

Introductory Chemistry I

MASS, MOLES, & CONCENTRATIONS

NUMBER OF MOLES OF A

 $n_A = \frac{\text{Mass, } m_A}{\text{Molar mass, } M_A} = \frac{\text{# of particles}}{6.022 \times 10^{23}}$

MOLE FRACTION OF A

 $X_A = \frac{\text{Moles of A}}{\text{Total moles}} = \frac{n_A}{\sum n_i}$

MASS FRACTION OF A

 $m_{fA} = \frac{\text{Mass of A}}{\text{Total mass}} = \frac{m_A}{\sum m_i}$

PARTS PER MILLION

 $ppm = \frac{\text{Mass of substance}}{\text{Total mass}} 10^6$

MOLARITY

 $[M] = \frac{\text{Moles dissolved solute}}{\text{Liters solution}}$

MOLALITY

 $m = \frac{\text{Moles dissolved solute}}{\text{Kilograms solvent}}$

CONVERSIONS

 $1ppm = 10^4 \text{ mass percent} = 10^6 \text{ mass fraction}$

$$X_A = \frac{n_A}{\sum n_i} \Rightarrow \frac{n_A M_A}{\sum n_i M_i} = m_{fA}$$
 where: $n_A M_A = m_A$, $\sum n_i M_i = \sum m_i$

$$m_{fA} = \frac{m_A}{\sum m_i} \Rightarrow \frac{m_A/M_A}{\sum m_i/M_i} = \chi_A$$
 where: $m_A/M_A = n_A$, $\sum m_i/M_i = \sum n_i$

Molarity \times Liters solution/Total moles = X_A

Molarity

Mass fraction of solvent × Density of solution (kg/L)

THE GASEOUS STATE

TEMPERATURE

 $^{\circ}$ C (Celsius) = $5/9(^{\circ}F - 32)$

 $^{\circ}F$ (Fahrenheit) = $(9/5)^{\circ}C + 32$

K (Kelvin) = °C + 273.15

 $^{\circ}$ R (Rankin) = $^{\circ}$ F + 459.67

Examples (K)

108 - H-Bomb

2000 - Bunsen burner (CH₄/O₂)

1000 - Cigarette

373 - Boiling point of H₂O

310 - Body temperature

273 – Freezing point of H₂O

Dalton's Law of Partial Pressures

• Partial pressure, p_{i} , = pressure exerted by individual component

90 - Boiling point of O₂

4.2 – Boiling point of He

0 – Absolute zero

at T and V of mixture

 $\sum pi = P_{\text{total}}$ (*T, V* are constant)

Gas 2

Amagat's Law of Partial Volumes

occupied by individual component

• Partial volume, V_{ii} = volume

 $\sum V_i = V_{total}$ (*T, P* are constant)

Gas 2

0.8 L

Density of Ideal Mixture

at T and P of mixture

GAS MIXTURES

Gas 1

Gas 1

PRESSURE

1 atm = 101325 Pa

= 1.01325 bar

= 14.6959 psi

= 760 mm Hg

= 760 Torr

Examples (atm)

107-Center of sun106-Center of earth500–1000-NH3 synthesis150-Gas cylinder50–75-CH4 pipeline1-Atmosphere10-6-Vapor pressure of Hg10-12-Laboratory vacuum

MOLECULAR PROPERTIES

Average Molecular Velocity

 $u=(3RT/M)^{1/2}$

 u_{N_2} (25°C) \cong 500 m/s

of Impacts per Second on 1 m²

100 molecules/cm³ (outer space)

C = 1/4(N/V)u (N = # of molecules)

 $C_{N_2} \cong 10^{28} \text{ collisions/m}^2 \cdot \text{s}$ (at 1 atm, 25°C)

Average Molar Mass of Mixture $M_{avg} = \sum n_i \bullet M_i / n_{tot}$ Average Distance Between Molecules = Mean Free Path

Gas 1 & 2

Gas 1 & 2

1.8 L

T, P

1 L

T, P_{Total}

 $\lambda = [\pi D^2_m \bullet (N/V)]^{-1}$

 D_m = diameter of molecule

 λ_{N_2} (1 atm) $\cong 10^{-7}$ m

Diffusion Coefficient

 $D = 1/3u\lambda$

 D_{N_2} (1 atm, 25°C) \cong 0.17 cm²/s

GRAHAM'S LAW OF DIFFUSION/EFFUSION

Rate of Transport of 1 = $\sqrt{\frac{\text{Molar Mass of 2}}{\text{Molar Mass of 1}}}$

SINGLE GASES

Output Boyle's Law PV = Constant (at constant T, n)

2 Law of Charles & V/T = ConstantGay-Lussac (at constant P, n)

Avogadro's Hypothesis
 At constant T and P, equal volumes of different gases contain

the same number of particles V/n = Constant (at constant T, P)

4 Ideal Gas Law PV = nRT (at low P, high T)

Molar Volume $V_{\text{Molar}} = 22.414 \text{ L at STP}$ of an Ideal Gas (STP = 0°C, 1 atm)

6 Density of an d = PM/RT Ideal Gas

7 Gas Constant, $R = 0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$

= 82.0578 cm³•atm/mol•K

= 8.3145 J/mol•K

= 8.3145 L•kPa/mol•K

= 1.9859 cal(I.T.)/mol•K

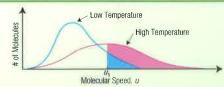
= 0.73024 ft³•atm/lb-mol•°R

VAN DER WAALS EQUATION FOR REAL GASES

a = measure of attractive force

b = measure of repulsive force or excluded volume

MAXWELL'S VELOCITY DISTRIBUTION OF GASEOUS MOLECULES



 As temperature increases, the average molecular speed increases, causing the curve to shift to the right and become broader

$d_{mixture} = P \cdot M_{avg} / RT$

0 C ø

Е

THE LIQUID & SOLID STATES

PROPERTIES OF LIQUIDS & CRYSTALLINE SOLIDS

	Orderedness	Diffraction Pattern	Rigidity	Molecular Movement	Separation Energy
Liquids	Low	Diffuse	Yielding	Yes	Low
Solids	High	Sharp	Rigid	No	Low to high

COMMON CRYSTAL STRUCTURES







Alkali Metals Li, Na, K, Rb **Ferrous Metals** Fe, Cr, Mn, V, Mo Simple Cubic Body-Centered Cubic



Noble Metals Ag, Au, Pt, Pd, Rh Other Metals Al, Ca, Sr, Ni, Cu Close-Packed Cubic (Face-Centered)



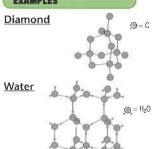
Hydrogen Halides HCI, HBr, HI Metals Be, Mg, Zn Close-Packed **Hexagonal**

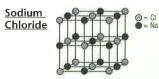
CRYSTAL TYPES & PROPERTIES

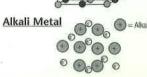
Bond Type	lonic	Covalent	Molecular	Metallic
Particles	Cations & anions	Atoms	Molecules or atoms	Atoms
Hardness	Hard, brittle	Hard	Soft	Soft to hard
Melting	High	High	Low	Low to high
Conduction*	Poor	Poor**	Poor	Good
Examples	NaCl	Diamond	Water	Li, Fe

^{*}Heat and electrical conduction **Except diamond products

EXAMPLES







LOCAL PACKING ARRANGEMENTS

Linear **Tetrahedral** Triangular © B3+

Coordination Number	Cation/Anion Radius
2	0 - 0.155
3	0.155 - 0.225
4	0.225 - 0.414

- At the lower limit of the radius ratio, cations and anions touch each other As the ratio increases, the structure opens up • At the upper limit, transition to the next higher coordination
- number occurs For ratios of 0.414 -0.732, the structure becomes octahedral; beyond this range, the structure becomes cubic (coordination number = 8)

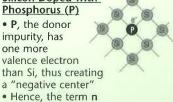
SEMI-CONDUCTORS: SILICON CHIPS

Silicon Doped with Phosphorus (P)

impurity, has one more valence electron than Si, thus creating a "negative center"

(for negative)-type

semiconductor



Silicon Doped with Boron (B)

 B, the acceptor impurity, has one less valence electron than Si, thus creating a "positive hole"



• Hence, the term p (for positive)

-type semiconductor

CHEMICAL EQUATIONS

BALANCING SIMPLE CHEMICAL EQUATIONS

KClO₃ → KCl + O₂ $KCIO_3 \rightarrow KCI + 3/2O_2$ $2KCIO_3 = 2KCI + 3O_2$

 First balance oxygen • Then balance potassium and chlorine • Finally, go back and re-balance oxygen

Tip: When balancing simple chemical equations, start with elements that occur the least number of times

CALCULATING MASS, MOLES & CONCENTRATIONS

Principle: Ratio of number of moles = ratio of number of particles

Irreversible Reaction

	Zn	+	2SO ₂	= ZnS ₂ O ₄
Mass (g)	X		y	1000
Moles	x/65.4		y/64	1000/193.4
Mole Ratios	x/65.4 1000/193.4	= 1:1	\Rightarrow	x = 338 g Zn
	y/64 1000/193.4	= 2:1	\Rightarrow	$y = 662 \text{ g SO}_2$

Irreversible Reaction with Limiting Reagent

	Zn +	$2SO_2 =$	ZnS ₂ O ₄
Initial Mass (g)	130.8	128	0
Initial Moles	$\frac{130.8}{65.4} = 2$	$\frac{128}{64} = 2$	0
Moles Left Over	1	0 (limiting)	1

Reversible Reaction

	CaCO ₃	\rightleftharpoons	CaO	+	CO ₂
Initial Moles	2		0		0
Reacted Moles	-0.5		+0.5		+0.5
Moles Left Over	1.5		0.5		0.5

Simultaneous Reactions

	CuO	1.00				Cu .839	2
Reaction 1	CuO	+	H ₂	=	Cu	+	H ₂ O
Mass (g)	Х				У		
Moles	x/79.	5			y/6	3.5	
Reaction 2	Cu ₂ O	+	H ₂	=	2Cu	+	H ₂ O
Mass (g)	1- x				0.839	y - y	
Moles	1 - x/1	43			(0.839	-y)/	63.5
Mole Ratios	$\frac{x/79}{y/63.}$	$\frac{5}{5} = 1$	2	1:2	x = 0. $1 - x =$		g CuO 5 g Cu ₂ O

Titration

	5Fe ²⁺	+ MnO ₄	→ Mr	n ²⁺ + 3	5Fe ³⁺
Volume (mL) 20.8	16			
Molarity	X	0.130			
Moles		16.0×0.13	0		
_	10^{3}	10 ³			
Mole Rati	$\frac{20.8}{}$		⇒	x = 0.	50 M
	16.0×0	.130	_	Λ – 0.	30 101

(0.839 - y)/63.5

BALANCING REDOX EQUATIONS

Principle: Split reaction into oxidation/reduction half-reactions and balance each in turn with H₂O, H⁺, and electrons (e⁻) • Recombine half-reaction equations algebraically so as to cancel e's (electrons are conserved in redox reactions)

• Multiply right side by 3 (electrons must cancel) and add:

 $3HCHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3HCOOH + 2Cr^{3+} + 4H_2O$

GENERAL CHARACTERISTICS

- The same principles apply as for Phase Equilibria In addition:
- (I) The concentrations at equilibrium stand in a fixed ratio called the Equilibrium Constant, Kc: $aA+bB \iff cC+dD \qquad K_c = \left\{ \frac{\left[C\right]^c \left[D\right]^a}{\left[A\right]^a \left[B\right]^b} \right\}_c$
- The concentrations at the start of a reaction constant ratio called the Reaction Quotient, Q: $aA+bB \iff cC+dD \quad Q_c = \left\{ \begin{bmatrix} C \end{bmatrix}^c \begin{bmatrix} D \end{bmatrix}^d \\ \begin{bmatrix} A \end{bmatrix}^a \begin{bmatrix} B \end{bmatrix}^b \right\}_{initial}$ (II) The concentrations at the start of a reaction stand in a similar
- (III) If $Q_c < K_{c'}$, then the reaction proceeds from left to right If $Q_c = K_c$, then the system is at equilibrium If $Q_c > K_{c'}$, then the reaction proceeds from right to left

THE EQUILIBRIUM CONSTANT, K

- (I) For gaseous reactions, K is often expressions of partial pressures: $K_p = \frac{[P_c]^c [P_D]^a}{[P_A]^a [P_B]^b}$ is often expressed in
- (II) The relation between K_p and K_c is given by: $K_p = K_c (RT)^{\Delta n}$

 $\Delta n = (c+d) - (a+b)$

known K's of component reactions: $2NO + O_2 \stackrel{\leftarrow}{\Rightarrow} 2NO_2 \quad K_1 = [NO_2]^2/[NO]^2[O_2]$ $2NO_2 \stackrel{\leftarrow}{\rightarrow} N_2O_4 \qquad K_2 = [N_2O_4]/[NO_2]^2$ $2NO + O_2 \stackrel{\longleftarrow}{\rightarrow} N_2O_4$ $K_x = K_1 K_2$

(IV) Unknown K's can be calculated from

(III) In heterogeneous reactions, solid

 $CaCO_3(s) \leq CaO(s) + CO_2$

 $K_c = [C O_2]$

concentrations are constant and can be included in the constant, K:

CALCULATIONS USING K

- Calculate p's and P_{Tot} at equilibrium and the % yield
- $K_p = 116 \ (T = constant)$

$$K_p = 116 = \frac{X^2}{152 - X} \Rightarrow$$

$$X^2 + 116X - (152)(116) = 0$$

Solve for X, P_{Tot} , and % yield

$$X = P_{PCI_3} = P_{CI_2} = 87.3 \text{ kPa}$$

 $P_{Tot} = (152 - 87.3) + 2 \cdot 87.3$

$$P_{Tot} = (132 - 87.3) + 2$$

= 239.3 kPa

PCI₅ Reaction PCl₃, Cl₂ PCI₅ $(P^{\circ}=152kPa)$

	PCl ₅ ≤	PCI ₃	+ Cl ₂	
Initial	152	0	0	
Reaction	-X	+X	+X	
At Eq	152-X	+X	+X	

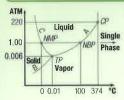
% yield = $\frac{87.3}{152}(100) = 57.4\%$

PHASE EQUILIBRIA

GENERAL CHARACTERISTICS

- Temperature, pressure, composition, and other properties of the system do not change with time
- Equilibrium results when the rates of two opposing processes (e.g., freezing/melting) become equal
- (III) Properties of a particular equilibrium state are independent of how that state was reached
- (IV) Le Chatelier's Principle: A system at equilibrium reacts to a change in a variable by minimizing that change

SINGLE COMPONENT SYSTEMS: THE WATER PHASE DIAGRAM



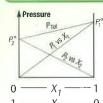
- A...... Boiling point or vapor pressure curve
- B...... Sublimation or solid vapor pressure curve
- C..... Melting point or freezing point curve

NBP/...Boiling/melting point at NMP "normal" pressure of 1 atm

CP..... Critical Point

TP.....Triple Point

TWO COMPONENT SYSTEMS: VAPOR-LIQUID EQUILIBRIA



Raoult's Law of Ideal Solutions

• The partial pressure, P_{ii} of a component in the vapor phase equals mole fraction, X_1 , in the liquid phase multiplied by the pure component vapor pressure, P_1° : $P_1 = X_1 \cdot P_1^{\circ}$

CALCULATIONS USING RADULT'S LAW

• Given P_1° , P_2° X_1 , at constant T, calculate X_2 , P_1 , P_2 , P_{Tot} , and the vapor phase mole fractions, Y_1 and Y_2

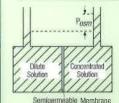
Solve X ₂	$X_1 + X_2 = 1 \implies X_2 = 1 - X_1$
Solve P ₁ , P ₂ , P _{Tot}	$\underbrace{P_1 = X_1 P_1^\circ \Rightarrow P_2 = X_2 P_2^\circ}_{\text{Raoult's Law}} \qquad \Rightarrow \underbrace{P_{Tot} = P_1 + P_2}_{\text{Dalton's Law}}$
Apply Ideal Gas Laws	$\underbrace{P_1 = n_1 RT/V \ \Rightarrow \ P_2 = n_2 RT/V \ \Rightarrow \ P_{Tot} = n_{Tot} RT/V}_{\text{Ideal Gas Laws}}$
Solve for Y ₁ , Y ₂	$Y_1 = P_1/P_{Tot} \Rightarrow Y_1 + Y_2 = 1 \Rightarrow Y_2 = 1 - Y_1$

COLLIGATIVE PROPERTIES

 Properties of phase equilibria which depend on the concentration of a non-volatile solute

Dissolved Substance	Changes Depend on m, M
Lowers the vapor pressure of solvent	$\Delta P_{V} = K_{V} m$
Raises the boiling point of solvent	$\Delta T_b = K_b m$
Lowers the freezing point of solvent	$\Delta T_f = K_f m$
Responsible for osmotic pressure	$P_{osm} = MRT$

OSMOTIC PRESSURE



- Water permeates from left to right across the semipermeable membrane until Posm stops the
- In reverse osmosis, extra pressure is applied on the concentrated side of the membrane, forcing water to flow from right to left
- An example of reverse osmosis is desalinated seawater

IONIC EQUILIBRIA (THE SOLUBILITY PRODUCT, Kon)

SPARINGLY SOLUBLE SOLIDS

• K_{sp} = Equilibrium Mg(OH)₂(s) \leftrightarrows Mg²⁺ + 2OH⁻ constant of sparingly soluble $K_{sp} = \left[Mg^{2+} \right] \left[OH^{-} \right]^{2} = 1.2 \times 10^{-11}$ ionic substances

CALCULATING ION CONCENTRATIONS

 $Mg(OH)_2 \subseteq Mg^{2+} + 2OH_0$

$$[Mg^{2+}]/[OH^{-}] = 1/2$$
 :: $[Mg^{2+}] = \frac{1}{2}[OH^{-}]$

$$K_{sp} = \frac{1}{2}(OH^{-})^{3} = 1.2 \times 10^{-11}$$

$$[OH^{-}] = 2.9 \times 10^{-4} \frac{\text{mol}}{1}$$

$$[Mg^{2+}] = \frac{1}{2}[OH^{-}] = 1.45 \times 10^{-4} \frac{mol}{L}$$

CALCULATING SOLUBILITY, S

 s = Mass of dissolved solids (g/L) ${\rm Mg(OH)_2}_{\rm dissolved} \rightarrow {\rm Mg^{2+}} = 1.45 \times 10^{-4} \frac{\rm mol}{\rm L}$ $s = 1.45 \times 10^{-4} \times Molar Mass = 8.5 \times 10^{-3} \frac{g}{l}$

COMMON ION EFFECT

 An increase in the ion concentrations reduces the solubility (Le Chatelier)

Solubility of Mg(OH)₂ in 1 M NaOH:

$$[Mg^{2+}][1]^2 = 1.2 \times 10^{-11} \implies s = 7 \times 10^{-10} \frac{g}{L}$$

SELECTIVE PRECIPITATION



Ag+, Cl-, CrO₄-AgCl Ag₂CrO₄ Example: Pour solution of silver ions (i.e., AgNO₃) into a beaker containing chlorine and chromium anions • Which will precipitate first, AgCl or Ag₂CrO₄? • How complete is the separation? • Possible equilibria are:

$$AgCl(s) \iff Ag^+ + C\Gamma$$

$$K_{sp} = 2.8 \times 10^{-10}$$

$$Ag_2Cr0_4(s) \leq 2Ag^+ + Cr0_4^{2-}$$

$$K_{sp} = 1.9 \times 10^{-12}$$

• [Ag+] required for precipitation to start

$$\left[Ag^{+}\right]_{AgCl} = \frac{K_{sp}}{\left[C\Gamma\right]} = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9} \quad \begin{array}{c} AgCl \text{ precipitates} \\ \text{first} \end{array}$$

$$\left[Ag^{+}\right]_{AgCrO_{4}} = \left\{\frac{\kappa_{sp}}{\left|CrO_{4}^{2-1}\right|}\right\}^{1/2} = \left\{\frac{1.9 \times 10^{-12}}{0.01}\right\}^{1/2} = 1.4 \times 10^{-5}$$

• [Cl-] remaining when Ag₂CrO₄ starts to

$$\left[\text{CF}\right]_{\text{rem}} = \frac{K_{\text{sp}}}{\left[\text{Ag}^{+}\right]} = \frac{2.8 \times 10^{-10}}{1.4 \times 10^{-5}} = 2 \times 10^{-5} \Rightarrow 0.002\%$$

IONIC EQUILIBRIA (ACIDS & BASES

LOWRY-BRONSTED DEFINITIONS

Bronsted Acid = Proton Donor

$$\frac{\text{HNO}_3}{\text{Acid}} \rightarrow \frac{\text{H}^+}{\text{Proton}} + \text{NO}_3^-$$

Bronsted Base = Proton Acceptor

$$\underbrace{OH^{-}}_{\text{Base}} + \underbrace{H^{+}}_{\text{Proton}} \rightarrow \text{H}_{2}\text{O}$$

ION PRODUCT OF WATER, KW

 K_w = Dissociation equilibrium constant of

 $H_20 \hookrightarrow H^+ + 0H^-$

$2H_2O \iff H_3O^+ + OH^- \quad K_W = [H_3O^+][OH^-] = 10^{-14} \text{ (at 25°C)}$

$K_w = [H^+][0H^-] = 10^{-14}$ (at 25°C)

PH OF SOME FLUIDS

THE PH SCALE

water

$$pH = -log[H^+] pOH = -log[0H^-]$$

pH+pOH = 14 (at 25°C)

For pure water at 25°C:

$$pH = pOH = 7$$
 and $[H^+] = [0H^-] = 10^{-7} \frac{mol}{L}$

DISASSOCIATION CONSTANTS OF

 $HA \stackrel{\leftarrow}{\hookrightarrow} H^+ + A^- \qquad K_a = \frac{H^+ A^-}{[HA]}$

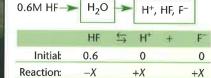
BOH \leftrightarrows B⁺ + OH⁻ $K_b = \frac{B^+ \text{ OH}^-}{\text{ [BOH]}}$

Indicators are Weak Acids or Bases

$$\underbrace{\text{HIn}}_{\text{color 1}} \stackrel{\leftarrow}{\hookrightarrow} \text{H}^+ + \underbrace{\text{In}^-}_{\text{color 2}}$$
(weak acid)

 $[nOH] \hookrightarrow OH^- + [n^+]$ (weak base)

CALCULATING ION CONCENTRATIONS WITH K.



At Eq:
$$0.6 - X + X$$

$$K_a = \frac{[H^+][F^-]}{[HF]} = \frac{X^2}{0.6 - X} = 7.1 \times 10^{-4}$$

$$X^2 + 7.1 \times 10^{-4} X - 4.32 \times 10^{-4} = 0$$

$$X = [H^+] = [F^-] = 0.021 \frac{\text{mol}}{\text{L}}$$

HCI (1M) 3.0 Vinegar Milk 7.0 Pure water Blood 7.4 ± 0.05 NaOH (1M) 14.0

Gastric juice 1 - 2Lemon juice 2.4 Urine 4.8 - 7.56.4 - 6.9Saliva

STRONG ACIDS & BASES (TOTAL DISSOCIATION)

HCI	LiOH
HBr	NaOH
HI	КОН
HNO ₃	Ca(OH) ₂
H ₂ SO ₄	Ba(OH) ₂

WEAK ACIDS & BASES (PARTIAL DISSOCIATION)

HF	NH ₃
HNO ₂	CH ₃ NH ₂
HCN	C ₂ H ₅ NH ₂
НСООН	$CO(NH_2)_2$
CH ₃ COOH	C_6H_5N
Aspirin	Caffeine

SOLUTIONS OF SALTS OF A WEAK ACID OR BASE: HYDROLYSIS

- Salts of weak acids and bases initially dissociate completely, then hydrolyze ("split") water, resulting in a basic or acidic
- The hydrolysis constant can be calculated from the component K's (i.e., K_a or K_b) and K_w

SOLUTIONS OF A SALT & ITS PARENT WEAK ACID OR BASE: BUFFERS

- Buffer solutions minimize changes in pH caused by addition of an acid or base
- Their pH can be calculated from the Henderson-Hasselbach equation

$$pH = log \frac{A^{-}}{IHA} - log K_0$$

 $pH = log \frac{A^{-}}{[HA]} - log K_a \qquad pOH = log \frac{B^{+}}{[BOH]} - log K_b$





Contributors: Prof. D. Basmadjian, PhD, T. K. Varga, MASc

ISBN: 1-55080-804-4 \$3.95 U.S./\$5.35 CDN your dealer, look up Permacharts.com, or call (1.800.387.3626 U.S. & Canada) This product is © Mindsource Technologies Inc., 2003.05. All rights reserved.



NEW-POWE 84 DISP-CHARTS

Ш

0

5

D

4

Ü

D

E

ø