Separations

Separations is the art of maximizing separative transport while minimizing diffusive transport
…J.C. Giddings.

MODEL 1 Entropy of Separations

$$\Delta S = nR \ln (V_f/V_i).$$

1. If the final volume (V_f) is larger than the initial volume (V_i), is the entropy of the process favored? Explain.

2. Is dilution a thermodynamically favorable or unfavorable process? Explain.

3. Is mixing an entropically favorable or unfavorable process. Explain.

4. If 50 mL of EtOH is mixed with 50 mL of water, what is the entropy of mixing?

MODEL 2 Thermodynamics of Separations

The equilibrium constant for transferring compound X from an aqueous to an organic solvent is called the partition coefficient.

$$X_{(aq)} \Leftrightarrow X_{(org)}$$

1. Write an expression for the partition constant (K_D) in terms of activities of X.

2. What factors determine the enthalpy and entropy (or chemical activity) of compound X in the two solvents?

MODEL 3 Intermolecular Forces

Substance	Boiling Point (K)
Ar	87.3
He	4.22
Butane	273
Acetone	329
Propanol	370
Hexane	342
2-pentanone	375
1-pentanol	410

1. Using the idea of intermolecular forces, suggest why the boiling points of Ar and He are different.

2. Why is the following statement not quite accurate? Xenon has a higher boiling point than neon because xenon atoms are heavier than neon atoms.

3. Which compounds interact *primarily* by London (van der Waals forces).

4. Which compounds interact *primarily* by dipole-dipole forces.

5. Which compounds interact *primarily* by hydrogen bond forces.

6. Explain why propanol and 1-pentanol boil at different temperatures. Explain why acetone and 1-2-pentanone boil at different temperatures. Compare the bp *differences* for these two pairs. Why is the difference so similar?

7. The three intermolecular forces described above are all $1/r^6$ forces because they fall off as the distance between them to the sixth power. ion-London, ion-dipole and ion-hydrogen bond forces all fall off as $1/r^2$. What does this suggest about the magnitude of ion interactions as compared with non-ion interactions?

MODEL 4 Hildebrand solubility parameter

The Hildebrand parameter is defined by the following equation:

$$\delta = \left(\frac{\Delta H_{vap} - RT}{V_m} \right)^{1/2}$$

Compound	**δ** (kJ/m^3)$^{1/2}$	**ΔH_{vap}** (kJ/mole)	**V_{molar}** (mole/m^3)
Hexane	14.2	28.9	1.3x10^{-4}
Benzene	19.0	34.7	8.9x10^{-5}
Water	46.0	40.7	1.8x10^{-5}

1. Conceptually, why is ΔH_{vap} in the numerator?

2. The enthalpy of mixing solute i in solvent β can be calculated from the following formula:

$$\Delta \overline{H}_{i\beta} = \overline{V}_i (\delta_i - \delta_\beta)^2$$

Is it possible to have a negative value for the enthalpy of mixing? Why or why not? Does this make physical sense?

3. Based on the formula, is benzene more soluble in hexane or water?

4. How would you calculate molar volume given density and molecular mass?

5. Conceptually, why is molar volume in the denominator in the solubility parameter equation and a term in the enthalpy of mixing?

6. How might molar volume relate to entropy effects?

MODEL 5 Distribution Coefficients

Compound	Log K_{OW}	pH	Log D	D
Hexane	4.18	0-14	4.18	15,000
Ethylamine	0.751	4	-0.07	0.85
Ethylamine	0.751	10	0.75	5.6
Acetic acid	0.994	4	0.923	8.4
Acetic acid	0.994	10	-4.26	$5.5x10^{-5}$
Acetamide	-0.672	0-14	-0.672	0.21

1. Why are some compounds distribution functions (D) insensitive to pH and others more sensitive?

2. Cocaine has the following properties:

Physical properties	Free base	Cocaine-HCl
Melting point	98°C	>195°C
Water solubility, g/ml	1.67x10-3	2.5
$CHCl_3$ solubility, g/ml	1.43	0.08
Ether solubility, g/ml	0.29	insoluble

a. How do the molecular properties relate to the methods that addicts might use for ingestion when this drug is abused?

b. Devise a procedure by which you would convert the HCl form to the free base form.

c. Why are criminal penalties more sever for the free base form (crack) than the HCl form?

3. The pK_b of cocaine is 5.6. How much cocaine would be partitioned into the aqueous phase at pH 4 and pH 10?

4. Devise a two-step procedure for purifying cocaine from coca plant leaves using the following: 0.1 M HCl, 0.1 M $NaHCO_3$, and ether or chloroform.