
A REVIEW OF SOME RESEARCH PRESENTED
AT THE TWENTIETH TOBACCO CHEMISTS'
RESEARCH CONFERENCE: PART 1.
A CELEBRATION OF THE FORTIETH
ANNIVERSARY OF THE APPLICATION OF GAS-
PARTICLE PARTITIONING THEORY TO THE
CIGARETTE MAINSTREAM SMOKE AEROSOL

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Outline for presentation

- Background
- Objectives
 1. Review experimental work done by Vekris
 2. Review gas-particle partitioning (GPP) theory developed by Vekris and compare with Pankow's
 3. Value of results in 2006 context
- Conclusions

Background – 1

- Selective filtration became a popular topic in early 1960s because of potential to reduce biological effects of smoking
 - To be selectively filtered, compounds needed to be at least partly in the gas-vapor phase (GVP) (e.g., a semivolatile compound (SVC) of the mainstream cigarette smoke (MSS) aerosol
 - Transfer from particulate phase (PP) to GVP assumed to be via distillation mechanism
 - Equilibrium between PP and GVP assumed to be established very rapidly

Background – 2

- To aid in the design of selective filters, data on concentrations in PP and in GVP for SVCs of interest were needed
 - Such concentration information could also be indirect test of hypothesis that PP-GVP equilibrium rapidly established
 - Ideal conditions also assumed in the development of theoretical relationships
 - Estimations had been done that showed effect of curvature on vapor pressure outside of aerosol droplet was not significant

Objective 1 – Review Vekris’s experimental work

- Experimental approach
 - Part 1 – GPP of SVCs in MSS aerosols
 - SVC (e.g., cyclic ketones) spiked on cigarettes
 - SVC generated from nonvolatile precursors spiked on cigarettes
 - Part 2 – Supporting studies
 - Measurement of concentration of GVP-compounds in free cigarette smoke aerosol (a/k/a MSS)
 - Estimation of rates of transfer between PP and GVP

Generation of SVCs for GPP studies

Compound	Precursor	Solvent
Pentaldehyde	Pentaldehyde 2,4-DNPHydrazone + levulinic acid	Benzene
Hexaldehyde	Hexaldehyde 2,4-DNPHydrazone + levulinic acid	Benzene
Heptaldehyde	Heptaldehyde 2,4-DNPHydrazone + levulinic acid	Benzene
Heptaldehyde	Castor oil	N/A
Pyridine	Sodium nicotinate	Water
Pyridine	Clathrate with Dianin's compound	Pyridine
3-Methylpyridine	Clathrate with Dianin's compound	3-Methylpyridine
2,3-Dimethylpyridine	Clathrate with Dianin's compound	2,3-Dimethylpyridine
2,6-Dimethylpyridine	Clathrate with Dianin's compound	2,6-Dimethylpyridine
Cyclopentanone	Barium adipate	Water
Cyclohexanone	Barium pimelate	Water

Some data for SVCs for GPP studies

Compound	Vapor pressure (torr @ 298°K)	pK _a	Log _{Kow}
Pentaldehyde	26		1.31
Hexaldehyde	11		1.78
Heptaldehyde	3.5		2.29
Pyridine	21	5.23	0.64
3-Methylpyridine	6.1	5.63	1.20
2,3-Dimethylpyridine	3	6.56	0.65
2,6-Dimethylpyridine	5.7	6.75	1.20
Cyclopentanone	11		0.24
Cyclohexanone	5		1.68

Data from various sources, including estimation equations

Test articles for GPP studies

■ All flue-cured (CN102)

- Nonfilter
- 70 mm long
- 25.6 mm circumference
- 1140 mg weight
- 8.6 cm WG pressure drop
- 34.5 mg/cig TPM
- 2.19 mg/cig nicotine
- 10.5 puffs/cig
- 240 μg /cig total SVC phenols
- 990 μg /cig GVP aldehydes
- 1.24 mg/cig total volatile acids calculated as HOAC

■ All burley

- Nonfilter
- 72 mm long
- 25 mm circumference
- 740 mg weight
- 10.1 cm WG pressure drop

Experimental conditions for GPP studies

	Burley	Flue-cured
Number of cigarettes per experiment	20	20
Number of puffs per cigarette	7	10
Number of cigarettes per Cambridge filter	5	4
Number of Cambridge filters per experiment	4	5
Cambridge filters preheated to remove artifacts caused by organic binder		
After smoking Cambridge filters were weighed and stored under mixture of acetone and ether. After concentration, solutions analyzed by GC.		
The GVP passing through the Cambridge filter was trapped in a spiral glass trap cooled with liquid oxygen. The trap was extracted at room temperature with solvent, and solution brought to a known volume and analyzed by GC.		

GPP results with flue-cured blend

Compound	Concentration ratios (F) x 10 ⁻⁵		<u>Experimental</u> Theoretical
	Theoretical	Experimental	
Pentaldehyde	25.6	52.8	2.1
Hexaldehyde	7	18.8	2.7
Heptaldehyde	1.9	7.3	3.7
Pyridine	13.2	6.1	0.5
3-Methylpyridine	4.0	1.3	0.3
2,3-Dimethylpyridine	1.8	0.8	0.5
2,6-Dimethylpyridine	3.3	2.6	0.6
Cyclopentanone	7.6	12.7	1.7
Cyclohexanone	3.2	5.9	1.7

Flue-cured versus burley GPP results

Compound	Concentration ratios (F) x 10 ⁻⁵		
	Flue-cured	Burley	$\frac{\text{Burley}}{\text{Flue-cured}}$
Cyclopentanone	12.7	16.0	1.3
Cyclohexanone	5.9	8.3	1.4
Hexaldehyde	18.8	65.0	3.5
Heptaldehyde	7.3	27.5	3.8
Pyridine	6.1	8.6	1.4

Measurement of GVP components in MSS

- Experimental proof of applicability of GPP theory to MSS required measurement of concentration of GVP components
- Measurements made on absorption of pyridine vapor from whole smoke and from smoke passed through normal or heat-treated (to remove organic binder) Cambridge filter pads
- Heat-treated Cambridge filter pads were shown to have minimal effect of pyridine vapor concentrations

Equilibrium in a burning cigarette?

- GPP theory assumes equilibrium conditions
- Can there be equilibrium in a system so dynamic as a burning cigarette?
- This is very important question
 - If compounds rapidly transfer between PP and GVP, dynamic equilibrium would exist and GPP is valid
 - If GPP is valid for MSS, then Pankow's theory of absorptive partitioning is valid for MSS
 - If Pankow's theory is valid, then existing data on MSS shows that nicotine will remain in the PP except when MSS is very dilute (1-mg product smoked under FTC/ISO conditions)

Evidence for rapid dynamic equilibrium

- Vekris cited the following observations
 - Particle-size growth in the MSS aerosol by condensation of existing particles
 - Selective filtration by the distillation mechanism is dependent on evaporation rate from PP to GVP
 - Displacement of low-volatility flavors from tobacco rod or filter tip is more efficient with MSS than air
 - Selective filtration of phenol by plasticized CA filters occurs even though less than 5% of phenol in GVP
 - Distribution of an SVC in MSS phases after Cambridge filter is constant and approximates calculated equilibrium distribution

Vekris transfer rate experiments

■ Experiment 1

- A small quantity (one puff of NF cigarette) was deposited on a Cambridge filter pad; nitrogen was drawn through the pad and concentration of volatiles in gas stream measured

■ Experiment 2

- Two streams, one of aerosol particles dispersed in nitrogen and the other of organic vapor, were mixed in a jet. The GVP concentrations of the organic material at two points in the system were measured by absorption of ultraviolet light

Results of Experiment 1

Conditions	Vapor pressure (torr)	Half-life (milliseconds)	Accommodation coefficient for $r = 10^{-4}$ cm	Calculated half-life for $r = 2 \times 10^{-5}$ cm (milliseconds)
From equilibrium data	0.012			
From flow rate of 5 L/min		3	2×10^{-4}	0.6
From flow rate of 10 L/min		7	1×10^{-4}	1.4

Half-lives were estimated for particles of radius 2×10^{-5} cm, the weight-average value for MSS. For comparison, normal puff flow rate, a small volume of smoke passes through a cigarette in about 100 milliseconds and through a 15-mm long filter in about 20 milliseconds.

Results of Experiment 2

		Half-life $\alpha = 1$	Half-life $\alpha = 0.1$	Half-life $\alpha = 0.01$	Half-life $\alpha = 0.0001$
Aerosol dispersed phase	Organic vapor	(milliseconds)	(milliseconds)	(milliseconds)	(milliseconds)
Paraffin	Mesitylene	0.09	0.3	2	200
Paraffin	<i>o</i> -chlorophenol	0.09	0.3	2	200
Dibutyl phthalate	Mesitylene	0.2	0.5	3	300

Vekris described the data above as follows. “The data show the calculated half-lives for particle radii 0.44μ in the case of paraffin and 0.61μ in the case of dibutyl phthalate, for four values of α .”

“Since the aerosol particles are made up of pure nonvolatile organic liquids, and organic vapors are also pure and of low volatility, α is likely to be relatively high. This is particularly true for the hydrocarbon system paraffin/mesitylene. The probable half-lives are, therefore, considerably less than 2 ms; and the concentrations within 13 ms are probably within 10% of equilibrium values.”

Objective 2 – Review Vekris's GPP theory

- Derivation started with Raoult's Law
 - $p = P \times X$, where p = solution vapor pressure; P = vapor pressure pure compound; X = mole fraction
- Dalton's law of partial pressures gives
 - $y = p/A$ where y = mole fraction in vapor phase; A = atmospheric pressure; then $y = (P \times X)/A$ and one $\text{cm}^3 @ T^\circ\text{K} = 273 \times A / (T \times 760 \times 22400)$ mol
 - Hence $y = w_v / m / (v_v \times 273 \times A) / (T \times 760 \times 22400)$
 - $y = (w_v \times T \times 760 \times 22400) / (m \times v_v \times 273 \times A)$
 - where, w_v = weight (g) component in GVP, v_v is volume (cm^3) of GVP, m is mol. wt. of component and T = room temperature in $^\circ\text{K}$

Review Vekris's GPP theory – 2

- Bringing in average molecular weight of PP
 - $X = w_p / m / v_p / m = w_p \times M / m \times v_p$ where w_p is the weight (g) of the component in PP, v_p is the volume (cm^3) of PP and M is average molecular weight of PP
 - $y = (P \times w_p \times M) / (m \times v_p \times A)$
 - $w_v / w_p = (P \times v_v \times M \times 273) / (T \times 760 \times v_p)$
 - $c_v / c_p = w_v / v_v / w_p / v_p = (P \times M \times 273) / (T \times 760 \times 22400)$
 - where c_v is the concentration in the GVP (g/cm^3)
 - where c_p is the concentration in the PP (g/cm^3)
- Thus,
 - $c_v / c_p = F = (1.6 \times 10^{-5} \times P \times M) / T$
 - At constant T , $F = KP$, where K is constant

Vekris – Pankow theory comparison – 1

■ Vekris

- $c_v / c_p = (P \times M \times 273) / (T \times 760 \times 22400)$
- where c_v is the concentration in the GVP (g/cm^3)
- where c_p is the concentration in the PP (g/cm^3)
- where P = vapor pressure of component of interest & M is MW (g/mol) of PP & T = temperature ($^\circ\text{K}$)

■ Pankow

- $c_p / c_g = 760RT / 10^6 MW_{om} Y_i p^o_L$,
- where c_p is concentration in PP ($\text{ng}/\mu\text{g}$)
- where c_g is concentration in GVP (ng/m^3)
- where p^o_L = vapor pressure of component of interest & MW_{om} is MW of PP (g/mol) & T = temperature ($^\circ\text{K}$)

Vekris – Pankow theory comparison – 2

- Vekris
 - $c_v / c_p = K$ – a dimensionless equilibrium constant
- Pankow
 - $c_p / c_g = K$ – an equilibrium constant with dimensions of $m^3 / \mu g$
 - In addition to Pankow's equilibrium constant being the inverse of Vekris's, Pankow uses the gas constant, R , because his units of PP concentration are ng/ug (weight/weight instead of weight/volume as used by Vekris)
 - Included activity coefficient (dimensionless)
- In essence, Vekris was there first

Objective 3 – Value of results in 2006 context

- Was research done by Vekris significant?
 - When work was first reported it appeared to generate little interest
 - Project was apparently terminated when Vekris left BAT mid-1968
 - Vekris's work is now better known as several authors have cited the work in recent publications
 - Key findings from Vekris's research
 - Ratio of concentrations (F) in the two phases is independent of total amount present
 - There is dynamic equilibrium between the two phases that is rapidly achieved
 - F-ratio for similar compounds depends on vapor pressure

Conclusions

- Susan Vekris was the developer of GPP theory; Pankow's development of GPP theory came much later
- Vekris recognized that GPP theory was based on thermodynamics, not kinetics, and thus had to bring in concept of dynamic equilibrium
- Vekris showed that dynamic equilibrium was attained on a time frame that was short (probably less than 10 milliseconds)
- Vekris showed that removing organic binder on Cambridge pad was important for accurate measurement of GVP concentrations

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