH_3)_2CO$	NH_3	2.87	1.47	315	32.3	185
$(CH_3)_2CO$	H_2O	2.87	1.84	493	34.5	135

Theory suggests that repulsion potential should be exponential function of *r*.

But for mathematical convenience,

$$\Gamma = \frac{A}{r^n} \tag{4-23}$$

$$\boxed{\Gamma_{\text{total}} = \Gamma_{\text{repulsive}} + \Gamma_{\text{attractive}} = \frac{A}{r^n} - \frac{B}{r^m}} \tag{4-24}$$

proposed by Mie.

Lennard-Jones potential: $n = 12$, $m = 6$

4.5 Mie's Potential-Energy Functions for Nonpolar Molecules

Mie's potential

$$\Gamma = \frac{\varepsilon\left(n^n / m^m\right)^{1/(n-m)}}{n-m}\left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m\right] \qquad (4\text{-}25)$$ [13]

where $\varepsilon = -\Gamma_{\min}$ and $\Gamma(\sigma) = 0$

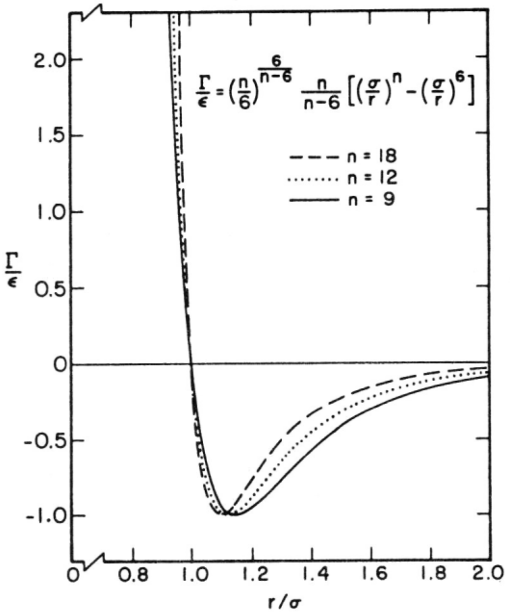


Figure 4-2 Three forms of Mie's potential for simple, nonpolar molecules.

Lennard-Jones (LJ) potential: n = 12, m = 6

$$\boxed{\Gamma = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]} \tag{4-26}$$

Two parameter model, LJ potential sometimes too repulsive

How to determine potential parameters

Spectroscopic and molecular-beam experiment

Compressibility and specific heat data

Viscosity, self-diffusivity

Second virial coefficient

4.6 Structural Effects

When molecules are nonspherical, there is the effect of molecular shape on thermodynamic effect.

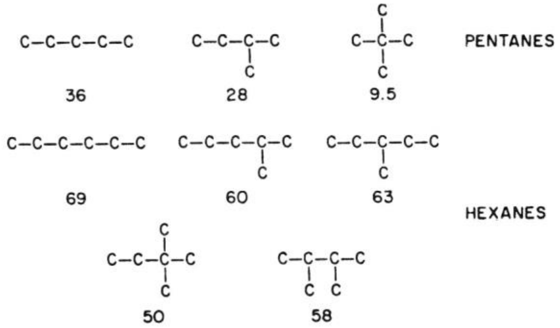
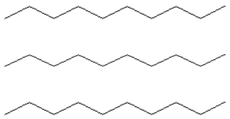


Figure 4-3 Boiling points (in °C) of some alkane isomers.

A branched isomer has a lower boiling point that a straight chain.

With branching, the surface area (for intermolecular contact) decreases as it becomes more spherical, and intermolecular attraction between two molecules becomes weaker.

There is an orientational order among long chains of n-alkane.



Mixing liquids of different degrees of order brings about a net decrease of attraction and order, positive $\Delta_{mix}h$ and $\Delta_{mix}s$

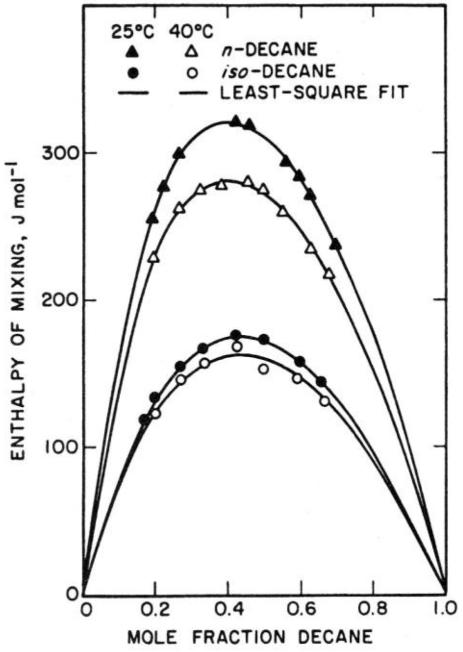
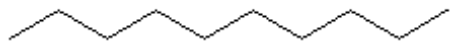
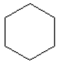
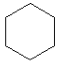


Figure 4-4 Effect of molecular structure on enthalpy of mixing: cyclohexane/*n*-decane and cyclohexane/isodecane (2,6-dimethyl octane).

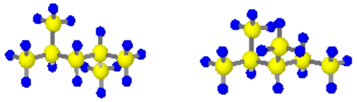
Upon mixing with cyclohexane (a globular molecule), short-range orientational order is destroyed.

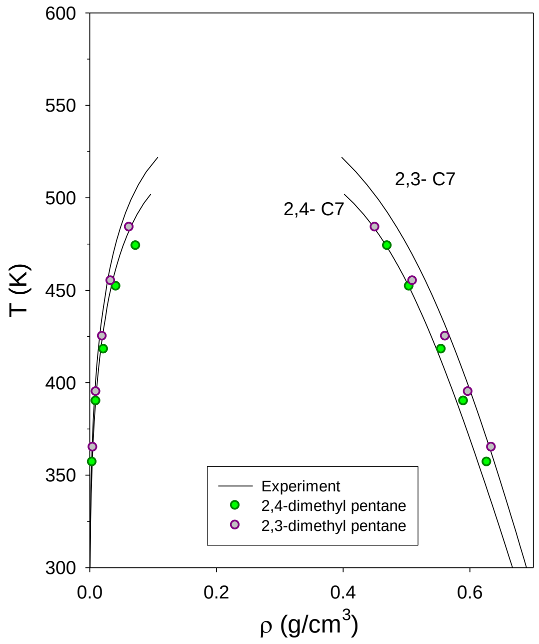
The mixing process requires more energy with linear alkanes.

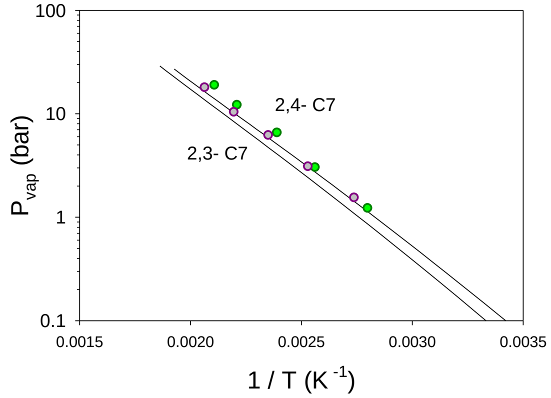
decane  + cyclohexane 

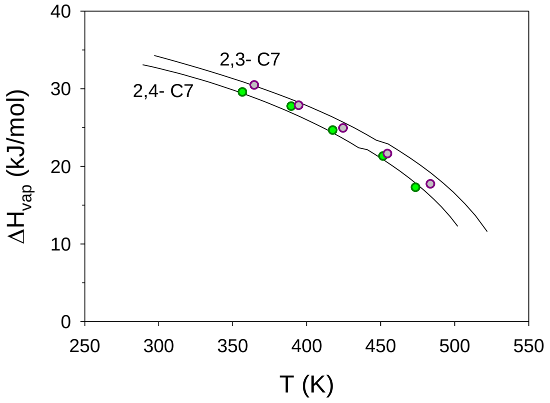
isodecane  + cyclohexane 

2,4-dimethylpentane and 2,3-dimethylpentane









2,4-dimethylpentane is more bulky (more spherical), and is less efficient for packing (lower liquid density).

4.7 Specific (Chemical) Forces

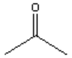
Examples of chemical effects on thermodynamics

The solubility of silver chloride in water rises by several orders of magnitude with adding ammonia.

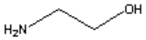
Formation of a silver/ammonia complex

Acetone is a better solvent for acetylene than ethylene.

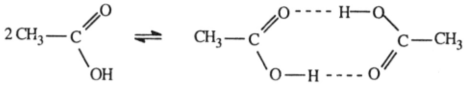
Formation of hydrogen bond with carbonyl oxygen



Absorption of CO_2 (acidic solute) in ethonal amine (basic solute)



Association: the tendency of molecules to form polymers



Dimerization of acetic acid

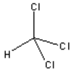
Methanol exists as dimer, trimer, and tetramer

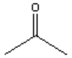
Solvation: the tendency of molecules of different species to form complexes

Sulfur trioxide (SO_3) in water forms sulfuric acid (H_2SO_4)

Weaker solvation

Chloroform/acetone solution

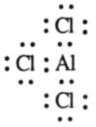


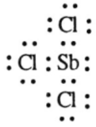


Hydrogen bonding between H…O

Negative deviation from Raoult’s law

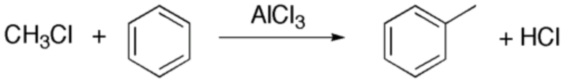
Aluminum trichloride solvates easily with an electron donor whereas atimony trichloride does not.





(saturated electronic structure)

Aluminum trichloride is an excellent catalyst for Friedel-Crafts reaction



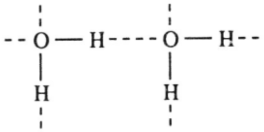
4.7 Hydrogen Bonds

X-H…Y (Y= F, O, N) acids, alcohols, amines

Hydrogen fluoride vapor

associated up to hexamer

Water



coordination number ~ 4 in ice crystal

Characteristic properties of hydrogen bonds

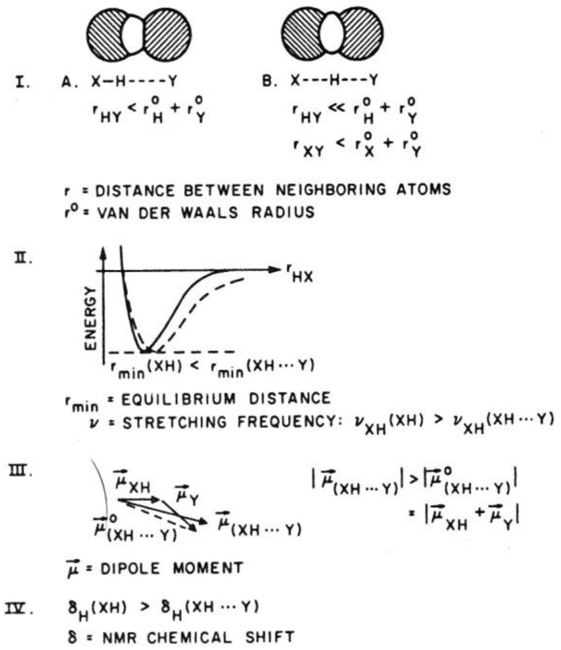


Figure 4-5 Characteristic properties of hydrogen-bonded systems: (I) intermolecular geometries: (A) ordinary, (B) strong hydrogen bonds; (II) vibrational spectra, XH stretching frequencies; (III) increase in polarity on complex formation; (IV) NMR deshielding effect observed at protons participating in hydrogen bonds. (P. Schuster, 1978, *The Fine Structure of the Hydrogen Bond in Intermolecular Interactions from Diatomics to Biopolymers*, B. Pullman, Ed., New York: Wiley & Sons).

I. H-bond distance is smaller than the sum of VDW radii.

II. X-H stretching at lower frequencies

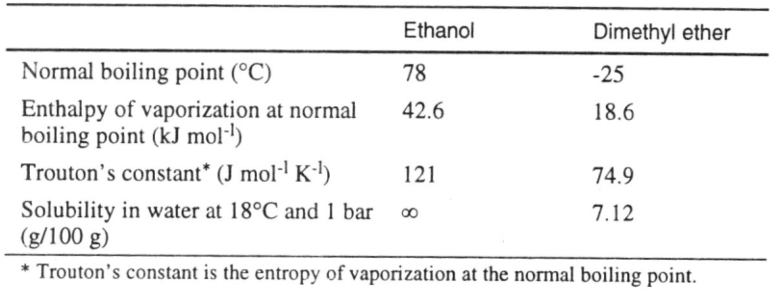
III. Increase of dipole moment

IV. Smaller NMR chemical shift of protons

The effect on physical properties

C_2H_6O isomers  (H-bond) 

Table 4-8 Some properties of the isomers ethanol and dimethyl ether.



	Ethanol	Dimethyl ether
Normal boiling point (°C)	78	-25
Enthalpy of vaporization at normal boiling point (kJ mol^{-1})	42.6	18.6
Trouton's constant* (J mol^{-1} K^{-1})	121	74.9
Solubility in water at 18°C and 1 bar (g/100 g)	∞	7.12

* Trouton's constant is the entropy of vaporization at the normal boiling point.

When ethanol (hydrogen bonded substance) is dissolved in cyclohexane (nonpolar solvent), hydrogen bonds are broken.

$$n\,A \leftrightarrow A_n$$

In the limit of infinite dilution, ethanol exists as monomers.

The fraction of monomers decreases with the increasing concentration.

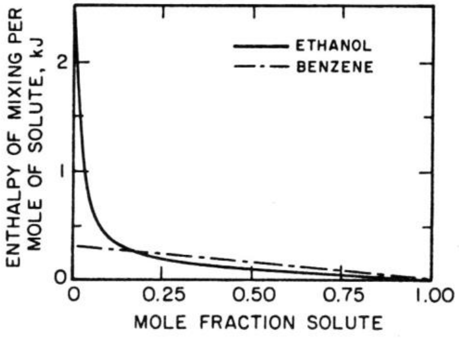


Figure 4-7 Hydrogen bonding in solution. Enthalpic effects for two chemically different solutes in cyclohexane at 20°C.

When ethanol is dissolved in “inert” solvent, breaking of hydrogen bonding requires absorption of energy (positive $\Delta_{mix}h$), which occurs at low concentration of solute.
But benzene does not show such a drastic dependence on the solute concentration.

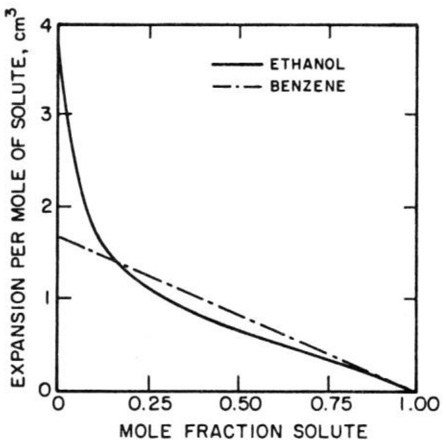
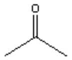
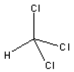


Figure 4-8 Hydrogen bonding in solution. Volumetric effects for two chemically different solutes in *n*-hexane at 6°C.

Because a hydrogen bonded network is compact, upon its breaking (ethanol at low concentration) there is a volume expansion of the mixture.

Hydrogen bonding between dissimilar molecules

Acetone  and chloroform 

The partial pressures for acetone/chloroform mixture is lower than those calculated from Raoult’s low. But, a negative deviation from ideality is not a completely convincing evidence for the formation of complex.

Measurement of freezing point

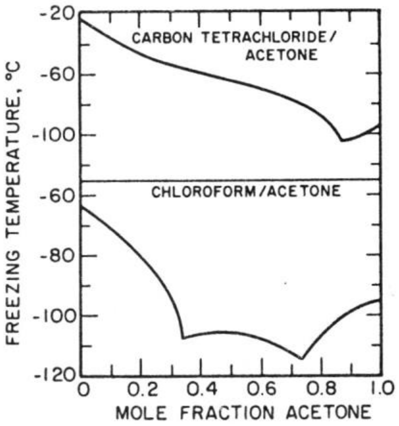
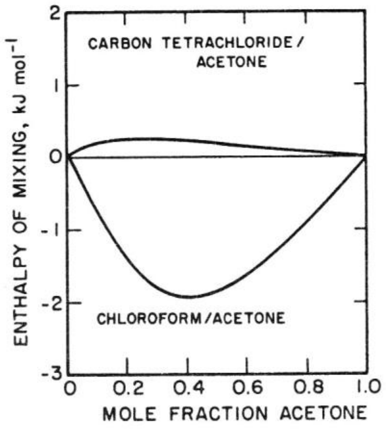


Figure 4-9 Evidence for hydrogen bonds: Freezing-point data.

Higher T_f means stronger interactions in the solid phase.

The maximum T_f at 50 mol % for acetone/chloroform mixture indicates that the compound $(CH_3)_2CO\ldots HCCl_3$ exists in the solid state.

Enthalpy of mixing



Heat is absorbed.

Heat is liberated due to the formation of hydrogen bond

Figure 4-10 Evidence for hydrogen bonds: Enthalpy-of-mixing data.

$$(CH_3)_2C{=}O + HCCl_3 \rightleftharpoons (CH_3)_2C{=}O - - - HCCl_3$$

Estimated Δh of hydrogen bond formation ~ 11.3 kJ mol^{-1}

c.f.) Thermal energy (RT) at 25°C ~ 2.5 kJ mol^{-1}

4.9 Electron Donor-Electron Acceptor Complexes (or charge-transfer complex)

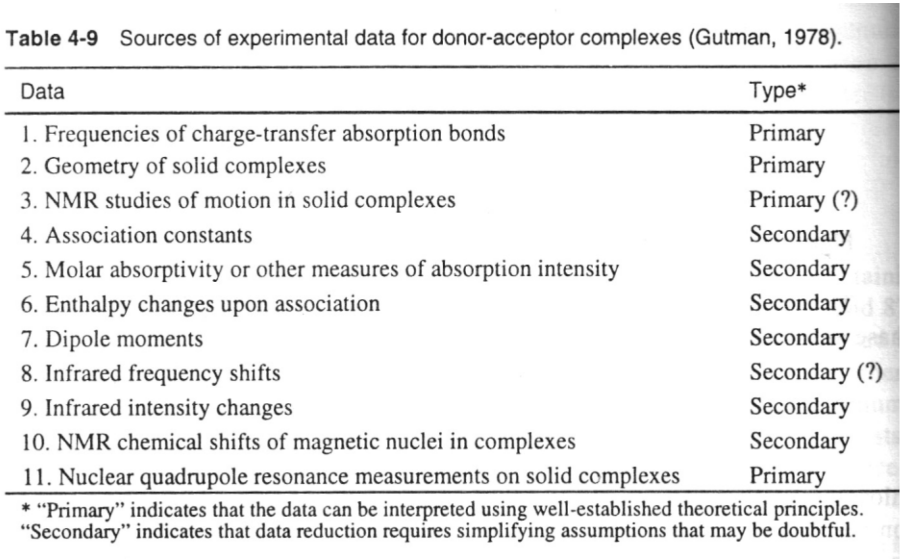


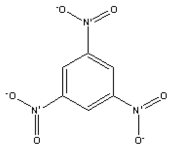
Table 4-9 Sources of experimental data for donor-acceptor complexes (Gutman, 1978).

Data	Type*
1. Frequencies of charge-transfer absorption bonds	Primary
2. Geometry of solid complexes	Primary
3. NMR studies of motion in solid complexes	Primary (?)
4. Association constants	Secondary
5. Molar absorptivity or other measures of absorption intensity	Secondary
6. Enthalpy changes upon association	Secondary
7. Dipole moments	Secondary
8. Infrared frequency shifts	Secondary (?)
9. Infrared intensity changes	Secondary
10. NMR chemical shifts of magnetic nuclei in complexes	Secondary
11. Nuclear quadrupole resonance measurements on solid complexes	Primary

* "Primary" indicates that the data can be interpreted using well-established theoretical principles. "Secondary" indicates that data reduction requires simplifying assumptions that may be doubtful.

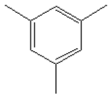
Complex formation between trinitrobenzene and aromatic compound

trinitrobenzene

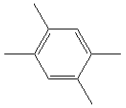


(electron acceptor)

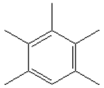
mesitylene



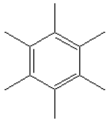
durene



pentamethylbenzene



hexamethylbenzene



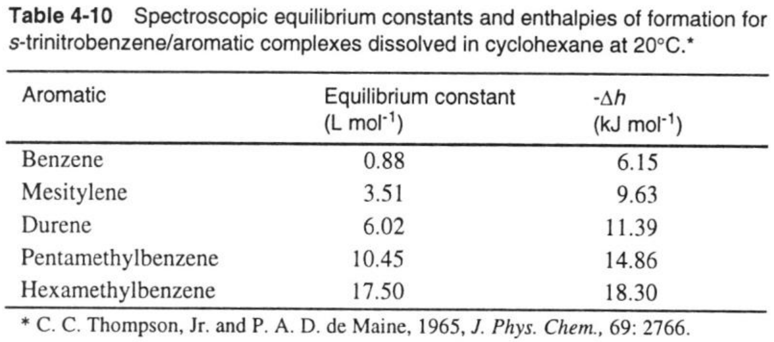


Table 4-10 Spectroscopic equilibrium constants and enthalpies of formation for *s*-trinitrobenzene/aromatic complexes dissolved in cyclohexane at 20°C.*

Aromatic	Equilibrium constant (L mol^{-1})	$-\Delta h$ (kJ mol^{-1})
Benzene	0.88	6.15
Mesitylene	3.51	9.63
Durene	6.02	11.39
Pentamethylbenzene	10.45	14.86
Hexamethylbenzene	17.50	18.30

* C. C. Thompson, Jr. and P. A. D. de Maine, 1965, *J. Phys. Chem.*, 69: 2766.

π-electrons on the aromatic ring become more easily displaced with more methyl groups.

Complex stability rises with the number of methyl groups on the benzene ring.

Complexes of aromatics with polar solvents

Saturated hydrocarbons do not form complex with polar solvent

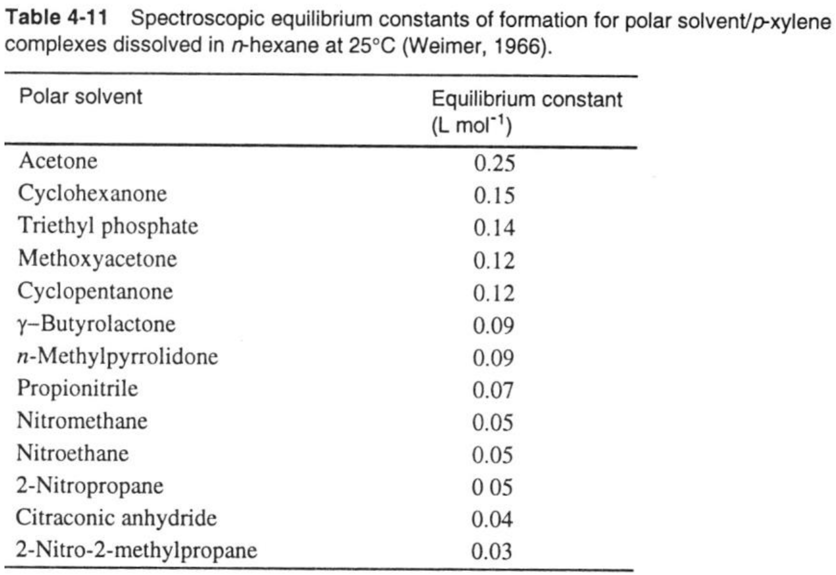
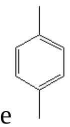


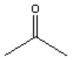
Table 4-11 Spectroscopic equilibrium constants of formation for polar solvent/*p*-xylene complexes dissolved in *n*-hexane at 25°C (Weimer, 1966).

Polar solvent	Equilibrium constant ($L\ mol^{-1}$)
Acetone	0.25
Cyclohexanone	0.15
Triethyl phosphate	0.14
Methoxyacetone	0.12
Cyclopentanone	0.12
γ–Butyrolactone	0.09
n-Methylpyrrolidone	0.09
Propionitrile	0.07
Nitromethane	0.05
Nitroethane	0.05
2-Nitropropane	0 05
Citraconic anhydride	0.04
2-Nitro-2-methylpropane	0.03

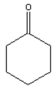
p-xylene



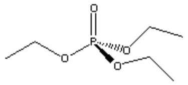
acetone



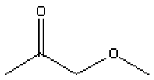
cyclohexanone



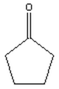
triethyl phosphate



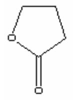
methoxyacetone



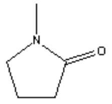
cyclopentanone



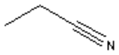
γ-butyrolactone



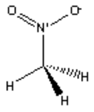
n-methylpyrrolidone



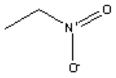
propionitrile



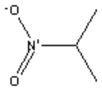
nitromethane



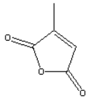
nitroethane



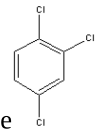
2-nitropropane

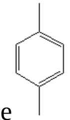
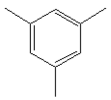


citraconic anhydride



Evidence of complex formation from thermo data

1,2,4-trichlorobenzene 

with benzene, toluene, p-xylene  mesitylene 

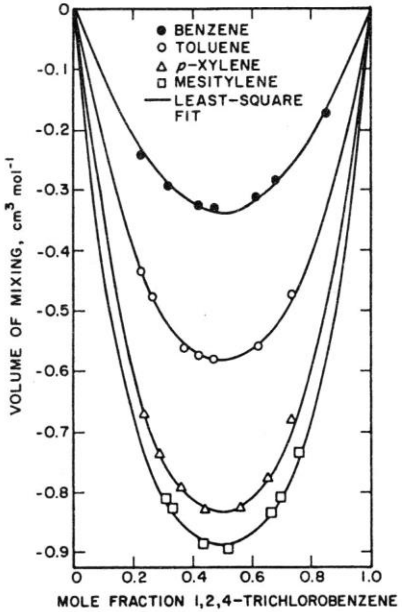


Figure 4-12 Effect of complex formation on volume of mixing. Binary systems containing 1,2,4-trichlorobenzene at 30°C.

The volume of mixing is negative (more favorable interactions between unlike molecules).

The attraction rises with increasing electron-donating power. (the highest for mesitylene)

Volume of mixing (at equimolar compositon) vs. Ionization potential

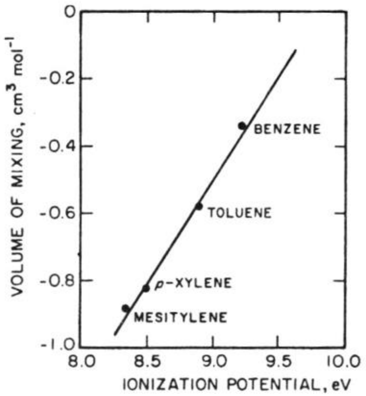


Figure 4-13 Correlation of volume of mixing with the ionization potential of the hydrocarbon. Equimolar 1,2,4-triclorobenzene/hydrocarbon mixtures at 30°C.

Strong correlation is a evidence for a donor-acceptor complex between trichlorobenzene and aromatics.

Misleading interpretation

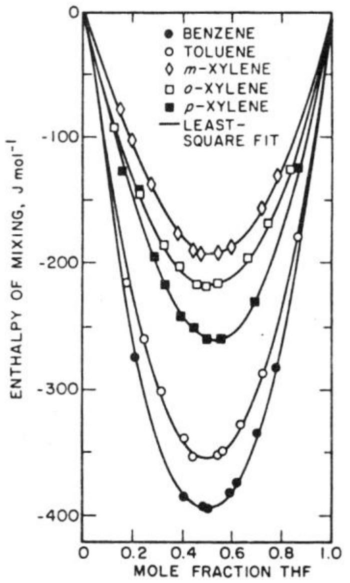


Figure 4-14 Effect of complex formation on enthalpy of mixing. Binary systems containing tetrahydrofuran (THF) at 25°C.

THF 

One might have expected that

$\Delta_{mix}h$ (with benzene) > $\Delta_{mix}h$ (with toluene) > $\Delta_{mix}h$ (with xylene)

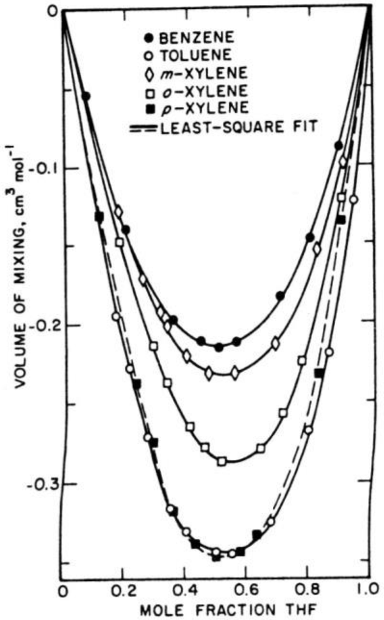


Figure 4-15 Effect of complex formation on volume of mixing. Binary systems containing tetrahydrofuran (THF) at 25°C.

For these mixtures, chemical and physical forces are of the same order of magnitude.

THF forms charge-transfer complexes with aromatic compounds, but precise order of the stability cannot be determined from the thermo data because of unknown(?) solvent effects.

4.10 Hydrophobic Interaction

Hydrophilic (water-loving 친수성), Hydrophobic (water-fearing 소수성), Amphiphilic

Micelle: an organized structure by amphiphilic molecules

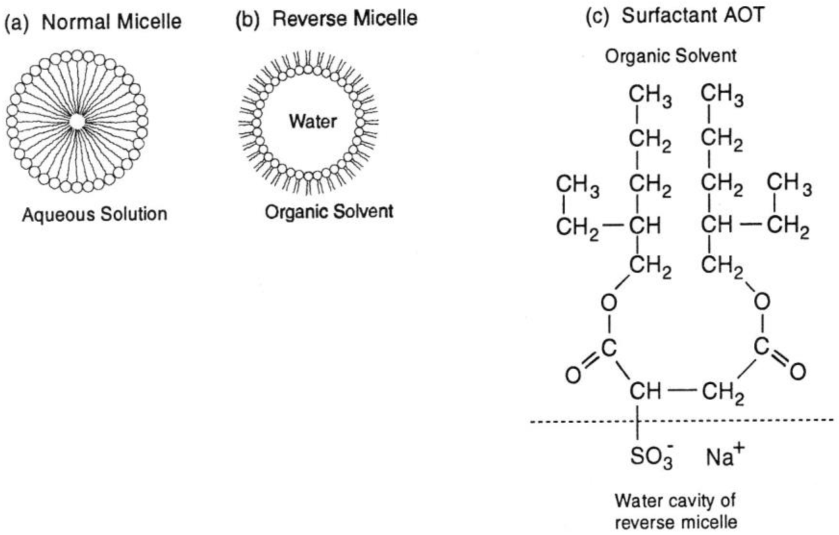


Figure 4-16 Schematic representation of a cross-section of micelles (a) and reverse micelles (b). In reverse micelles, the polar terminal group of the surfactant's molecules are directed towards the interior of the aggregate (forming an inner water core), and the hydrophobic chains are exposed to the organic solvent, as illustrated for the double-chained surfactant AOT (c).

Hydrophobic effect is an entropic phenomenon.

Upon solubilization of a solute, hydrogen bonds between water molecules are rearranged.

A higher degree of local order than in pure water is created

(a decrease in entropy called hydrophobic effect)

The hydrophobic effect is responsible for the immiscibility of nonpolar substances with water.

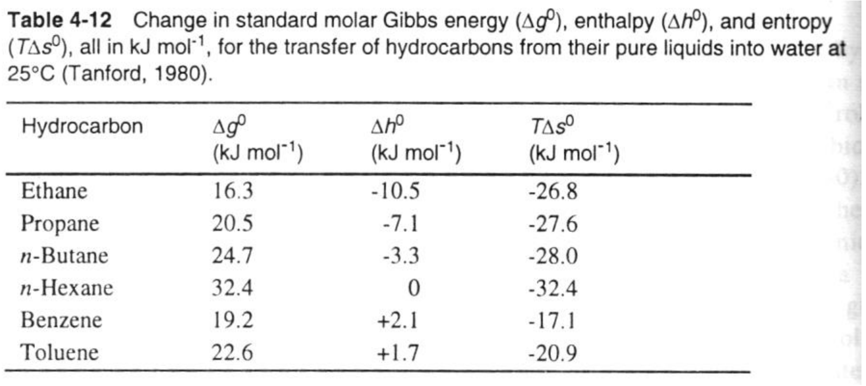


Table 4-12 Change in standard molar Gibbs energy (Δg^0), enthalpy (Δh^0), and entropy ($T\Delta s^0$), all in kJ mol^{-1}, for the transfer of hydrocarbons from their pure liquids into water at 25°C (Tanford, 1980).

Hydrocarbon	Δg^0 (kJ mol^{-1})	Δh^0 (kJ mol^{-1})	$T\Delta s^0$ (kJ mol^{-1})
Ethane	16.3	-10.5	-26.8
Propane	20.5	-7.1	-27.6
n-Butane	24.7	-3.3	-28.0
n-Hexane	32.4	0	-32.4
Benzene	19.2	+2.1	-17.1
Toluene	22.6	+1.7	-20.9

Longer alkanes are less soluble.

Benzene is more soluble in water than hexane

Hydrophobic interaction refers to the unusually strong attraction between hydrophobic molecules in water (stronger than in vacuo).

Potential energy for two contacting methane molecules

In vacuo, -2.5×10^{-21} J

In water, -14×10^{-21} J

4.11 Molecular Interactions in Dense Fluid Media

Interactions between two molecules in a vacuum − potential function (e.g. LJ potential)

Interactions between two molecules in a solvent medium − potential of mean force

The potential of mean force plays a major role in colloid and protein solutions.

The potential of mean force is an averaged intermolecular potential of two solute molecules over positions and orientations of surrounding solvent molecules

Osmotic Pressure (van't Hoff)

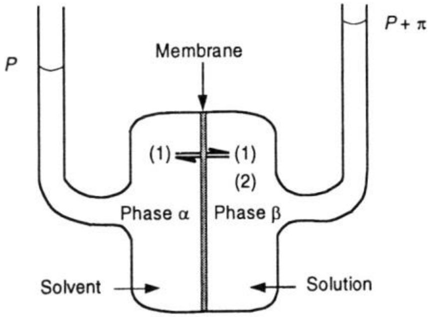


Figure 4-17 Schematic diagram of an osmotic-pressure measurement apparatus. The membrane is permeable to the solvent (1) but not to the solute (2).

At equilibrium,

$$\mu_1^\alpha = \mu_1^\beta \qquad (4\text{-}38)$$

$$\mu_1^\alpha = \mu_{\text{pure }1}^\alpha (T, P) \qquad (4\text{-}38a)$$

solute not present in phase α

$$\mu_1^\beta = \mu_{\text{pure }1}^\beta (T, P + \pi) + RT \ln a_1 \qquad (4\text{-}39)$$

$$a_1 = \gamma_1 x_1$$

For pure fluid $(\partial\mu/\partial P)_T = v$. and assuming that fluid is incompressible

$$\mu_{\text{pure }1}(P+\pi) = \mu_{\text{pure }1}(P) + \pi v_{\text{pure }1} \quad (4\text{-}40)$$

(4-38) is written as

$$-\ln a_1 = \frac{\pi v_{\text{pure }1}}{RT} \quad (4\text{-}41)$$

If solution is dilute, $x_1 \approx 1,\ \gamma_1 \approx 1$

$$-\ln x_1 = \frac{\pi v_{\text{pure }1}}{RT} \quad (4\text{-}42)$$

ln 1 ?

Since $x_2 << 1,\ \ln x_1 = \ln(1-x_2) \approx -x_2$. Talyor series: $\ln(1+t) = t - \frac{t^2}{2} + \frac{t^3}{3}\ldots \quad |t| \le 1$

$$\pi v_{\text{pure }1} = x_2 RT \quad (4\text{-}43)$$

Because $x_2 << 1$, $n_2 << n_1$ and $x_2 \approx n_2/n_1$.

$$\boxed{\pi V = n_2 RT} \quad (4\text{-}44)$$

van’t Hoff equation for osmotic pressure π

which can determine the solute’s molecular weight.

Other colligative-property measurement: boiling point elevation, freezing point depression.

For finite concentration

$$\boxed{\frac{\pi}{c_2} = RT\left(\frac{1}{M_2} + B^* c_2 + C^* c_2^2 + \cdots\right)} \quad (4\text{-}45)^{24}$$

$$\frac{P}{\rho} = RT(1 + B\rho + C\rho^2 + \cdots)$$

M_2 the molar mass of solute, B^* osmotic second virial coefficient, c_2 in g/L

Neglecting three-body interactions

$$\frac{\pi}{c_2} = RT\left(\frac{1}{M_2} + B_{22}^{*}\ c_2\right) \qquad \text{intercept} = RT/M_2, \quad \text{slope} = \quad RT\,B_{22}^{*}$$

Aqueous protein solutions

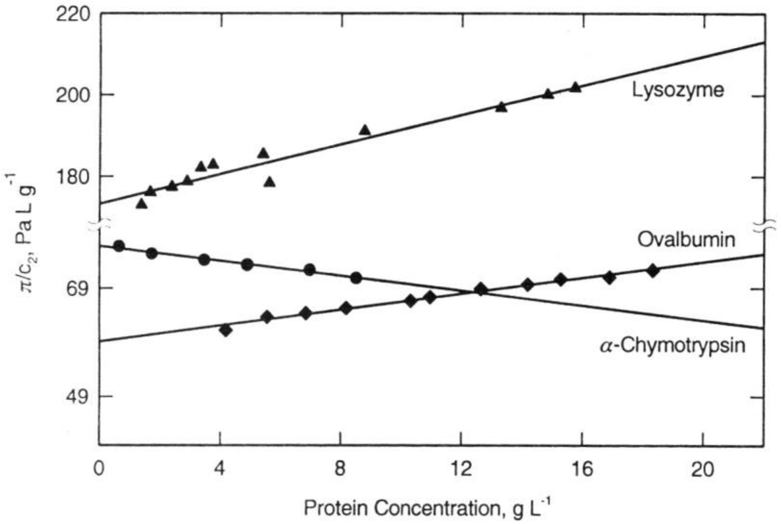
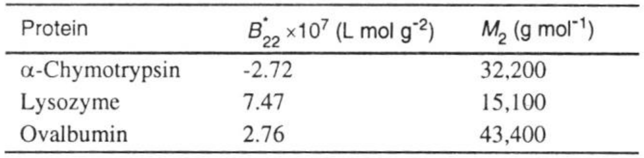


Figure 4-18 Osmotic-pressure data for α-chymotrypsin (●)(Haynes *et al.*, 1992) in 0.1 M potassium sulfate buffer, at pH 5 and 25°C, and for lysozyme (▲) and ovalbumin (◆) (McCarty and Adams, 1987) in 0.06 M cacodylate buffer, at pH 5.8 and 37°C.

Table 4-13 Osmotic second virial coefficients and number-average molecular weights for α-chymotrypsin, lysozyme, and ovalbumin in aqueous buffer solutions, regressed from the data shown in Fig. 4-18.



Protein	$B_{22}^{*} \times 10^{7}$ (L mol g^{-2})	M_2 (g mol^{-1})
α-Chymotrypsin	-2.72	32,200
Lysozyme	7.47	15,100
Ovalbumin	2.76	43,400

α-chymotrypsin molecules are slightly attracted to each other.

Donnan Equilibria

Thermodynamics of system containing an ion selective membrane

Additional criterion: electrical neutrality for each phase.

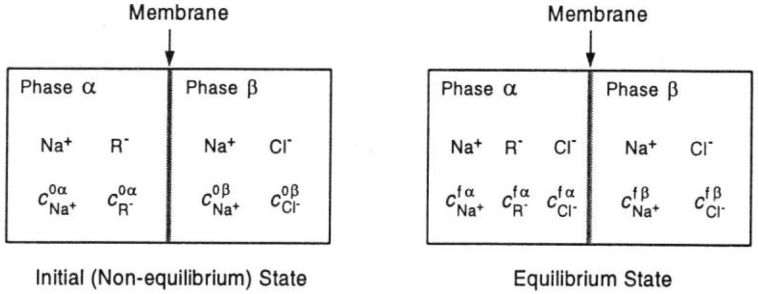


Figure 4-19 Schematic representation of Donnan equilibrium.

membrane is impermeable to R^-

If there is a difference in ion concentration across a membrane, an electrical potential will arise.

Nernst Equation

$\boxed{\mu_A^\alpha = RT\ln a_A^\alpha + z_A F E^\alpha}$ including average electrical potential of the compartment

$$\mu_{Na^+}^\alpha = RT\ln a_{Na^+}^\alpha + FE^\alpha \qquad \mu_{Cl^-}^\alpha = RT\ln a_{Cl^-}^\alpha - FE^\alpha$$

at equilibrium $\Delta\mu_{Na^+} = \mu_{Na^+}^\alpha - \mu_{Na^+}^\beta = 0$ $\qquad \Delta\mu_{Cl^-} = \mu_{Cl^-}^\alpha - \mu_{Cl^-}^\beta = 0$

$$RT\ln\frac{a_{Na^+}^\alpha}{a_{Na^+}^\beta} + F\left(E^\alpha - E^\beta\right) = 0 \qquad RT\ln\frac{a_{Cl^-}^\alpha}{a_{Cl^-}^\beta} - F\left(E^\alpha - E^\beta\right) = 0$$

$$RT\ln\frac{a_{Na^+}^\alpha a_{Cl^-}^\alpha}{a_{Na^+}^\beta a_{Cl^-}^\beta} = 0 \qquad a_{Na^+}^\alpha a_{Cl^-}^\alpha = a_{Na^+}^\beta a_{Cl^-}^\beta$$

for dilute solutions

$c_{Na^+}^\alpha c_{Cl^-}^\alpha = c_{Na^+}^\beta c_{Cl^-}^\beta$ Donnan equilibrium

At initial state, electroneutrality requires that

$$c^{0\alpha}_{\mathrm{Na}+} = c^{0\alpha}_{\mathrm{R}-} \quad \text{and} \quad c^{0\beta}_{\mathrm{Na}+} = c^{0\beta}_{\mathrm{Cl}-} \qquad (4\text{-}46)$$

Let δ be the change in Na^+ concentration in α, then $-\delta$ be the change in Cl^- concentration in β

After attaining equilibrium

$$\text{In } \alpha\text{:} \qquad c^{f\alpha}_{\mathrm{Na}+} = c^{0\alpha}_{\mathrm{Na}+} + \delta \qquad c^{f\alpha}_{\mathrm{Cl}-} = \delta \qquad c^{f\alpha}_{\mathrm{R}-} = c^{0\alpha}_{\mathrm{R}-} \qquad (4\text{-}47)$$

$$\text{In } \beta\text{:} \qquad c^{f\beta}_{\mathrm{Na}+} = c^{0\beta}_{\mathrm{Na}+} - \delta \qquad c^{f\beta}_{\mathrm{Cl}-} = c^{0\beta}_{\mathrm{Cl}-} - \delta \qquad c^{f\beta}_{\mathrm{R}-} = 0 \qquad (4\text{-}48)$$

How to calculate δ from the known original concentrations?

For solvent,

$$\mu^{\alpha}_{s} = \mu^{\beta}_{s} \qquad (4\text{-}49)^{27}$$

$$\mu^{\alpha}_{s} = \mu^{*}_{s} + P^{\alpha} v_s + RT \ln a^{\alpha}_{s} \qquad (4\text{-}50)$$

* for pure solvent state

$$\frac{RT}{v_s} \ln\left(\frac{a^{\beta}_{s}}{a^{\alpha}_{s}}\right) = P^{\alpha} - P^{\beta} = \pi \qquad (4\text{-}51)$$

$$\mu^{\alpha}_{\mathrm{NaCl}} = \mu^{\beta}_{\mathrm{NaCl}} \qquad (4\text{-}52)$$

?   NaCl is totally dissociated into ions

$$\mu^{\alpha}_{\mathrm{Na}+} + \mu^{\alpha}_{\mathrm{Cl}-} = \mu^{\beta}_{\mathrm{Na}+} + \mu^{\beta}_{\mathrm{Cl}-} \qquad (4\text{-}53)$$

can be written from $\mu^{\alpha}_{Na^+} - \mu^{\beta}_{Na^+} = 0 = \mu^{\alpha}_{Cl^-} - \mu^{\beta}_{Cl^-}$

Writing osmotic pressure for ions and substituting into (4-53)

$$\pi = \frac{RT}{\overline{v}_{Na+} + \overline{v}_{Cl-}} \ln\left(\frac{a^{\beta}_{Na+}\ a^{\beta}_{Cl-}}{a^{\alpha}_{Na+}\ a^{\alpha}_{Cl-}}\right) \tag{4-54}$$

from (4-51)

$$\frac{a^{\beta}_{Na+}\ a^{\beta}_{Cl-}}{a^{\alpha}_{Na+}\ a^{\alpha}_{Cl-}} = \left(\frac{a^{\beta}_{s}}{a^{\alpha}_{s}}\right)^{\frac{\overline{v}_{Na+} + \overline{v}_{Cl-}}{v_s}} \tag{4-55}$$

for very dilute solution

$a^{\alpha}_{s} = a^{\beta}_{s} = 1$ (nearly pure solvent)

for solute

$a_i = c_i$ (different units?)

(4-55) becomes

$$c^{\alpha}_{Na+}\ c^{\alpha}_{Cl-} = c^{\beta}_{Na+}\ c^{\beta}_{Cl-} \tag{4-56}$$

In terms of initial concentrations

$$(c^{0\alpha}_{Na+} + \delta)\,\delta = (c^{0\beta}_{Na+} - \delta)^2 \tag{4-57}$$

solving for δ

$$\boxed{\delta = \frac{(c^{0\beta}_{Na+})^2}{c^{0\alpha}_{Na+} + 2c^{0\beta}_{Na+}}} \tag{4-58}$$

The fraction of the original NaCl β that has move to α

$$\frac{\delta}{c^{0\beta}_{\mathrm{Na}^+}} = \left(2 + \frac{c^{0\alpha}_{\mathrm{Na}^+}}{c^{0\beta}_{\mathrm{Na}^+}}\right)^{-1} \tag{4-59}$$

Osmotic pressure $\pi = \left(\sum_{in\ \alpha} c_i - \sum_{in\ \beta} c_j\right) RT$

$$\pi = 2RT\left(c^{0\alpha}_{\mathrm{Na}^+} - c^{0\beta}_{\mathrm{Cl}^-} + 2\delta\right) \tag{4-60}$$

The difference in electric potential across the membrane

$$\Delta\phi = \frac{RT}{N_A\, e\, z_{\mathrm{Na}^+}} \ln \frac{a^{\beta}_{\mathrm{Na}^+}}{a^{\alpha}_{\mathrm{Na}^+}} \tag{4-61}$$

$$= E^{\alpha} - E^{\beta}$$

Setting activities equal to concentration for dilute conditions

$$\Delta\phi = \frac{RT}{N_A\, e\, z_{\mathrm{Na}^+}} \ln \frac{c^{0\beta}_{\mathrm{Na}^+}}{c^{0\alpha}_{\mathrm{Na}^+} + c^{0\beta}_{\mathrm{Na}^+}} \tag{4-61a}$$

important in biology, electrodialysis, reverse osmosis

4.12 Molecular Theory of Corresponding States

Classical (macroscopic) theory of corresponding states (van der Waals)

At critical point

$$\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0 \qquad (4\text{-}62)$$

there exists a universal function that is valid for all substances.

$$F\left(\frac{v}{v_c}, \frac{T}{T_c}, \frac{P}{P_c}\right) = 0 \qquad (4\text{-}63)$$

e.g.) for van der Waals EOS $F = P_R - \frac{8T_R}{3v_R - 1} + \frac{3}{v_R^2} = 0$

Molecular (microscopic) theory of corresponding states

If there is a universal function for intermolecular potential

$$\frac{\Gamma_{ii}}{\varepsilon_i} = F\left(\frac{r}{\sigma_i}\right) \qquad (4\text{-}64)$$

then there exists a universal equation of state

$$\tilde{P} = F^*(\tilde{T}, \tilde{v}) \qquad (4\text{-}77)$$

where $\tilde{T} = \frac{kT}{\varepsilon} \qquad \tilde{v} = \frac{V}{N\sigma^3} \qquad \tilde{P} = \frac{P\sigma^3}{\varepsilon} \qquad (4\text{-}76)$

Derivation with some statistical mechanics

Canonical partition function $Q(N,T,V)$

$$Q = Q_{\text{int}}(N,T)\,Q_{\text{trans}}(N,T,V) \qquad (4\text{-}65)$$

Q_{int} is internal contribution including rotation, vibration, electronic contributions.

Simple product of an isolated molecule

Translational part depends on volume given by

$$Q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2}\right)^{(3N/2)} \frac{1}{N!}\int \underset{V}{\cdots}\int \exp\left[-\frac{\Gamma_t(\mathbf{r}_1,\ldots,\mathbf{r}_N)}{kT}\right] d\mathbf{r}_1\ldots d\mathbf{r}_N \qquad (4\text{-}66)$$

Γ_t is the potential energy of the entire system, and is frequently assumed to be $\Gamma_t = \sum_{i<j}\Gamma_{ij}(r_{ij})$

Configurational integral $Z_N(N,T,V)$ is

$$\boxed{Z_N = \int \underset{V}{\cdots}\int \exp\left[-\frac{\Gamma_t(\mathbf{r}_1,\ldots,\mathbf{r}_N)}{kT}\right] d\mathbf{r}_1\ldots d\mathbf{r}_N} \qquad (4\text{-}67)$$

difficult to calculate directly for real fluids

but for ideal gas $\Gamma_t = 0$ and $Z_N^{\text{id}} = V^N$.

Since $A = -kT\ln Q$ and $P = -\left(\dfrac{\partial A}{\partial V}\right)_T$

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} = kT\left(\frac{\partial \ln Z_N}{\partial V}\right)_{T,N} \qquad (4\text{-}68)$$

Substituting the universal potential (4-64) into

$$\Gamma_t = \sum_{i<j} \Gamma_{ij}(r_{ij})$$

(4-69

Then

$$Z_N = \sigma^{3N} \int \underset{V/\sigma^3}{\cdots} \int \exp\left[-\frac{\varepsilon}{kT} \sum_{i<j} F\left(\frac{r_{ij}}{\sigma}\right)\right] d\left(\frac{r_1}{\sigma^3}\right) \cdots d\left(\frac{r_N}{\sigma^3}\right) \qquad (4\text{-}70)$$

$$Z_N = \sigma^{3N} Z_N^{*}\left(\frac{kT}{\varepsilon}, \frac{V}{\sigma^3}, N\right) \qquad (4\text{-}71)$$

…

$$\tilde{P} = F^{*}(\tilde{T}, \tilde{v})$$

(4-77

But But

It is not strictly true for most substances.

$$\frac{\Gamma_{ii}}{\varepsilon_i} = F\left(\frac{r}{\sigma_i}\right) \qquad (4\text{-}64)$$

two parameter theory for simple molecules

4.13 Extension of Corresponding-States Theory to More Complicated Molecules

Simple molecules: argon, krypton, xenon, methane, oxygen, nitrogen, carbon monoxide

A need of third parameter for complex molecules

For simple fluids, it is observed that

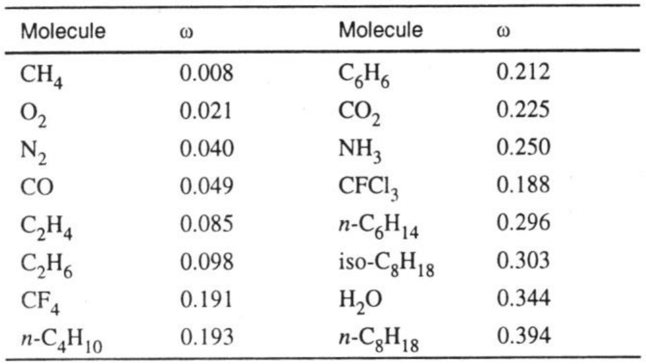
$$\frac{P^s}{P_c} = \frac{1}{10} \quad \text{at} \quad \frac{T}{T_c} = 0.7 \tag{4-85}$$

Pitzer defined the acentric factor by

$$\boxed{\omega \equiv -\log\left(\frac{P^s}{P_c}\right)_{T/T_c=0.7} - 1.000} \tag{4-86}$$

a useful empirical measure of noncentral nature of intermolecular forces

Table 4-14 Acentric factors.



Molecule	ω	Molecule	ω
CH_4	0.008	C_6H_6	0.212
O_2	0.021	CO_2	0.225
N_2	0.040	NH_3	0.250
CO	0.049	$CFCl_3$	0.188
C_2H_4	0.085	$n\text{-}C_6H_{14}$	0.296
C_2H_6	0.098	iso-C_8H_{18}	0.303
CF_4	0.191	H_2O	0.344
$n\text{-}C_4H_{10}$	0.193	$n\text{-}C_8H_{18}$	0.394

The three-parameter corresponding-states theory

All fluids having the same acentric factor have the same reduced configurational properties at the same reduced temperature and pressure.

For the compressibility factor, Pitzer used a truncated Talyor series in ω

$$z(P_R,T_R,\omega) = z^{(0)}(P_R,T_R,\omega = 0) + \omega\, z^{(1)}(P_R,T_R) \qquad (4\text{-}87)$$

Lee and Kesler used a referenc fluid (n-octane) explicitly.

$$z(T_R,v_R,\omega) = z^{(0)}(T_R,v_R,\omega = 0) + \frac{\omega}{\omega^{(r)}}[\, z^{(r)}(T_R,v_R,\omega^{(r)}) - z^{(0)}(T_R,v_R,\omega = 0)] \quad (4\text{-}88)$$

using BWR equation of state

$$z = \frac{P_R v_R}{T_R} = 1 + \frac{b^*}{v_R} + \frac{c^*}{v_R^2} + \frac{d^*}{v_R^5} + \frac{c_4}{T_R^3 v_R^2}\left(\beta + \frac{\gamma}{v_R^2}\right)\exp\left(-\frac{\gamma}{v_R^2}\right) \qquad (4\text{-}89)$$

A third parameter very much improves the accuracy of corresponding-state correlations.
The accuracy of the gas-phase compressibility for normal fluids (except for highly polar fluids) ~ 2% or better when Lee and Kesler’s table is used.