5.7 Virial Coefficients from Corresponding-State Correlations

Assuming that the potential can be written in dimensionless form by

$$\frac{\Gamma}{\varepsilon} = F\left(\frac{r}{\sigma}\right) \tag{5-49}$$

where F is a universal function of the reduced intermolecular separation. Then B in dimensionless form

$$\frac{B}{2\pi N_A \sigma^3} = \int_0^\infty \left[1 - \exp\left(\frac{-\varepsilon F(r/\sigma)}{kT}\right) \right] \left(\frac{r}{\sigma}\right)^2 d\left(\frac{r}{\sigma}\right)$$
(5-50)

If we set $\sigma^3 \propto v_c = \varepsilon/k \propto T_c$, we obtain

$$\frac{B}{v_c} = F_B \left(\frac{T}{T_c}\right) \tag{5-51}$$

The reduced second virial coefficient is a generalized function of reduced temperature.

From empirical correlation for methane, argon, krypton, and xenon,

$$\frac{B}{v_c} = 0.430 - 0.866 \left(\frac{T}{T_c}\right)^{-1} - 0.694 \left(\frac{T}{T_c}\right)^{-2}$$
(5-52)

For a mixture

$$B_{\text{mixt}} = \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j B_{ij}$$
(5-53)

for cross-coefficient B_{ij} we assume

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \tag{5-54}$$

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \tag{5-55}$$

Then it follows that

$$v_{c_{ij}} = \frac{1}{8} \left(v_{c_i}^{1/3} + v_{c_j}^{1/3} \right)^3$$
(5-56)

$$T_{c_{ij}} = (T_{c_i} T_{c_j})^{1/2}$$
(5-57)

using (5-52) we get B_{ij}

 Table 5-7
 Experimental and calculated second virial coefficients for an equimolar mixture of argon/nitrogen.

Temperature	B _{mixt} (cm ³ mol ⁻¹)	
(°C)	Calculated	Experimental
0	-16.5	-16.3
-70	-41.3	-40.4
-130	-89.4	-88.3

using (5-52), (5-53), (5-56), and (5-57)

Experimental correlation for normal alkanes and $\alpha\text{-olefins}$

$$\frac{B}{v_c} = 0.430 - 0.886 \left(\frac{T}{T_c}\right)^{-1} - 0.694 \left(\frac{T}{T_c}\right)^{-2} - 0.0375(n-1) \left(\frac{T}{T_c}\right)^{-4.5}$$
(5-58)

where n is number of carbon atoms

For critical volume

$$v_c (\text{cm}^3 \text{ mol}^{-1}) = 25.07 + 50.38n + 0.479n^2$$
 (5-59)



Figure 5-21 Corresponding-states correlation of McGlashan for second virial coefficients of normal paraffins and α -olefins.

This clearly shows the need for a third parameter in a corresponding-states correlation.

Combining rule for chain length

$$n_{12} = \frac{1}{2}(n_1 + n_2)$$
 (5-60)
of little theoretical basis, an *ad hoc*



Figure 5-22 Second virial coefficients of a mixture containing 50.05 mole percent propene and 49.95 mole percent α -heptene.

If we naively assume

$$B_{12} = \frac{1}{2}(B_{11} + B_{22}) \tag{5-61}$$

then we obtain erroneous results

$$B_{\text{mixt}} = y_1 B_{11} + y_2 B_{22} \tag{5-62}$$

which is in significant disagreement with experiment as in Fig. 5-22

Pitzer-Tsonopoulos Correlation

Acentric factor: a macroscopic measure of how much the force field around a molecule deviates from spherical symmetry.

$$\omega = -\log\left(\frac{P^s}{P_c}\right)_{T/T_c=0.7} - 1.000$$
(5-63)

when applied to the second virial coefficient

$$\frac{B}{N_A \sigma^3} = F_{\omega} \left(\frac{kT}{\varepsilon}\right)$$
(5-64)

upon replacing σ and ϵ/k

$$\frac{BP_c}{RT_c} = F_{\omega} \left(\frac{T}{T_c}\right) \tag{5-65}^{14}$$

Schreiber and Pitzer proposed

$$\frac{BP_c}{RT_c z_c} = c_1 + c_2 T_R^{-1} + c_3 T_R^{-2} + c_4 T_R^{-6}$$
(5-66)

where

$$T_R = T/T_c \qquad z_c = 0.291 - 0.08\,\omega$$

$$c_i = c_{i,0} + \omega \ c_{i,1} \tag{5-67}$$

i	$c_{i,0}$	<i>c</i> _{<i>i</i>,1}
1	0.442259	0.725650
2	-0.980970	0.218714
3	-0.611142	-1.249760
4	-0.00515624	-0.189187

except for highly polar fluids such as water, nitriles, ammonia, and alcohols except for quantum gases such as helium, hydrogen, and neon

Tsonopoulos proposed another form

$$\frac{BP_c}{RT_c} = F^{(0)}\left(\frac{T}{T_c}\right) + \omega F^{(1)}\left(\frac{T}{T_c}\right)$$
(5-68)

where

$$F^{(0)}\left(\frac{T}{T_c}\right) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} - \frac{0.000607}{T_R^8}$$
(5-69)
$$F^{(1)}\left(\frac{T}{T_c}\right) = 0.0637 + \frac{0.331}{T_R^2} - \frac{0.423}{T_R^3} - \frac{0.008}{T_R^8}$$
(5-70)

 $\left(\frac{T_c}{T}\right)^2$

4

Figure 5-23 Reduced second virial coefficients.

-1.6

-20

-2.4

0

1

For polar and hydrogen-bonded fluids



Figure 5-24 Correlating constant *a* for some polar fluids. Top curve for ketones, aldehydes, alkyl nitriles, ethers, and carboxylic acid esters; lower curve for alkyl halides, mercaptans, sulfides, and disulfides.

for ketones, aldehydes, alkyl nitriles, ethers, and carboxylic acid esters,

$$a = -2.14 \times 10^{-4} \mu_R - 4.308 \times 10^{-21} (\mu_R)^8$$
 (5-73) (top curve)

for alkyl halides, mercaptans, sulfides, and disulfides

$$a = -2.188 \times 10^{-11} (\mu_R)^4 - 7.831 \times 10^{-21} (\mu_R)^8$$
 (5-74)
(bottom curve)

reduced dipole moment is defined as

$$\mu_R = 0.9869 \times 10^5 \, \frac{\mu^2 P_c}{T_c^2} \tag{5-75}$$

for water a = -0.019

For strongly hydrogen-bonded fluids, the virial equation is not useful for describing vaporphase imperfections. Third virial coefficient Skip

Quantum Gases

Corresponding-states correlations for virial coefficient may be applied to quantum gases (helium, hydrogen, and neon) by using effective critical constant and $\omega = 0$ The effective critical constants depend on temperature, given by

$$T_{c} = \frac{T_{c}^{0}}{1 + \frac{21.8}{MT}}$$

$$P_{c} = \frac{P_{c}^{0}}{1 + \frac{44.2}{MT}}$$

$$\upsilon_{c} = \frac{\upsilon_{c}^{0}}{1 - \frac{9.91}{MT}}$$
(5-88)

These equations are empirical. *M* is the molar mass (gram per mol) As *MT* becomes large, $T_c \rightarrow T_c^0$, $P_c \rightarrow P_c^0$ and $v_c \rightarrow v_c^0$.

Table 5-9	"Classical"	critical	constants	for	quantum	gases
-----------	-------------	----------	-----------	-----	---------	-------

	<i>Т</i> _c ⁰ (К)	P_c^0 (bar)	v_c^0 (cm ³ mol ⁻¹)
Ne	45.5	27.3	40.3
He ⁴	10.47	6.76	37.5
He ³	10.55	6.01	42.6
H ₂	43.6	20.5	51.5
HD	42.9	19.9	52.3
HT	42.3	19.4	52.9
D ₂	43.6	20.4	51.8
DT	43.5	20.6	51.2
T ₂	43.8	20.8	51.0

For mixture containing quantum gases

$$T_{c_{ij}} = \frac{(T_{c_i}^0 T_{c_j}^0)^{1/2} (1 - k_{ij})}{1 + \frac{21.8}{M_{ij}T}}$$
(5-89)

$$P_{c_{ij}} = \frac{P_{c_{ij}}^{0}}{1 + \frac{44.2}{M_{ij}T}}$$
(5-90)

$$P_{c_{ij}}^{0} = \frac{z_{c_{ij}}^{0} R(T_{c_{i}}^{0} T_{c_{j}}^{0})^{1/2} (1 - k_{ij})}{\upsilon_{c_{ij}}^{0}}$$
(5-91)

$$(v_{c_{ij}}^{0})^{1/3} = \frac{1}{2} \left[(v_{c_i}^{0})^{1/3} + (v_{c_j}^{0})^{1/3} \right]$$
(5-92)

$$z_{c_{ij}}^{0} = 0.291 - 0.08 \left(\frac{\omega_{i} + \omega_{j}}{2} \right)$$
(5-93)

$$\frac{1}{M_{ij}} = \frac{1}{2} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)$$
(5-94)

The critical volume can be estimated by

$$\upsilon_c^0 = \frac{RT_c^0}{P_c^0} (0.291 - 0.08\omega)$$

5.8 The Chemical Interpretation of Deviations from Gas-Phase Ideality

Chemical viewpoint considers the forces between molecules to be of chemical, rather than physical. It attempts to explain nonideal behavior in terms of the formation of new chemical species.

 $2A \rightleftharpoons A_2$, $3A \rightleftharpoons A_3$, etc.

Polymerization reactions results in negative deviation (z < 1) from ideal-gas behavior. // the number of molecules is reduced by the reactions.

5.9 Strong Dimerization: Carboxylic Acids



We define an equilibrium constant in terms of the partial pressure as we assume true species (monomers and dimers) behaves as an ideal gas.

$$K = \frac{P_{A_2}}{P_A^2} = \frac{y_{A_2}P^0}{y_A^2 P}$$
(5-95)
$$= \frac{a_{A_2}}{a_A^2} = \frac{y_{A_2}P/P^0}{\left(y_A P/P^0\right)^2}$$

where *P* is total pressure, P^0 is the standard-state pressure (= 1 bar)

The total number of true moles n_T is given by

$$n_T = n_A + n_{A_2} = (1 - \alpha) + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$
(5-96)

where n_A is the number of moles of monomer, n_{A_2} is the number of moles of dimmer, and

 α is the fraction of molecules that dimerize.

with the restraint that $n_A + 2n_{A_2} = 1$ (mass balance).

By assumption, $PV = n_T RT$

$$n_T = \frac{PV}{RT} = 1 - \frac{\alpha}{2}$$

$$\alpha = 2 - \frac{2PV}{RT} \tag{5-97}$$

Since

$$y_{A} = \frac{n_{A}}{n_{T}} \qquad \qquad y_{A_{2}} = \frac{n_{A_{2}}}{n_{T}}$$

substituting into (5-95) $K = \frac{\frac{\alpha/2}{1-\alpha/2}P^{0}}{\left(\frac{1-\alpha}{1-\alpha/2}\right)^{2}P}$ $K = \frac{\alpha(1-\alpha/2)P^{0}}{2(1-\alpha)^{2}P}$ (5-100)

Since K is a function only of temperature, α must go to zero as P approaches zero. Dimerization decreases as the pressure falls (Le Chatelier's principle)



Figure 5-27 Dimerization equilibrium constants for acetic acid and propionic acid.

Dimerization is strong even at very low pressures.

For example, at 40°C and P = 0.016 bar, α (acetic acid) = 0.8, α (propionic acid) = 0.84

Cross-dimerization

$$CH_{3}-C \bigvee_{OH}^{O} + CH_{3}-CH_{2}-C \bigvee_{OH}^{O} \rightleftharpoons CH_{3}-C \bigvee_{O-H}^{O} - ---H-O C - CH_{2}-CH_{3}$$

$$1/2A_{2} + 1/2B_{2} \rightleftharpoons AB$$

We assume that there is zero enthalpy change for the reaction. The entropy change is given by $R \ln 2$ because distinguishability has been lost. (A₂ and B₂ are distinguishable, but two AB's are indistinguishable)

The standard Gibbs energy of forming AB dimmers from A and B monomers

$$2A \iff A_2 \qquad \Delta g_{A_2}^0 = -RT \ln K_{A_2} \tag{5-101}$$

$$2B \iff B_2 \qquad \Delta g_{B_2}^0 = -RT \ln K_{B_2} \tag{5-102}$$

A + B
$$\implies$$
 AB $\Delta g^{0}_{AB} = -\frac{1}{2}(\Delta g^{0}_{A_2} + \Delta g^{0}_{B_2}) - RT \ln 2 = -RT \ln K_{AB}$ (5-103)

which gives

$$K_{\rm AB} = 2 \sqrt{K_{\rm A_2} K_{\rm B_2}} \; . \label{eq:KAB}$$

This is reasonable only when mixture's components are chemically similar.

$2A \implies A_2$	Ι	
$3A \rightleftharpoons A_3$	II	
$2W \iff W_2$	III	
A+W 🛁 AW	IV	

Using PVT data of acetic acid vapor, K's for I and II are evaluated. Using PVT data of water, K's for III are evaluated. K for IV is assumed to be the same as K for III.

From these chemical Equilibria,

$$\varphi_1 = \frac{p_W}{p_1}$$
(5-104)

 $\varphi_2 = \frac{p_A}{p_2}$
(5-105)

where p_w is the partial pressure of acetic acid monomer, and p_A is partial pressure of acetic acid monomer.



Figure 5-28 Vapor-phase fugacity coefficients for saturated mixtures of water (1)/acetic acid (2) at 1 bar.

Although the total pressure is low, deviation from ideal-gas behavior are large.

5.10 Weak Dimerizations and Second Virial Coefficients

We consider a pure polar gas and assume that the forces between molecules can be divided into two classes: "normal" intermolecular forces (dispersion forces) and chemical association forces leading to the formation of new chemical species.

The equation of state is

$$PV = n_T (RT + BP) \tag{5-106}$$

with

$$B = B_{\text{nonpolar}} + B_{\text{polar}}$$

$$B_{\text{polar}} = -RTK / P^{0}$$
(5-107)
(consider later again)

 B_{polar} is much larger in magnitude that $B_{nonpolar}$.

In order to consider the excluded volume effect

$$P(V - n_T b_m) = n_T R T (5-108)^{19}$$

where n_T is the true total number of true moles, and $n_T b_m$ is the excluded volume due to the finite size of the molecules.

Suppose that there is one mole of A in the absence of dimerization. For small degrees of association ($\alpha \ll 1$). Eq. (5-100) becomes

$$K = \frac{\alpha P^0}{2P} \tag{5-109}$$

Then n_T is

$$n_T = 1 - \frac{\alpha}{2} = 1 - \frac{PK}{P^0} \tag{5-110}$$

Rewriting the equation of state

$$\frac{PV}{RT} = 1 + \frac{P}{RT} \left(n_T b_m - \frac{RTK}{P^0} \right)$$
(5-111)

The excluded volume is the sum of monomers and dimers

$$n_T b_m = (n_{\rm A} + 2n_{\rm A_2})b \tag{5-112}$$

where b is the excluded volume for the monomer.

As
$$n_A + 2n_{A_2} = 1$$
, $n_T b_m = b$.

Comparing with
$$\frac{PV}{RT} = 1 + \frac{BP}{RT}$$
 (for a total of 1 mole of A)

The second virial coefficient is

$$B = b - \frac{RTK}{P^0}$$
 (5-113) for small degrees of dimerization ($\alpha \ll 1$)

For strongly hydrogen-bonded fluids, the condition ($\alpha \ll 1$) is attained only at low pressure. For example, at 40°C and P = 0.016 bar, α (acetic acid) = 0.8 For α to be small (say, 0.01), it is necessary to reduce the pressure to 1.3 Pa. Other hydrogen-bonded fluids (alcohols, aldehydes, esters) begin to dimerize an appreciable extent only at normal pressures (close to 1 bar)

Chemical theory is limited to moderate pressures because trimers and higher aggregates are formed as pressure rises and few quantitative data are available beyond dimerization.

When data are available over a range of temperature, we can obtain enthalpy and entropy

$$-\ln K = \frac{\Delta h^0}{RT} - \frac{\Delta s^0}{R}$$
(5-114)

K is determined from experimental second virial coefficient *B* and volume of molecules *b* from atomic radii, Eq (5-113)

	<i>b</i> (cm ³ mol ⁻¹)	$-\Delta h^0$ (kJ mol ⁻¹)	$-\Delta s^0$ (kJ mol ⁻¹ K ⁻¹)
Methyl acetate	170.2	10.04	0.0562
Acetonitrile	113.5	18.07	0.0703
Diethyl amine	223.4	12.00	0.0598
Diethyl ether	206.0	8.463	0.0526
Ammonia	54.3	8.995	0.0662
Nitromethane	121.9	15.13	0.0648
Water	45.9	13.91	0.0713

 Table 5-10
 Excluded volumes (obtained from the method of Bondi), standard enthalpies and entropies of dimerization (from second virial coefficients) for some polar gases.

For mixtures

$$B_{12} = \frac{1}{2} (b_1^{1/3} + b_2^{1/3})^3 - \frac{1}{2} \frac{RTK_{AB}}{P^0}$$
(5-115)

we assumed that $b_{AB}^{1/3} = b_{12}^{1/3} = (1/2)(b_1^{1/3} + b_2^{1/3})$

The factor 1/2 of the last term is a symmetry factor



Figure 5-29 Second cross virial coefficients (Olf *et al.*, 1989a) of methanol/methyl acetate and acetonitrile/methyl acetate. ●, ■ Experiment; —— Calculated from chemical theory.

Acetonitrile/Acetaldehyde system

It was found that experimental second-virial cross coefficient for mixture is much more negative than that of either pure component.



Figure 5-30 Second virial coefficients for the acetonitrile/acetaldehyde system.

The enthalpy of formation for the acetonitrile/acetaldehyde complex is considerably larger than that for either pure-component dimmer.

	Δu^0 (energy of formation, kJ mol ⁻¹)		
	Calculated		
Complex	Parallel Structure (a)	End-to-end Structure (b)	Observed
Acetaldehyde/acetaldehyde	22.11	44.21	21.39
Acetonitrile/acetonitrile	14.15	28.30	16.58
Acetonitrile/acetaldehyde	17.27	34.54	30.54
(+) (-) (+) (+) (+) (+) (+) (+) (+) (+) (+) (+		(+ -)(+ -	-)
Structure (a)		Structure	(b)

 Table 5-11
 Standard energies of complex formation in the acetonitrile/acetaldehyde system (Carter, 1960).

From electrostatic theory, the energy of formation of each of these structure is

(a)	$\Delta u^0 = -\frac{\mu^2}{4\pi\varepsilon_0 r^3}$	(or $-\frac{\mu_i \mu_j}{4\pi\varepsilon_0 r^3}$ if $i \neq j$)	(5-116) parallel
(b)	$\Delta u^0 = -\frac{2\mu^2}{4\pi\varepsilon_0 r^3}$	(or $-\frac{2\mu_i\mu_j}{4\pi\varepsilon_0 r^3}$ if $i \neq j$)	(5-117) end-to-end

It suggests that the structure of the complex is qualitatively different from that of the pure dimmers.

Ammonia/Acetylene

Only ammonia has a dipole moment. Nevertheless, there are strong complexing forces that are not present between like molecules.



Figure 5-31 Experimental second virial coefficients for acetylene (1) and for ammonia (2). B_{12} is the observed cross coefficient for binary mixtures of (1) and (2).

 B_{12} is considerably more negative than either B_{11} or B_{22} .

It can be explained by the formation of hydrogen bond between (acidic) acetylene and (basic) ammonia.

Chemical equilibrium constant *K* is found from

$$-\frac{1}{2}\frac{RTK}{P^0} = B_{12 \exp} - B_{12 \text{ physical}}$$
(5-118)



Figure 5-32 Second-virial cross coefficient for acetylene/ammonia mixtures. Calculated contributions from physical forces are insufficient to account for the observed large negative coefficient. $B_{12 \text{ physical}}$ is the sum of contributions a, b, c and d.

From the variation of K with temperature, enthalpy and entropy of complex formation are

 $\Delta h^0 = (-9250 \pm 1250) \text{ J mol}^{-1}$ $\Delta s^0 = (-75.3 \pm 3.8) \text{ J mol}^{-1} \text{ K}^{-1}$

in good agreement with statistical-mechanical calculation.

Trimethy amine/Methanol

There is strong interaction between alcohol and amine



Figure 5-33 Second virial coefficients for the system trimethyl amine (1)/methanol (2).

The large negative B₁₂ yields a remarkably low fugacity coefficient for methanol, infinitely dilute in trimethyl amine.



Figure 5-34 Fugacity coefficients for methanol at infinite dilution in trimethyl amine at 45°C (Stein and Miller, 1980).

Acetic acid / Formic acid



Figure 5-35 Fugacity coefficients for saturated mixtures of two carboxylic acids at 1 bar: formic acid (1)/acetic acid (2).

Although the total pressure is only 1 bar, deviations from ideal gas behavior are considerable.

Because both component associate, the two fugacity coefficients are well below unity.

Propionic acid / Methyl isobutyl ketone

Only propionic acid associate with each other.



Figure 5-36 Fugacity coefficients for saturated mixtures of propionic acid (1)/methyl isobutyl ketone (2) at 1 bar.

The weak minimum for propionic acid is due to two effects.

As concentration of acid rises, the tendency to associate increases.

As temperature rises, the association constant decreases.