Review of a few
Physical and Chemical Principles
Related to Exposure Modeling

If you need more details than given here, there's a lot of tutorials available on YouTube

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From High School and College General Chemistry

- The concentration of saturated vapor Csat is an important to know "upper bound" (usually) on exposure concentration

- A chemical's P_V value **increases** as the **temperature** of the system **increases**.
  For benzene: P_V = 75 mm Hg at 20 C and P_V = 96 mm Hg at 25 C so 95/75 = 1.3 X higher at 25 C

- Look up the Clausius–Clapeyron or Antoine equation or Wagner equation if you need P_V at other temperatures.   See Appendix II of "Mathematical Models …"

- Different chemicals will have different Antoine coefficients and thus different Pv vs T curves

- See a discussion with benzene as the example at:
 https://www.youtube.com/watch?v=YxplklxQDmI

2

- An opened 500 gram package of 1,4-dichlorobenzene moth balls is spilled and left in a tight closet.

- The closet has a tight sealing door and a volume of 3 cubic meters with no ventilation.

- A homeowner opens the door and gets exposed to the closet air.

- If at saturation what is the ppm concentration of 1,4-dichlorobenzene the person was exposed to in the first few breaths?

3
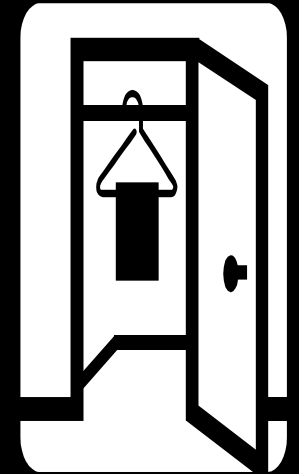
An Example of Applying the Saturation Vapor Pressure Model

We can assume:

- The person was exposed to a saturated concentration of 1,4-dichlorobenzene at 25 C.

- This implicitly assumes
  - Equilibrium vapor pressure was attained in the closet, <u>and</u>
  - The contaminated air was *not* significantly diluted by room air prior to inhalation

- The chemical formula is $C_6H_4Cl_2$ and the molecular weight is 147 g/mol.

- The vapor pressure is 1.36 mm Hg at 25 °C

- Csat (ppm) = [1.36*10^6]/760 = 1790 ppm (10,800 mg/m³)
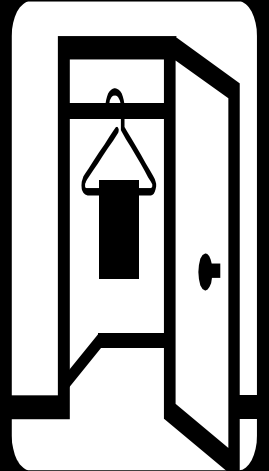
By mass balance is this possible? Yes. 500 grams = 500,000 mg in 3 m³

4

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Saturation Vapor Pressure of a Component in a Mixture

Raoult's "Rule" Commonly called Raoult's LAW

Chemical A is a component in a liquid mixture.
- Chemical A has a molecular structure similar to the other mixture components.
  - X_A denotes the **mole fraction** of A in the liquid.
    - # $Moles_A$ = ($grams_A$ / molecular $weight_A$)
    - Mole $fraction_A$ = (# $Moles_A$ / Sum of all Moles of all constituents)
  - $P_{V,A}$ denotes the **saturation vapor pressure** of pure chemical A
- In a closed system of air and excess liquid chemical, the *partial pressure* of chemical A's vapor in the airspace, denoted P_A, is given by:

$$P_A = X_A \cdot P_{V,A}$$

An Example

A solvent of mixed xylenes with 15% methylene chloride (MeCl) by weight --- (not a really similar compound mixture, but let us look at it)

What is C_{sat} for MeCl?

First, determine the mole fractions

- MW: MeCl = 84.9 g/mol, Xylene = 106 g/mol
- In 100 g,
  - 15 g ÷ 84.9 g/mol = 0.18 moles MeCl
  - 85 g ÷ 106 g/mol = 0.80 moles xylene
  - Total 0.98 moles
- Mole Fraction MeCl = 0.18/0.98 = 0.18
- Mole Fraction xylenes = 0.80/0.98 = 0.82

STEP 2: Saturation vapor pressures of
- MeCl is 350 torr at 20 °C
- Xylenes 7 torr at 20 °C

STEP 3: Activity Coefficient?
- Not a very pure mixture, neither X_{MeCl} and $X_{xylenes}$ approach 0.99….
- Use UNIFAC Calculator (a general method)… or alternate methods
- Measured activity coefficients are best, but UNIFAC estimates are OK, but there are limits to UNIFAC … do not use for mixtures containing polymers or for electrolyte mixtures. Do not use at more than a few atmospheres of pressure or above 150 °C

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Activity Coefficient Example 15% by weight Methylene Chloride in Mixed Xylenes

Note the exponents!

Or an Excel tool from The Netherlands

This older but reliable calculator has become hard to find. Write to me twa8hr@gmail.com for a copy, or download from my public Dropbox link.
https://www.dropbox.com/sh/flwa17da6trmemv/AACXHxp6OBcAaIMj3vtbqINTa?dl=0

Also see Mike Jayjock's coverage in his BLOG:
 Activity Coefficients an UNIFAC Calculator   or   From The Netherlands, XLunifac

In this example, both components deviate high, to different extents. In other mixtures, some deviations may be downward.

An Example

Apply Raoult's Rule to estimate MeCl vapor pressure in a mixture with xylenes

- **Without Activity Coefficient**

$$P_A = X_A \times P_{V,A} = 0.18 \times 350 = 63 \text{ torr}$$

$$C_{sat} = 63 \text{ torr} \times 10^6 \div 760 \text{ torr} = \textbf{83,000 ppm}$$

- **_With_ Activity Coefficient**

$$P_A = X_A \times P_{V,A} \times A_{coef} = 0.18 \times 350 \times 5.7 = 360 \text{ torr}$$

$$C_{sat} = 360 \text{ torr} \times 10^6 \div 760 \text{ torr} = \textbf{470,000 ppm}$$

Hmm! Might the difference of 5.7 x be IMPORTANT?!

Building Molecules in the UNIFAC Calculator

- See http://www.aim.env.uea.ac.uk/aim/info/UNIFACgroups.html for more information on molecular fragment contributions

- Example Phenol.   5 x ACH & 1 x ACOH It is then added to the local database

- This freeware calculator does not include all possible molecular groups.

- Unfortunately, we do not have time to talk much about the compound database or how to add new compounds.

Call or write to me after the course.   The XLUnifac

Spreadsheet takes a bit of study to use
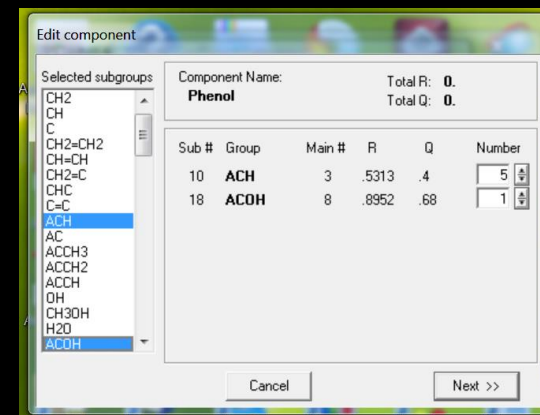
Summary: What did we just learn?

If we have **pure liquid in equilibrium**:

- Find the vapor pressure (at your temperature)

- Compute Saturation Concentration:

  - C_{sat} in PPM = P_v/760mm Hg x 10^6

  - If in *sealed* room or space, adjust denominator for the increase in pressure by the substance… (very very rarely necessary)

    - $C_{sat} = (P_v * 10^6)/(760mm\ Hg + P_v)$

If we have a mixture

- Use **Raoult's law** if the target chemical makes up >99% … or use if >90% **and** is similar to other components:

  $P_A = X_A \cdot P_{V,A}$

- Or use **Raoult's Rule with Known or Estimated Activity Coefficients if <90 to 99% or dissimilar (differing polarity or differing homologous series) materials**

- Use **Henry's law** if chemical exists in small proportion (<0.1%) and is in aqueous solution:

  $H_A = \dfrac{C_A(air)}{C_A(aq)}$

  Henry's Law can be used for non-aqueous systems, but few non-aqueous system coefficients are available.   Watch units when you look up H_A values.

Part 2.
Mass Balance, Evaporation Rates, Generation Rates, and Their Calculation

Within all types of Emission:

There is always some consideration of the time course of contaminant generation.

- Instantaneous (or approximately so)
- Constant (infinitely replenished) – (evap/inject)
    - Spill within containment
    - Vapor leak – constant pressure or limiting orifice
    - Slowly filling a partially full gasoline container
- Decreasing
    - Evaporation – decreasing in size or concentration
        - Spill after source is off- resulting in a shrinking pool
        - More volatile component of mixture in a pool.
    - Vapor leak – decreasing pressure

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IH MOD 2.0 handles the following:

❑ The Rate of <u>Emission is Constant</u>.

- Sometimes called "zero order"

❑ The Emission Rate is Decreasing with Time

- Some models in IH MOD can handle "first order" decreases in the source and require a value for k in $G = G_0 (-\exp kt)$
- Example: a spill with shrinking diameter

❑ The Emission is a Bolus or considered an instantaneous finite release in SOME of the Eddy Diffusion Models.

This will handle the BULK of what you want to do; however, if you want or need to get more sophisticated you will probably need a more advanced modeling platform like MathCAD or MATLAB or more specific advanced models.

Often, for a time-varying generation rate, an average or a maximum can be sufficient

14

Estimating G by a Material Mass Balance

Simple Material Mass Balance can be a useful estimate for a generation rate:

$$G = \frac{\text{Mass (mg) emitted into air in interval T}}{T \text{ (min)}}$$

- **Example of the Material Mass Balance**
  - 20 ml of adhesive containing 15% toluene vol/vol is used per 15 minute task. **All** the toluene is assumed to evaporate.
  - Toluene's liquid density is 0.866 g/mL
  - What is G or the <u>average</u> rate of release over T?

- **Answer**
  - 20 ml x 0.15 = 3 mL toluene
  - 3 mL x (866 mg/mL) = 2600 mg toluene
  - G = (2600 mg/15 min) = 173 mg/min

- Example 2. 1 kg of a degreasing solvent is lost over an 8 hour day (by how much is added to keep the degreaser at full.

  1000 grams/480 minutes = 2.1 grams/minute = 2100 mg/min

15

Estimating G by Rate of Injection into Air

Again,   G   =

$$\frac{\text{Mass (mg) emitted into air in interval T}}{\text{T (min)}}$$

- **Examples of Injection:**
    - Hair Spray: 5 grams of isopropanol per 2 seconds in a 1 m^3 sphere around the mouth and nose of the User.
    - Container Filling: Volume of the container is displaced into the air with vapors from the filling liquid. Example: pouring gasoline into a lawn tractor tank.
    - Sanding, sawing, sweeping or other ways of throwing particulate into the air.

    HYPOTHETICAL EXAMPLE: a metal finishing operation involves fine polishing.   By before and after weighing of parts, 0.1% of the mass is lost.   If 100 kg polished, 0.1 kg is released. If respirable, 100 grams/480 minutes =

    0.21 grams/minute = 208 mg/min

Estimating G by Evaporation from a small spill
Algorithm for Predicting the Vapor Mass Emission Rate from a Pure Liquid Surface

Hummel: $G =$
$$\frac{165.6 \; MW^{0.833} \; P_V \left(0.0345 + \dfrac{1}{MW} \right)^{0.25} A}{T^{.05}} \sqrt{\frac{U}{L \, P_{atm}}}$$

G = vapor emission rate (mg/min)

D_M = molecular diffusion coefficient in air (m²/sec)

ν = kinematic viscosity of air (m²/sec)… 1.52 x10⁻⁵ @ 20 C; 1.56x10⁻⁵ @ 25 C (m²/s)

U = air speed over the liquid pool (m/sec)

P_v = vapor pressure of evaporating chemical (Pascal, Pa)

P_{atm} = atmospheric pressure (Pa) [note: 1 atm = 101,325 Pa]

R = ideal gas constant, 8.314 Pa·m³·mol⁻¹·K⁻¹

MW = molecular weight of the chemical (g/mol)

A = surface area of liquid pool (m²)

L = surface length of liquid pool (m) *along airflow direction*

T = temperature of the liquid (K)

17

Hummel Vapor Emission Rate Algorithm Assumptions

- If we assume that the liquid temperature and pool size are **constant** as evaporation proceeds, this algorithm predicts a **constant vapor mass emission rate**.

- For simplicity, a **constant temperature** and constant **liquid pool size** are frequently assumed in generation rate algorithms and experiments.
  - These factors may **not** be constant.
  - Why?

- If the liquid's temperature and/or surface area **decrease** as evaporation proceeds, the vapor mass emission rate will also decrease. Sometimes all you really need though is an INITIAL Generation rate

- **VP is limited to 0.05 atm or 38 mm Hg**

IH Mod 2.0 — G : Hummel equation

		Initial values			
Overall system pressure	P	1 Atm	< >		1 Atm
Velocity of air	Vx	100 cm/sec	< >		100 cm/sec
Surface temperature of pool	T	20°C			20°C
Length of pool along airflow	Δx	100 cm	< >		100 cm
Surface area of pool	A	10000 cm²	< >		10000 cm²
Molecular weight	MW	85 g/mole			
Vapor pressure of substance	VP	0.1 Atm			

Evaporation rate   **74500 mg/min**

$$\left[\frac{\left(8.79 \times 10^{-5} (MW)^{0.833}(VP) \times (1/MW + 1/29)^{0.25}\right)}{T^{0.05}} \sqrt{\frac{V_x}{\Delta x p}} \right] \cdot A \cdot 6 \cdot 10^4$$

Version 1,0 : April 2018

This file has been created by Daniel Drolet and Tom W. Armstrong

19
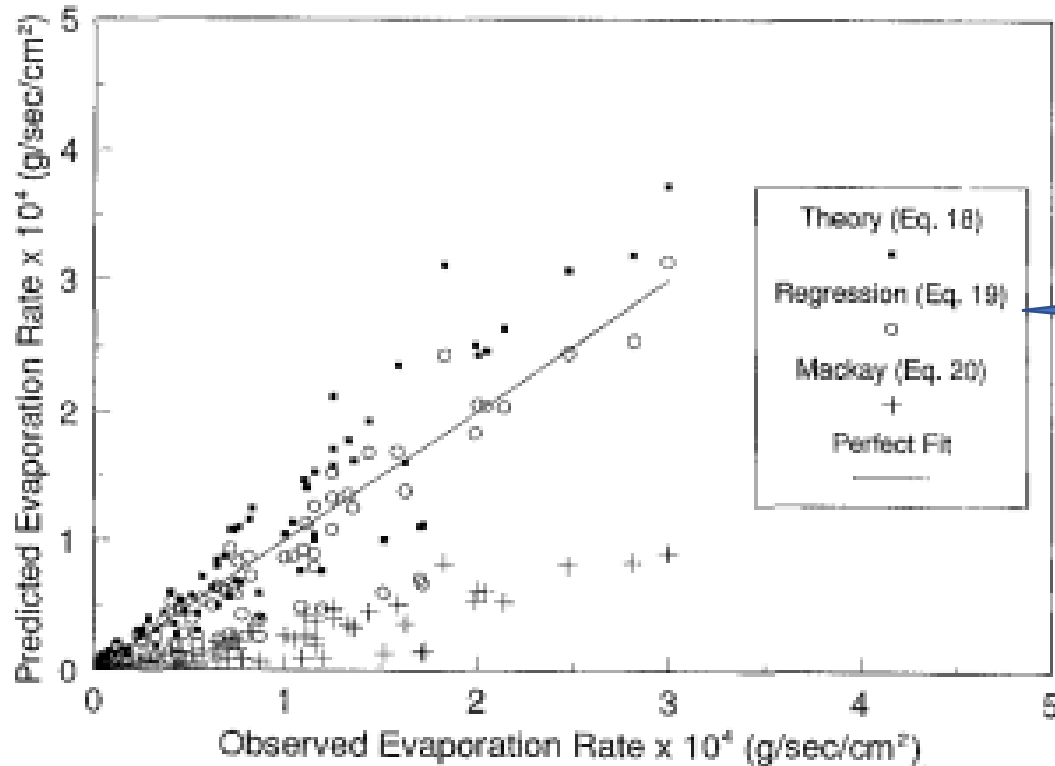
FIGURE 5. Comparison of the predicted versus observed experimental evaporation rates for the theoretical equation, a regression fit, and the Mackay equations

The black dots are the Hummel equation predictions

I have wondered how well this would do for an initial evaporation rate for a substance in a mixture if the mole fraction and activity coefficient were applied to get the partial pressure of the substance in the mixture. I may have missed it but I am not aware of reports on this.

20

How do I get G If?

- You are dealing with a particulate (e.g., dust from a power saw)?
    - Determine by experimental measurements
    - Back calculate from a survey report
    - Apply a "dustiness index"*

- You can not live with the limitation of Hummel? That is, must be a pure substance, must have VP less than .05 atm, or need better than "Ball Park" accuracy as described by the authors of the Hummel model.
    - Maybe estimate based on relative evaporation rate from an OK compound.
    - Determine experimentally or back calculate from a survey

*Schneider and Jensen, 2009 Relevance of aerosol dynamics and dustiness for personal exposure to manufactured nanoparticles. J. Nanopart. Res. 11, 1637–1650.

* Levin et al., 2014 Release and exposure assessment of four pharmaceutical powders based on dustiness and evaluation of damaged HEPA filters. J. Occup. Environ. Hyg. 11, 165–177.

Relative Evaporation Rate

- If you have a generation rate for a chemical with a published relative evaporation rate, you can use this to estimate the generation rate for another chemical with a published evaporation rate.

- This is shown in the IH Mod 2.0 Support File for estimating Alpha (See next slide) but can be used for a "relative" generation rate too

- This could be very useful when the chemical of interest is very toxic or otherwise hazardous

- The Hummel generation rate appears to give the right "order of magnitude" or better and is generally conservative but has an increasing error above its stated VP limits.

first order evaporation rate constant (aka Alpha in IH Mod 2.0), as given in the IH Mod 2.0 Support File

1 Alpha is a first order evaporation rate constant and gives the relationship between the initial contaminant mass (M_0) the remaining contaminant mass at time t (M_t)

$$M_t = M_0 * exp^{-\alpha t}$$

Rearranging,

$$\alpha = -[Ln(M_t/M_0)]/t$$

where

M_t = contaminant mass (grams) remaining at time t (minutes)
M_0 = the initial contaminant mass (grams) at time zero
t = the time at which Mt is determined
α = evaporation rate constant, (per minute)

To use this, we need an estimate of the evaporation time ot a given remaining portion, say 10% or the initial mass. Note 0% does not work

Calculating α

M_0 Initial mass	500 g
M_t Mass at Time t	51 g
Time t	10 min
Estimated Alpha, min^{-1}	0.228

ALPHA continued (from IH Mod 2.o Support File)

2 Keil and Nicas Algorithm to Estimate Alpha

The authors* measured α for a suite of compounds and different sizes of spill. They found that α can be estimated for organic compounds containing only C, H, and O with the equation:

$$\alpha = 0.000524\ VP + 0.0108\ SA/Vol$$

where
VP is the vapor pressure of the liquid
SA/Vol is the surface area to volume ratio.

This relationship was found for vapor pressures over the range of 6 to 400 mm Hg, yielding alphas of 0.0046 to 0.39 at 20⁰C and for an air velocity over the solvent of 3.4 m/min and GSD 1.9. Use outside that vapor pressure range, conditions or molecular composition may not give valid estimates

*Charles B. Keil & Mark Nicas (2003) Predicting Room Vapor Concentrations Due to Spills of Organic Solvents, AIHA Journal, 64:4, 445-454, DOI: 10.1080/15428110308984838

Keil & Nicas Estimate of α

Vapor Pressure	100 mm Hg
Surface Area	10 cm²
Volume	10 mL

| Estimated Alpha, min^{-1} | **0.0632** |

Chemical	VP mm Hg 20°C	α min^{-1}	Range
Ethyl ether	440	0,37	0.31 - 0.41
n-Pentane	400	0,39	0.35 - 0.43
Acetone	180	0,16	0.13 - 0.19
n-Hexane	124	0,14	0.12 - 0.16
Methyl alcohol	96	0,055	0.042 - 0.076
Methyl ethyl ketone	78	0,055	0.048 - 0.063
2-Propanol	33	0,028	0.024 - 0.033
Toluene	21	0,025	0.024 - 0.027
n-Butyl acetate	10	0,011	0.009 - 0.012
1-Butanol	6	0,0046	0.0037 - 0.0057
Methylene chloride	350	0,14	0.013 - 0.015
Chloroform	160	0,082	0.079 - 8.088
Carbon disulfide	297	0,11	0.10 - 0.11

3 If you have Alpha for Some Substances and Relative Evaporation Rate Data ...

Another type of data relevant available is called *Relative Evaporation Rate*
It is the evaporation rate in a lab test compared to butyl acetate or ether

Source used : **EASTMAN** Solvent Comparison Tool

Alpha for butyl acetate is 0.011 /min (Keil 2003)

	Evap Rate But. Ac. =1	estimated α
Acetone	6.3	6.3 * 0.011 = **0.069**
Toluene	1.9	1.9 * 0.011 = **0.021**
Methyl alcohol	3.5	3.5 * 0.011 = **0.039**

What if Exposure Controls are Present?

- **How effective are the controls?** For example, see Fransman, W., Schinkel, J., Meijster, T., Van Hemmen, J., Tielemans, E., Goede, H., 2008. Development and Evaluation of an Exposure Control Efficacy Library (ECEL). Ann. Occup. Hyg. 52, 567–575.

- **Proportionally reduce the generation rate estimated without controls**

- **Use the models developed and published by Ganser and Hewett**
  - Hewett P, Ganser GH. Models for nearly every occasion: Part I - One box models. J Occup Environ Hyg. 2017 Jan;14(1):49-57. doi: 10.1080/15459624.2016.1213392. PMID: 27869546.
  - Ganser GH, Hewett P. Models for nearly every occasion: Part II - Two box models. J Occup Environ Hyg. 2017 Jan;14(1):58-71. doi: 10.1080/15459624.2016.1213393. Erratum in: J Occup Environ Hyg. 2017 Aug;14(8):D139. PMID: 27869550.

References on Generation Rates

- US EPA "Ap42" but mostly industrial emissions
- Chapter 3, Modeling Pollutant Generation Rates in "Mathematical Models for Estimating Occupational Exposure to Chemicals", C. Keil et al, AIHA Press, 2009. Tasks approaches relevant to consumers
- In EU, approaches are evolving to standardize consumer exposure scenarios, but not much is available on specifics relevant to generation rates
- US EPA Exposure Factors Handbook
- Specific literature reports
- No known comprehensive compilations