Discussion: predicting optics carbonization from a knowledge of resist outgas composition

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Possible methods to estimate Carbonization Rate (*CR*)

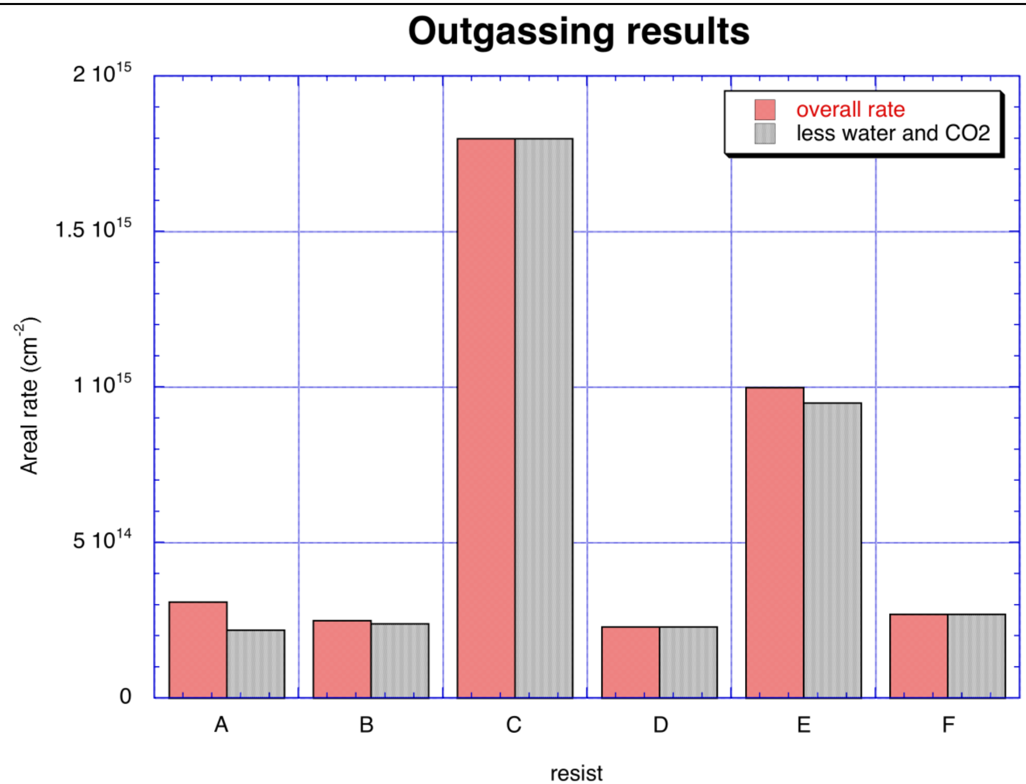
1. Semi-quantitative method
   a) Measure total outgas
   b) Analyze composition of outgas
   c) Determine the EUV-induced carbonization rate of organic components at some low pressure (nm/dose @ $P \geq 10^{-9}$ Torr)
   d) Sum contributions of organic components assuming carbonization rate scales linearly with pressure from that low pressure downward
2. "Improved" semi-quantitative method
   a) Perform 1. a) & b)
   b) Determine EUV-induced carbonization rate ***scaling factor*** (nm/(dose·Torr)) applicable* to conditions in the stepper (if possible)
   c) Sum contributions of organic components using ***scaling factor***

*** *P* of organics in stepper < 10^{-9} Torr + trace of H_2O in background**

An example of compositional analyses for 6 resists

Total outgas = Ω_X

Step 1.(a)



Significant components thus far O_i

Step 1.(b)

1. Isobutene
2. Benzene
3. Acetone
4. Toluene
5. Isobutane
6. Diphenyl sulfide
7. Hexane
8. Tert-butylbenzene

Step 1.(c): EUV-induced Carbonization Rates ($CR^{(m)}$)

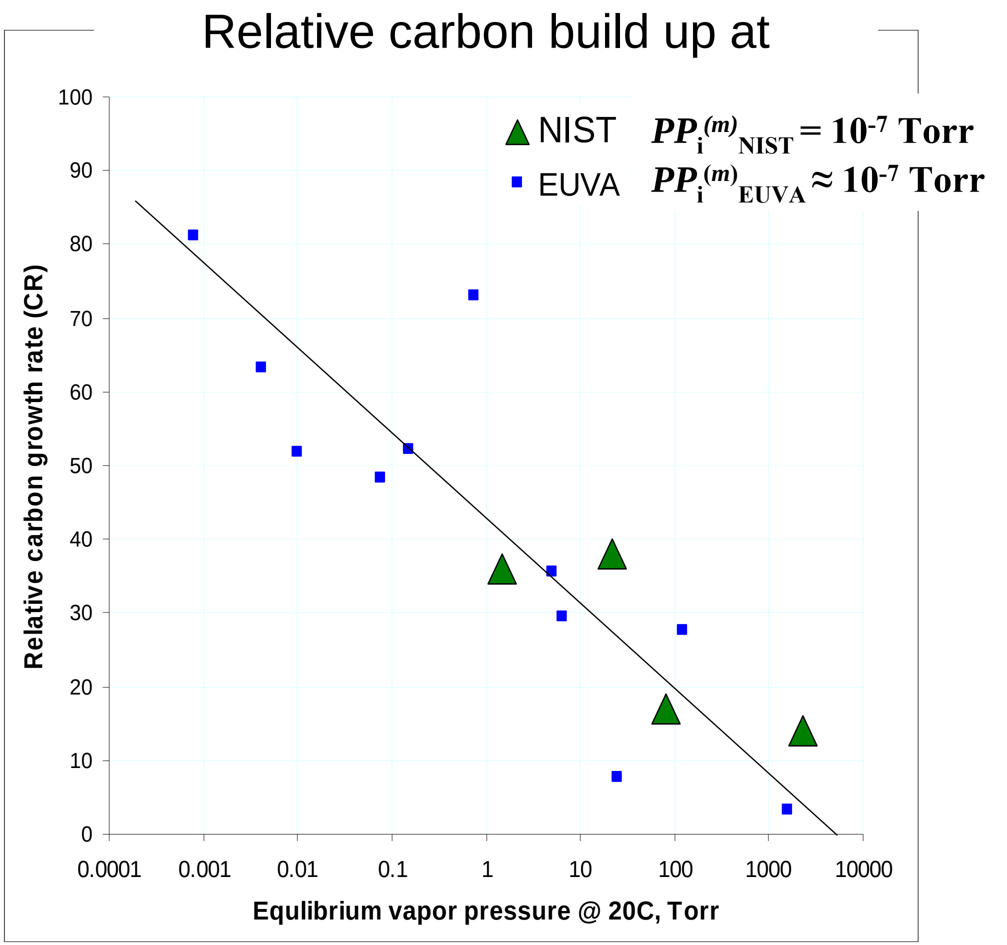
NIST Measurements (normalized)

Species	Vapor pressure at 20C, Torr	Relative C growth rate
Benzene	80.85	17
Toluene	21.86	38
isobutene	2267.55	14
Tert-butylbenzene	1.5	36

EUVA (Japan) Measurements *)

Butane	1556.54	3.3
Hexane	121.26	27.7
Methyl propionate	6.38	29.6
Polyfluorooctane	25	7.8
Butanol	5.02	35.7
Decane	0.15	52.2
Diethyl benzene	0.75	73
Methyl nonanoate	0.075	48.4
Decanol	0.01	51.8
Dimethyl phthalate	0.00417	63.3
Hexadecane	0.0008	81.1

*) Matsunari et al, SPIE Vol. 6517, 65172X, (207)



Desired result: $CR_i^{(m)}$ (nm/dose) at the lowest pressure $PP^{(m)}$ ($\approx 10^{-9}$ Torr)

Note: Somewhat systematic dependence on the log of the equil. vapor pressure

Step 1.(d): Combining resist data to rank damage potential

Assume:

1. Total outgas resist X = Ω_X
2. Fractional composition: Resist X = $f_{X1}\cdot O_1 + f_{X2}\cdot O_2 + f_{X3}\cdot O_3 + \cdots$
3. $CR^{(m)}$(nm/dose) = EUV-induced carbon build-up at $PP_i^{(m)}$ of O_i
4. Partial pressure at optic $PP_i^{(o)} \propto \Omega_X \cdot f_{Xi}$
5. Linear scaling: $CR_i^{(o)} \approx (PP_i^{(o)}/PP_i^{(m)})\cdot(CR_i^{(m)})$

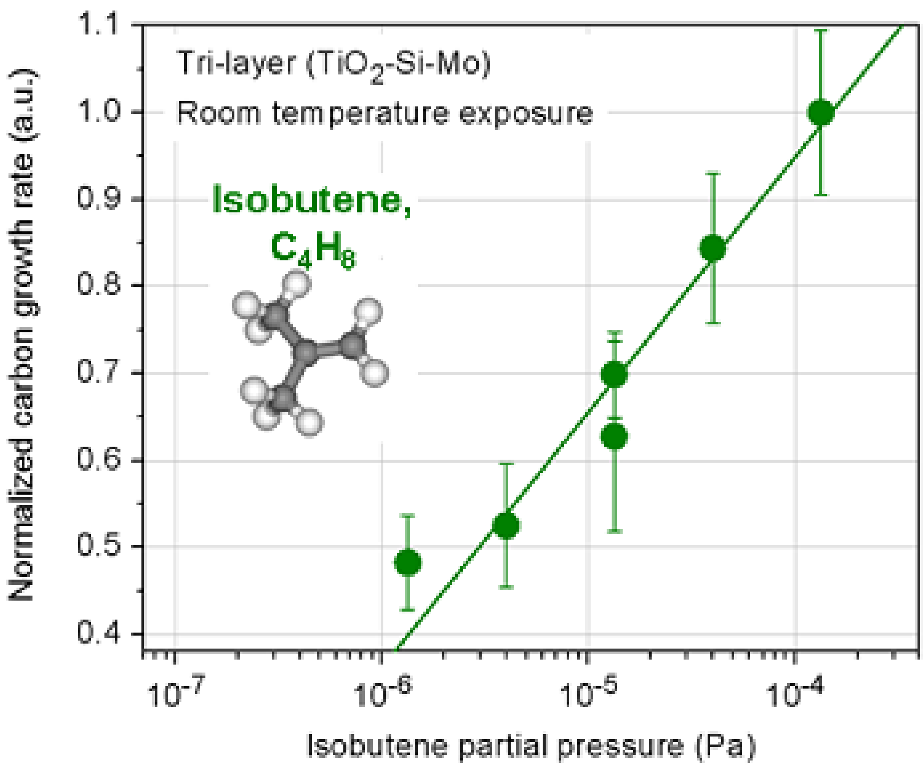
$$\textbf{Ranking factor} \approx \Omega_X \cdot \sum (f_{Xi}/PP_i^{(m)})\cdot CR_i^{(m)}$$

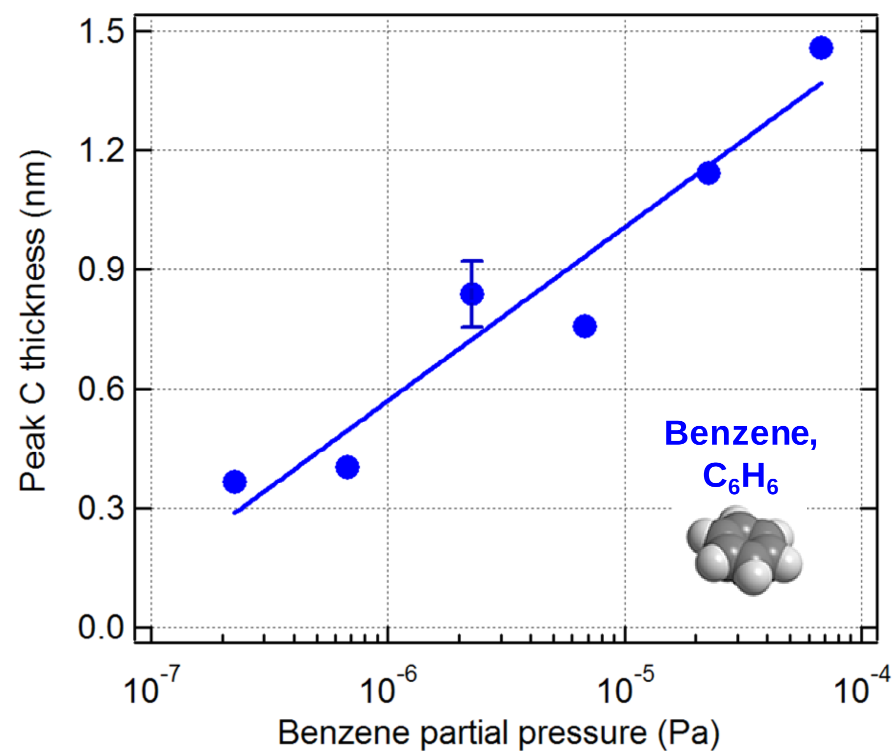
Weaknesses:

1. We have found 5. not true for several O_i on TiO_2 at $PP^{(m)}$ down to 3×10^{-9} Torr ;
2. Assumes each organic O_i acts independently; also ignores fact that water vapor in stepper will affect carbonization rates.

Scaling: $CR^{(o)} \neq (PP_i^{(o)}/PP_i^{(m)}) \cdot CR^{(m)}$

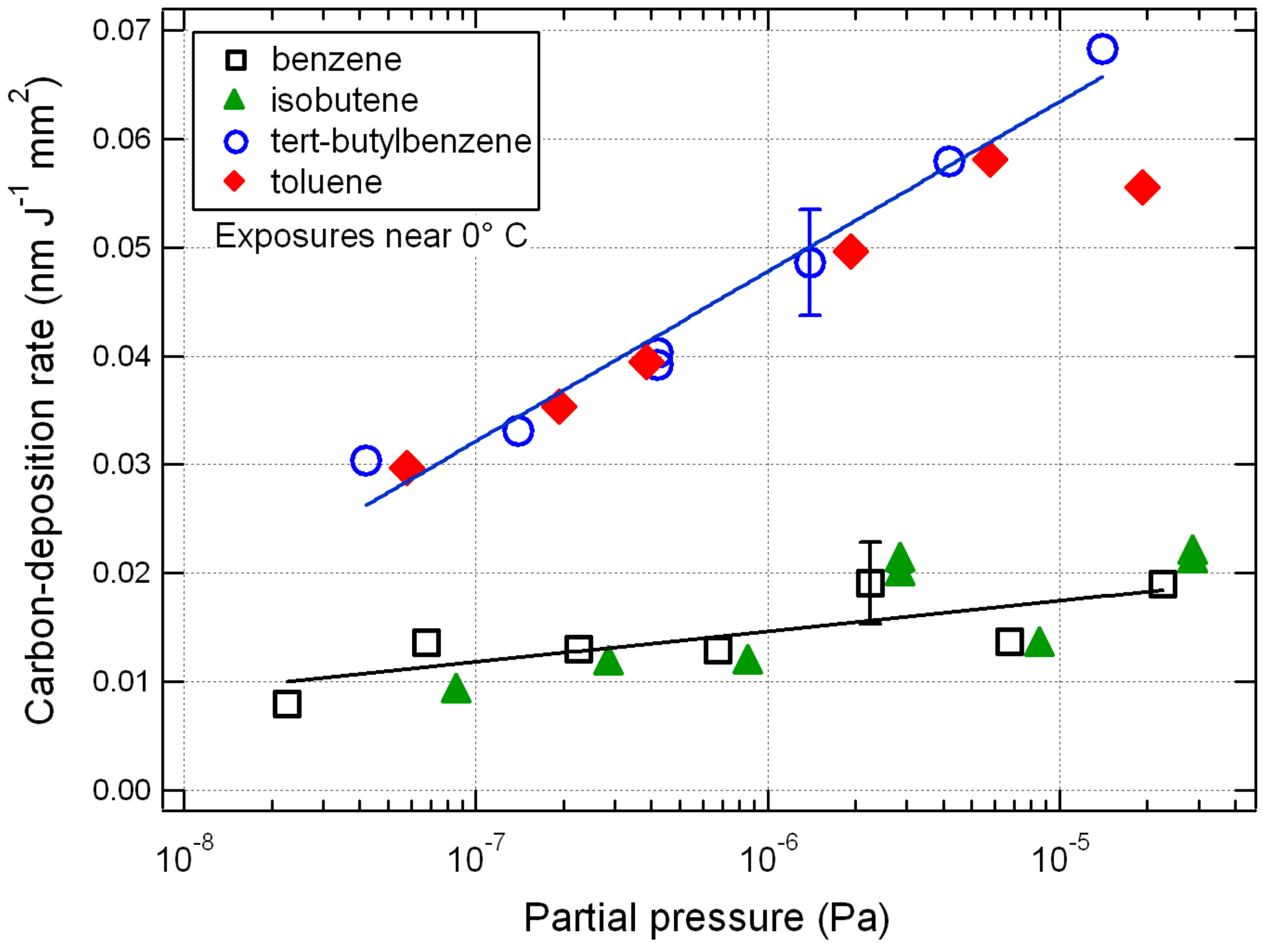
Log (P/P_x) dependence fits all organics thus far observed





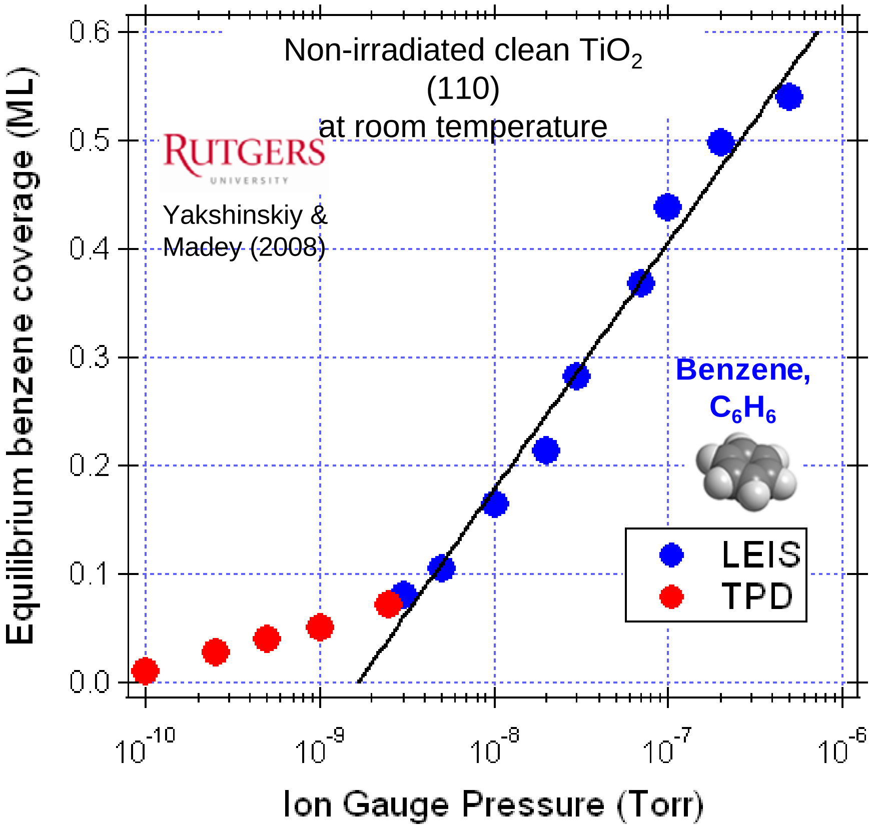
Isobutene and benzene

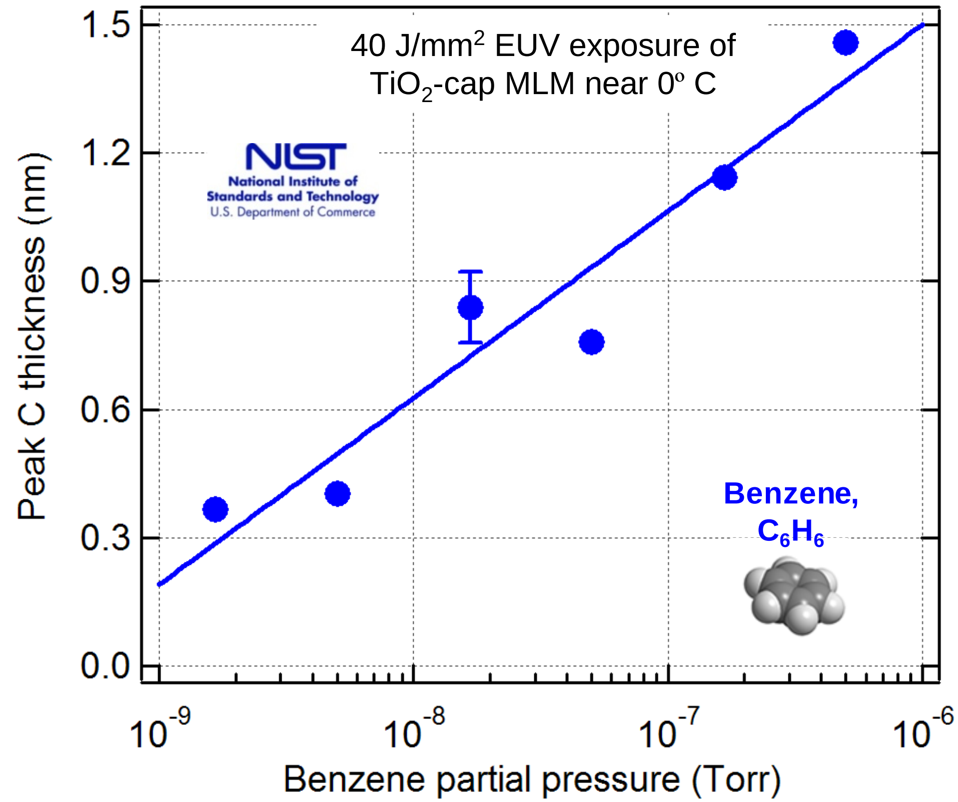
Scaling: $CR^{(o)} \neq (PP_i^{(o)}/PP_i^{(m)}) \cdot CR^{(m)}$ (cont.)



Tert-butylbenzene and toluene

Comparison to surface science experiments





- **Surface physics experiments can go to lower pressures**
- **However: Also requires effects of residual water vapor be included in carbonization rate measurements!**

Ranking by "improved" semi-quantitative method

Prerequisites:

- Knowledge of expected partial pressure of water vapor in stepper
- Determination of a carbonization scaling factor $\mathfrak{R}_i$(nm/(dose·Torr)) for organic $\mathbf{O}_i$ suitable for $PP << PP_i^{(m)}$ that also includes effect of water vapor (expected to be possible for very low pressures)

Other inputs:

3. Total resist X outgas = Ω_X
4. Fractional composition: Resist X = $f_{X1}\cdot\mathbf{O_1} + f_{X2}\cdot\mathbf{O_2} + f_{X3}\cdot\mathbf{O_3} + \cdots$

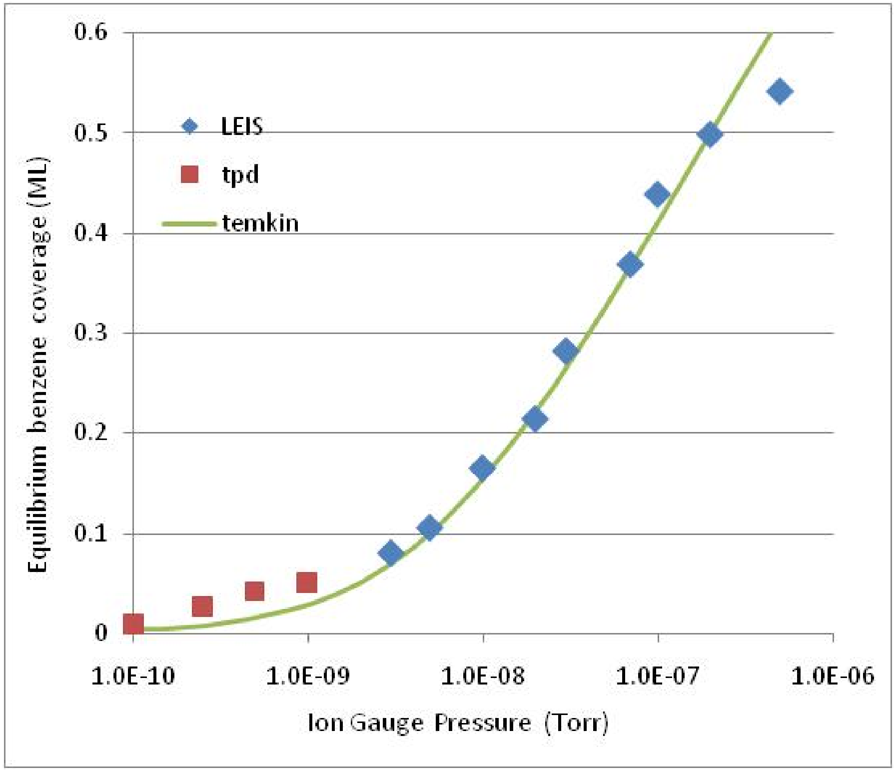
Improved Ranking Factor ≈ $\Omega_X\cdot\sum f_{Xi}\cdot\mathfrak{R}_i$

Discussion questions

1. What factors have been neglected in the improved version? Are they important?
   - Effect of large He background?
   - Other bi-molecular interactions e.g., $\mathbf{O_i} \times \mathbf{O_k}$ or $\mathbf{O_i} \times \mathbf{He}$?
   - Do we have to consider the possibility of mitigation schemes?
   - Effect of OOB radiation?
   - Effect of organics from tool components?
2. What is the best way to determine scaling factor $\mathfrak{R}_i$?
3. Will the community support experimental plus theoretical research to determine $\mathfrak{R}_i$ applicable at the low *PP*s expected in the stepper?
4. "Improved" ranking factor should be normalized to a measure of actual mirror carbonization in stepper. How should it be done?
   - Witness plate test?
   - Other possibilities?
5. What are the main threats to different optics in the chain?

Back-up slides

Isotherms and extrapolation to low pressures



<u>Temkin isotherm:</u>

$$\mathbf{Log(P) = A \cdot \theta + \log(\theta/(1 - \theta)) + B}$$

<u>Langmuir isotherm:</u>

$$\theta = \mathbf{D \cdot P/(1 + C \cdot P)}$$

Often seen for smooth surfaces with low coverages

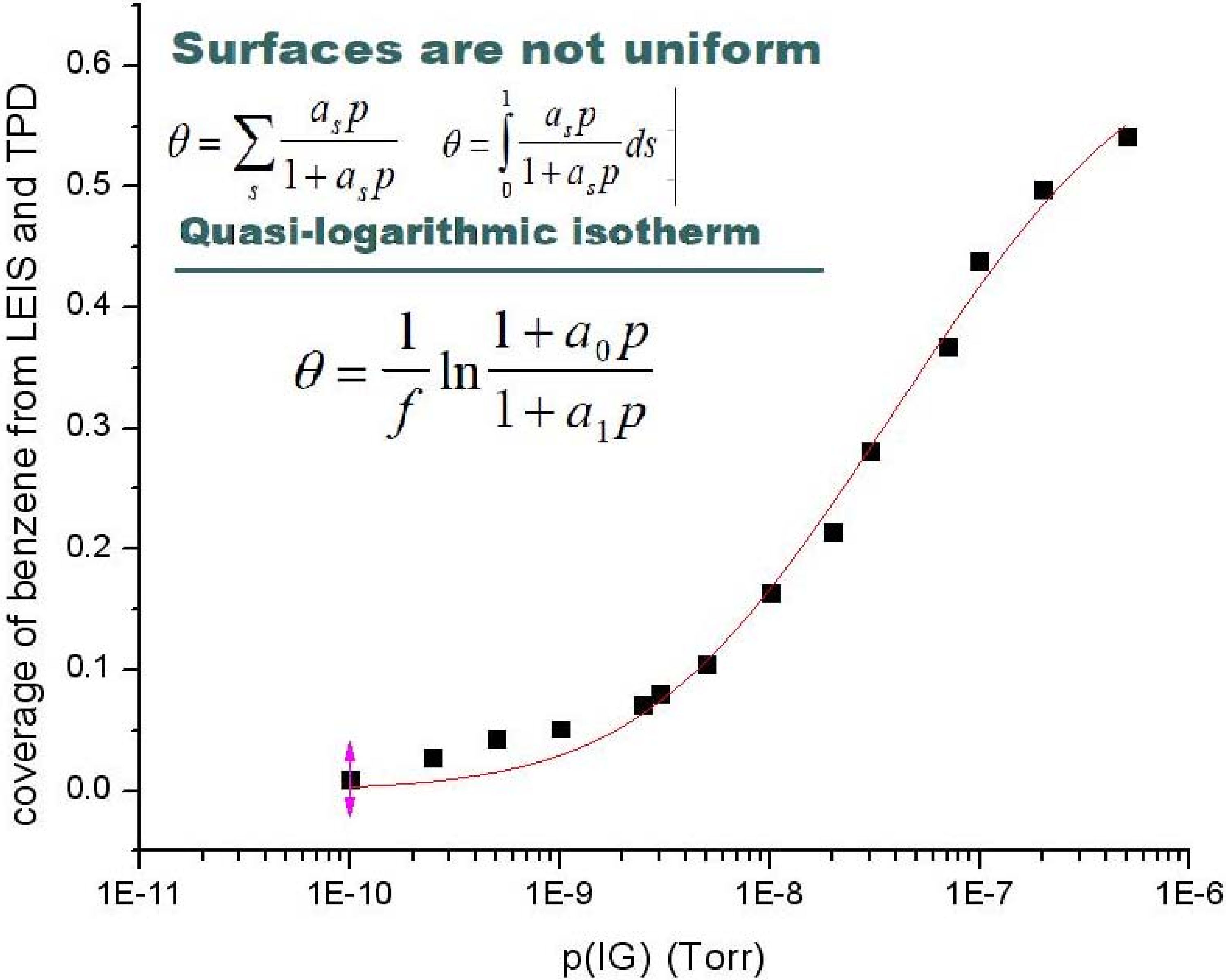
Both isotherms asymptotically approach

$$\theta = \mathbf{constant \cdot (P)}$$

at low coverage and low pressure:

Tools of basic surface science might provide method to evaluate coverage at very low P.

However: Applicability requires effects of residual water vapor be included in carbonization rate measurements!



Surfaces are not uniform
$\theta = \sum_s \frac{a_s p}{1 + a_s p}$
$\theta = \int_0^1 \frac{a_s p}{1 + a_s p} ds$
Quasi-logarithmic isotherm
$\theta = \frac{1}{f} \ln \frac{1 + a_0 p}{1 + a_1 p}$
coverage of benzene from LEIS and TPD
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1E-11
1E-10
1E-9
1E-8
1E-7
1E-6
p(IG) (Torr)