WESTERN RESEARCH INSTITUTE
"Providing solutions to highway building materials problems"

ASPHALT MICROSTRUCTURE MODEL

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43rd Petersen Asphalt Research Conference
Pavement Performance Prediction, P3-Symposium
June 21-23, 2005
Laramie, Wyoming
Models Used to Predict Pavement Performance
Compositional Models Session

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ACKNOWLEDGEMENTS

FHWA for their Financial Support under Contract No. DTFH61-98-R-00093

NCHRP 9-37: Using Surface Energy Measurements to Select Materials for Asphalt Performance

ICAR-505: Surface Energy Measurements as Performance Indicators of Hot-Mix Asphalts (HMA) and Portland Cement Concrete (PCC) Performance

Towards a Unified Physico-Chemical Model of Asphalt Binder

Asphalt Microstructure Model

Introduction to micro-Emulsion Colloid Mechanics
The Onion Model and Colligative Properties
Equilibrium Thermodynamics in micro-Emulsion Colloid Mechanics
Kinetics in micro-Emulsion Colloid Mechanics

Asphalt Solidification Model

Equilibrium Thermodynamics of Surfaces and Interfaces
Phase Transformations and Colligative Properties
non-Equilibrium Thermodynamics of Surface micro-Structuring
Dissipative Structure Theory
Application to Fracture Mechanics

Further Thoughts on Fatigue and Moisture Damage, Rutting, and Thermal Cracking

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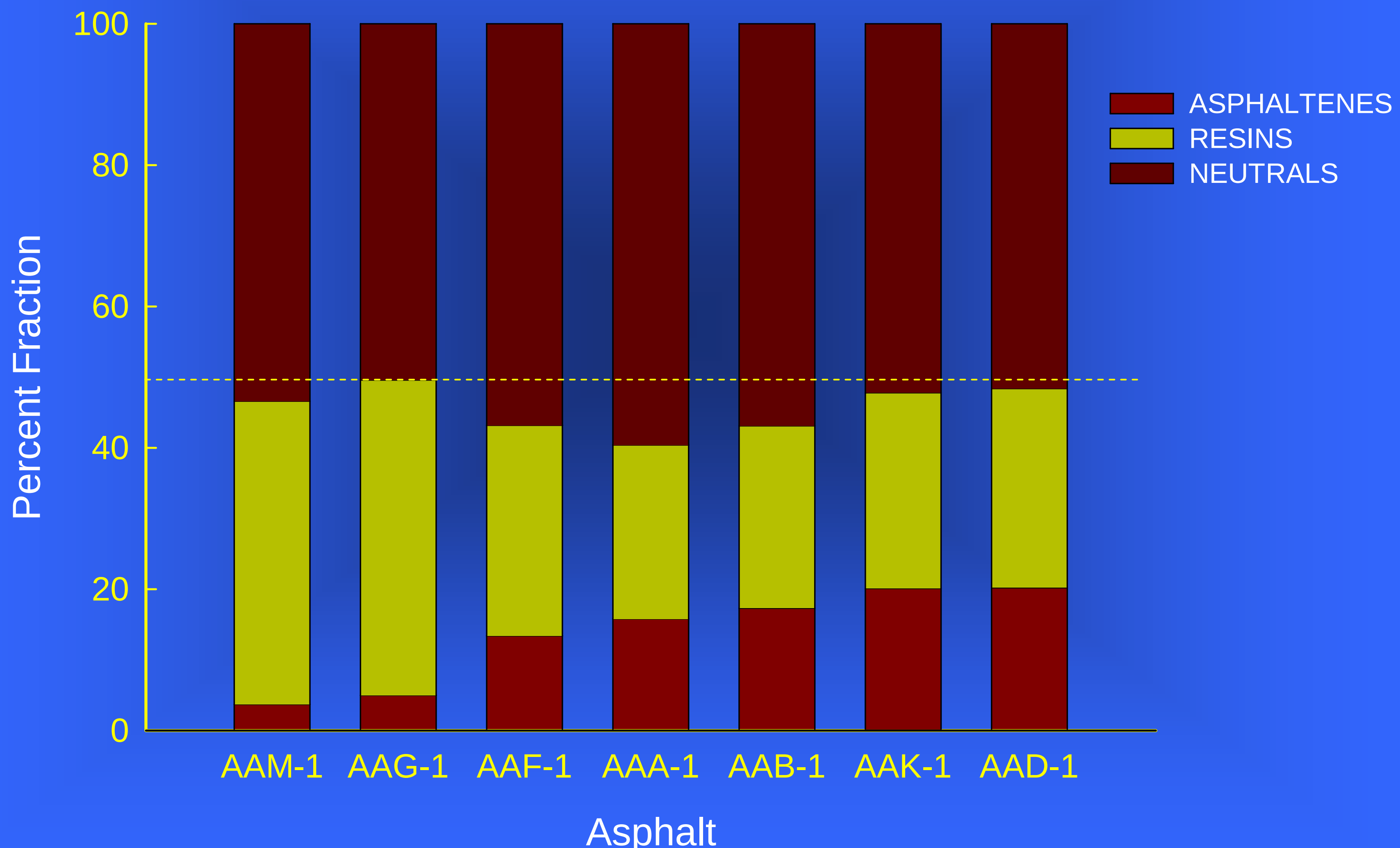
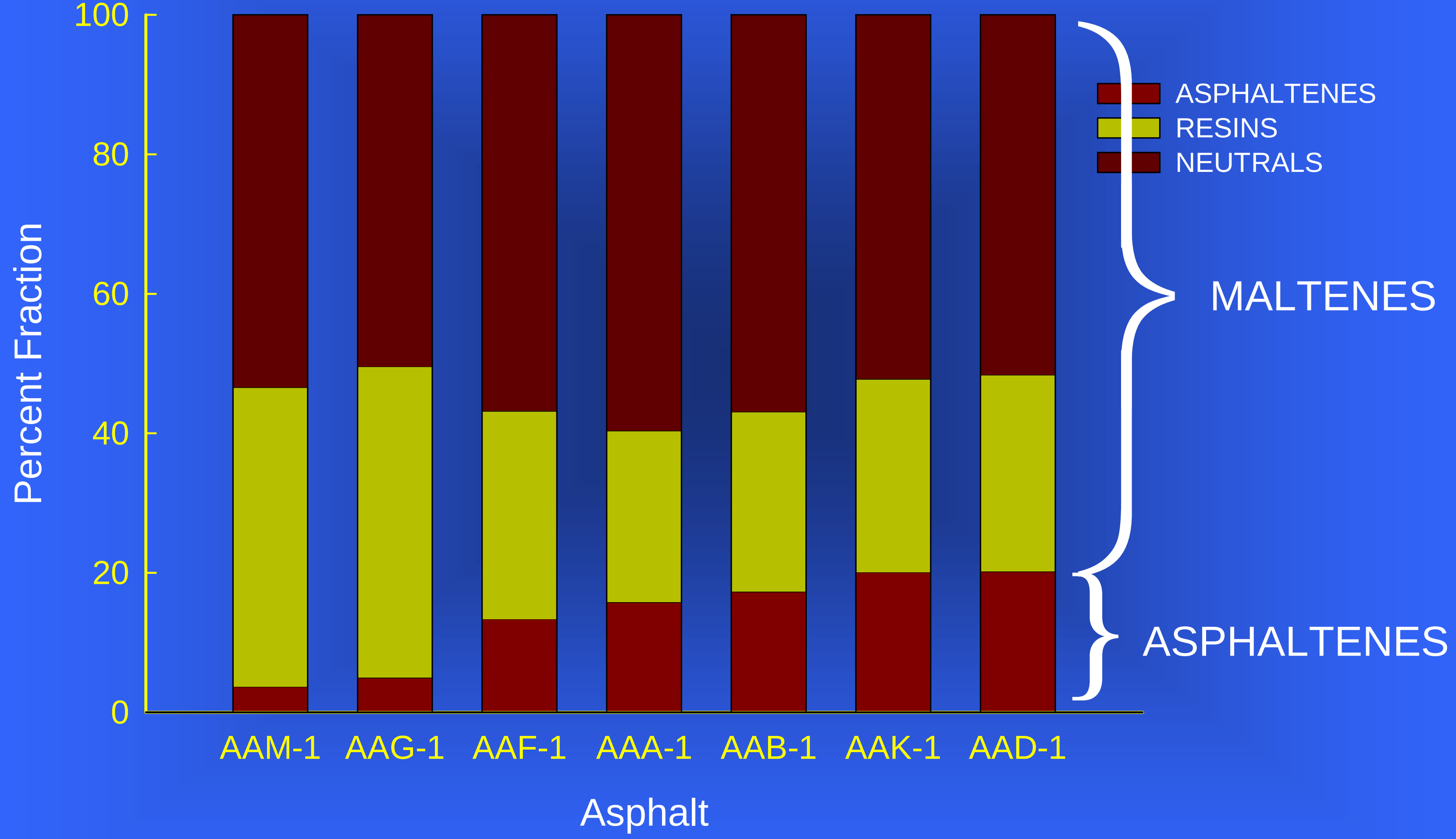
One Attempt to Define the Pertinent Components of an Asphalt

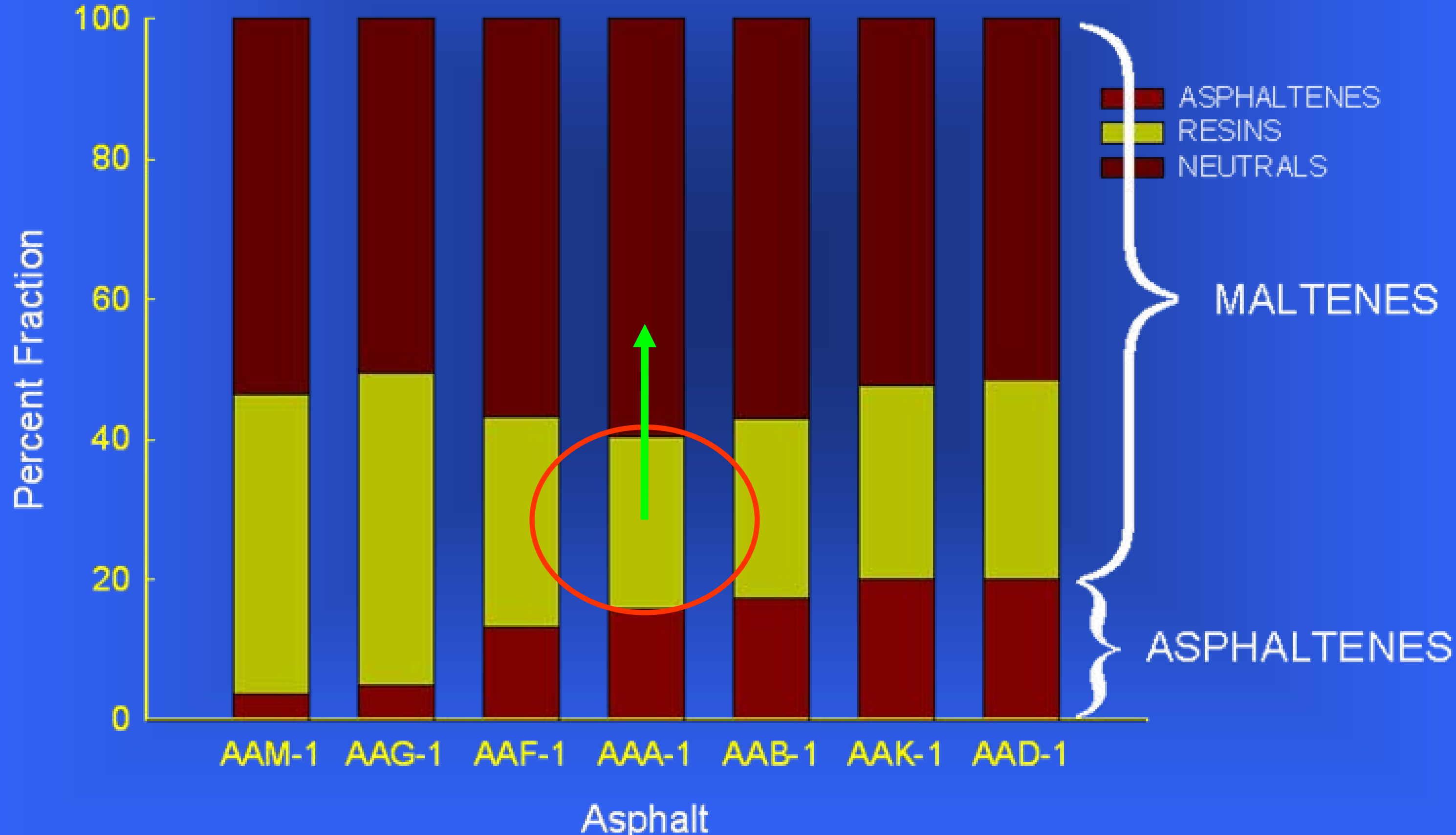


In this model, neutrals plus resins equals maltenes



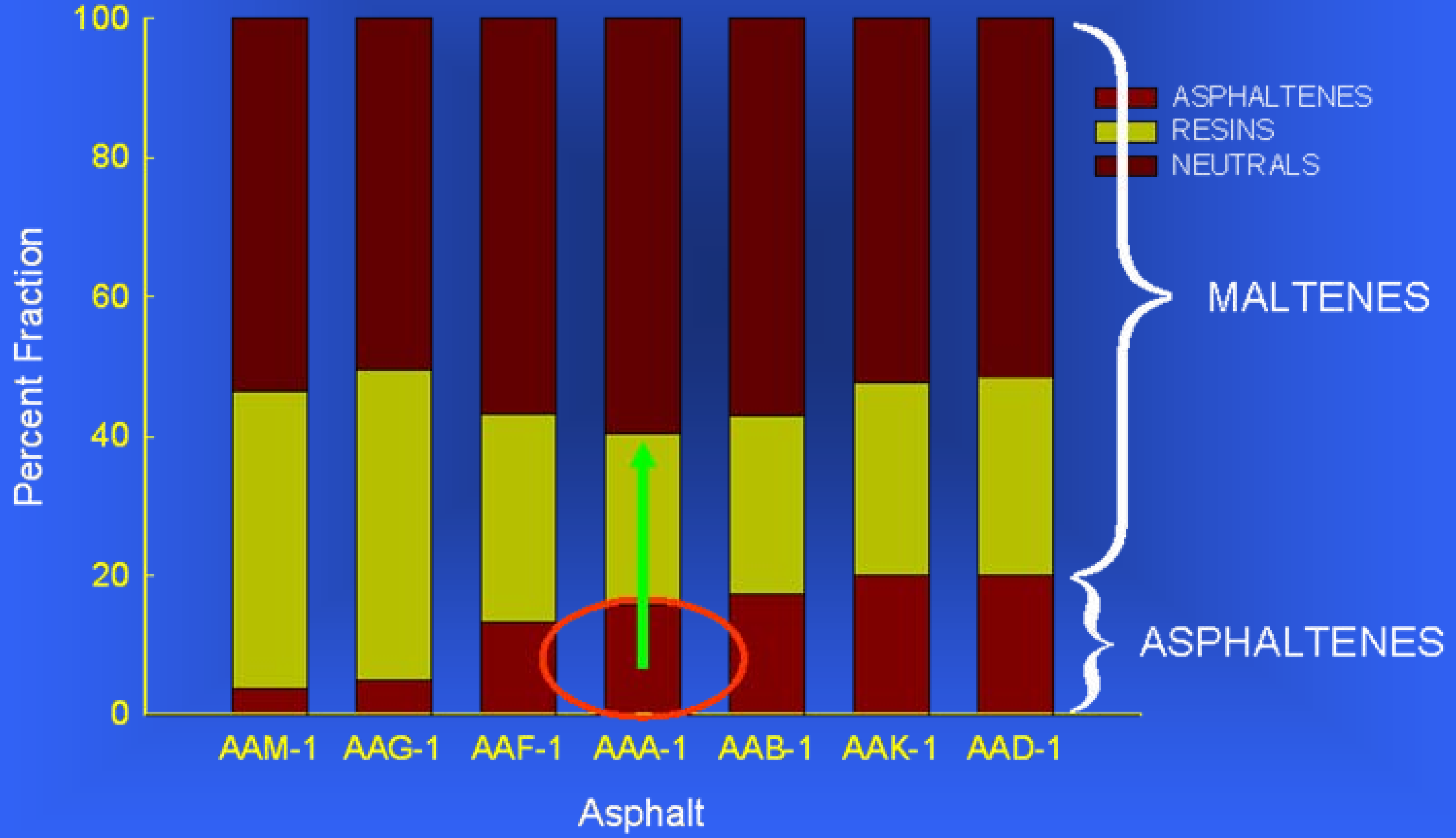
Effect of adding resins to neutrals

$$\Delta T = \frac{x_r R T^{*2}}{\Delta H_f}$$



Effect of adding asphaltenes to maltenes

$$\Delta T = \frac{x_a RT^{*2}}{\Delta H_f}$$



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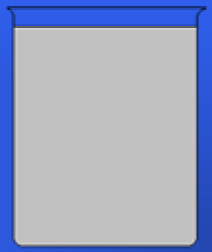
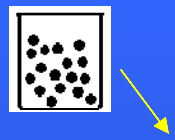
$$\eta_0 = A_0 e^{E_a^{\,0}/RT}$$

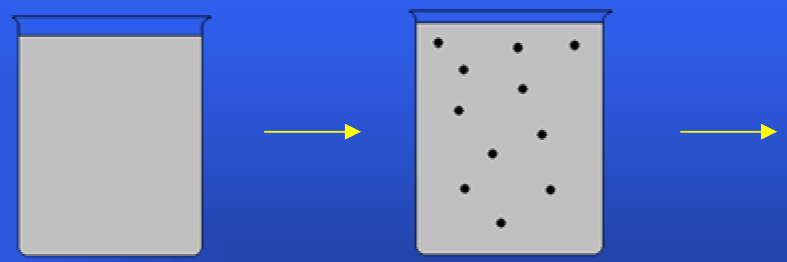
Eyring's Definition of Viscosity



η_0: Ideal Solvent Viscosity
A_0: pre-Exponential Factor
$E_a^{\,0}$: Activation Energy of Viscous Flow
R: Ideal Gas Constant
T: Temperature (Kelvin)



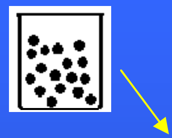
$$\eta_0 = A_0 e^{E_a^{0}/RT}$$



$$\eta_r \equiv \frac{\eta}{\eta_0} = 1 + \nu\phi$$

Einstein's Definition of a Colloidal Suspension

- η_r: Relative Viscosity
- η_0: Viscosity of the Solvent Phase
- η: Viscosity of the Suspension
- ϕ: Volume Fraction of Suspended Particles
- ν : Einstein Coefficient



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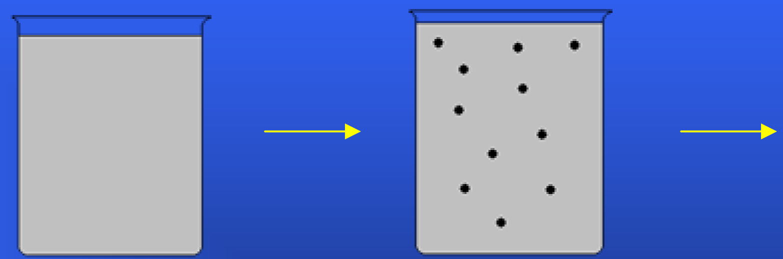
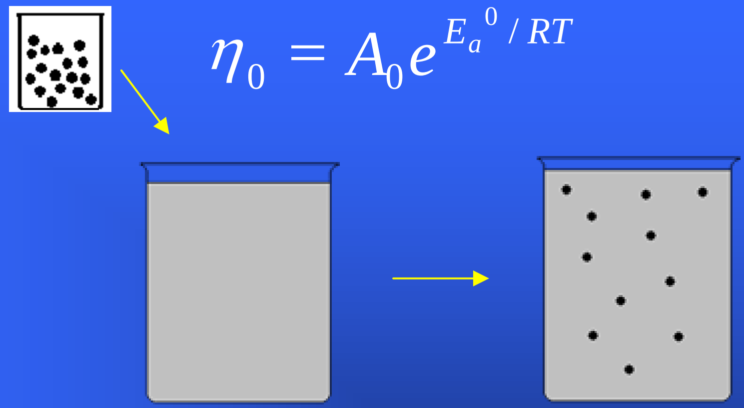


$$\eta_r \equiv \frac{\eta}{\eta_0} = 1 + \nu\phi$$

$$\phi_i = \frac{V_i}{V_S + V_i}$$

V_i: Volume Occupied by the Suspended Particles
V_S : Volume Occupied by the Solvent Phase

$$\eta_0 = A_0 e^{E_a^0 / RT}$$

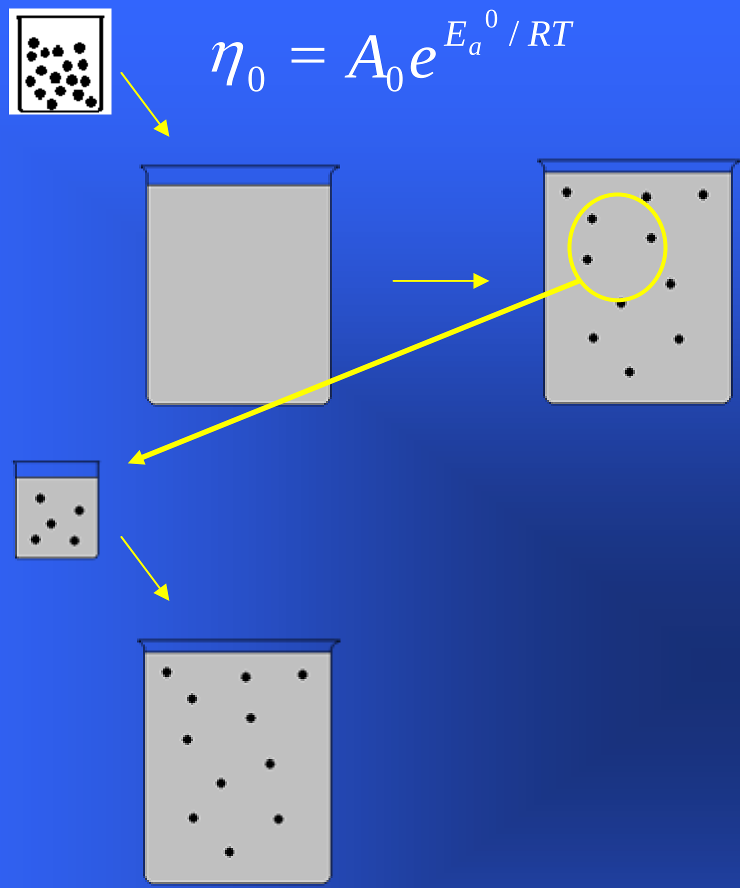


$$\eta_r \equiv \frac{\eta}{\eta_0} = 1 + \nu\phi$$

$$\phi_i = \frac{V_i}{V_S + V_i}$$

$$\lim_{\phi \to 0} \frac{1}{\phi}\left[\frac{\eta}{\eta_0} - 1\right] = \nu$$

ν: was defined by Einstein as the intrinsic viscosity, $[\eta]$, which is found to be equal to 5/2 for a dilute solution comprised of spherical particles



$$\eta_0 = A_0 e^{E_a^{\,0}/RT}$$

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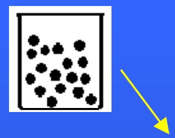
Pal and Rhodes
Thought Experiment



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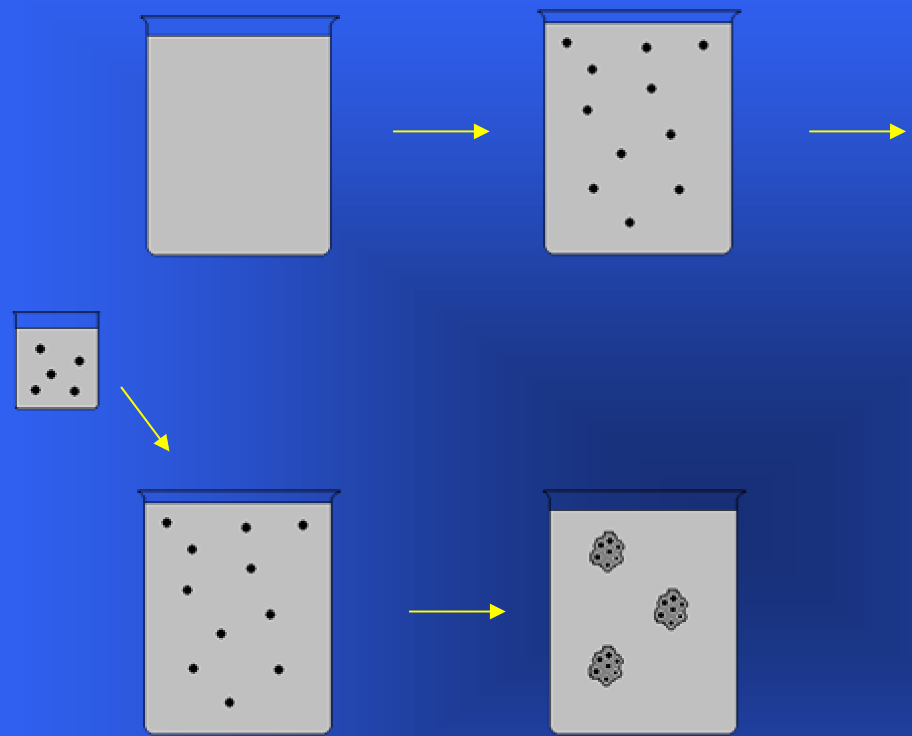

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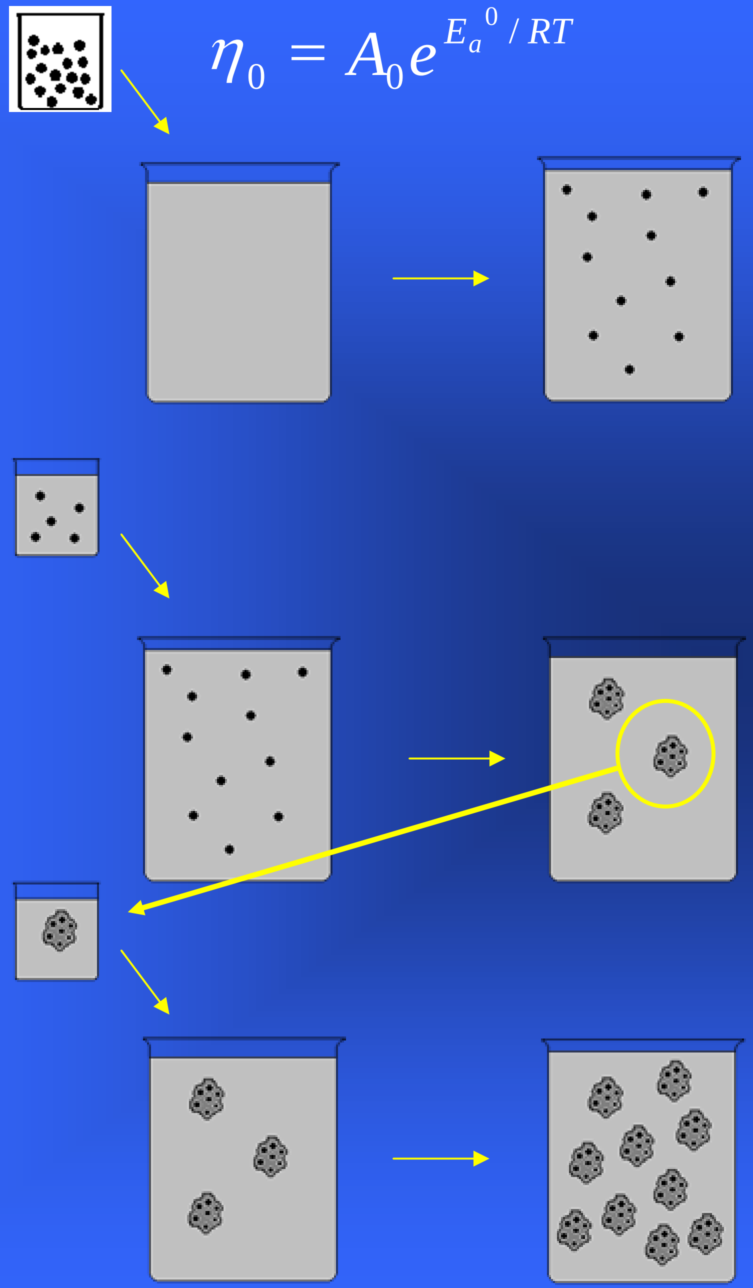

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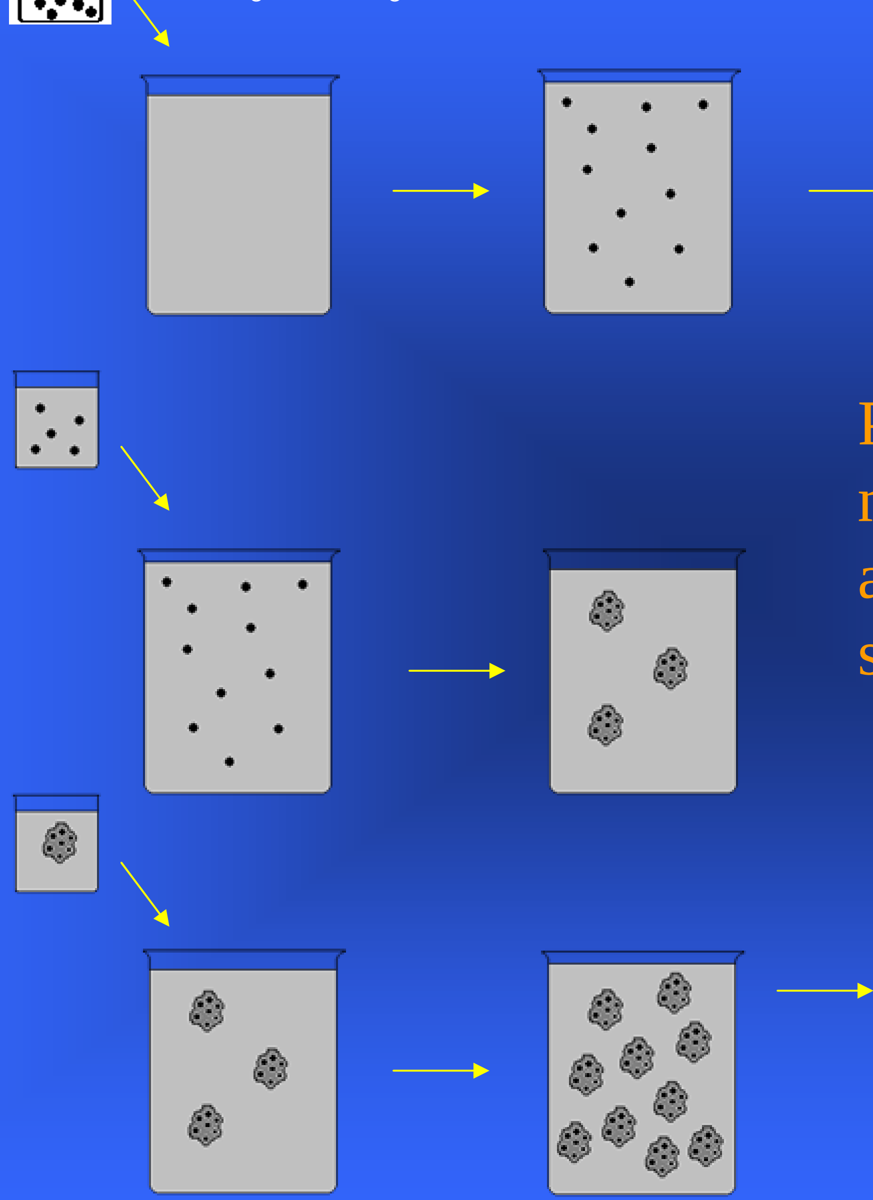
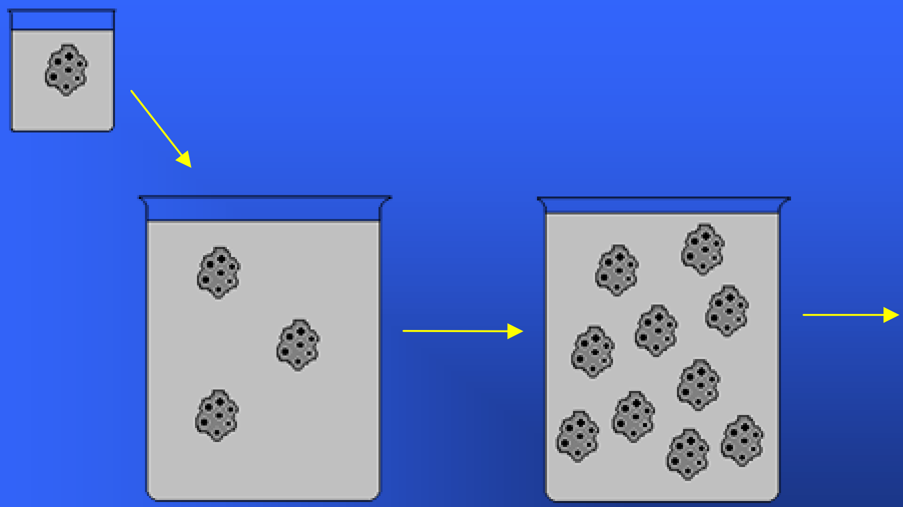


$$\eta_r \equiv \frac{\eta}{\eta_0} = 1 + \nu\phi$$

Pal and Rhodes mean-field approach to adjust for concentrated suspensions

$$\frac{\eta'}{\eta} \equiv \frac{\eta + \Delta\eta}{\eta} = 1 + \nu(\phi' - \phi)$$

$$= 1 + \frac{\Delta\eta}{\eta} = 1 + \nu\Delta\phi$$



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$$= 1 + \frac{\Delta\eta}{\eta} = 1 + \nu\Delta\phi$$

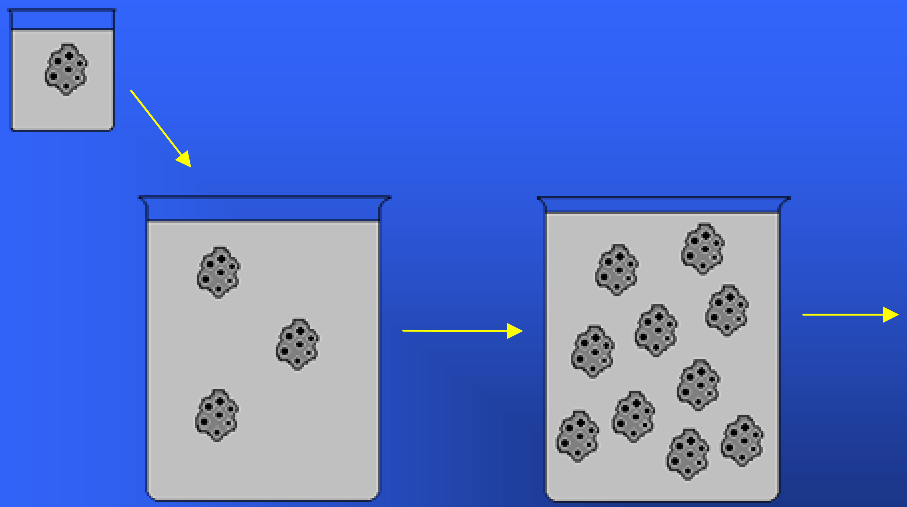
$$\phi' = \phi + \Delta\phi$$

$$= \frac{V'}{V_T + (V' - V)}$$

$$= \frac{V + \Delta V}{V_T + \Delta V}$$

$$\Delta\phi \approx \frac{d\phi}{(1 - K\phi)} = \frac{\Delta V}{V_T} \approx \frac{dV}{V_T}$$

$$V_T = V_S + KV_i$$



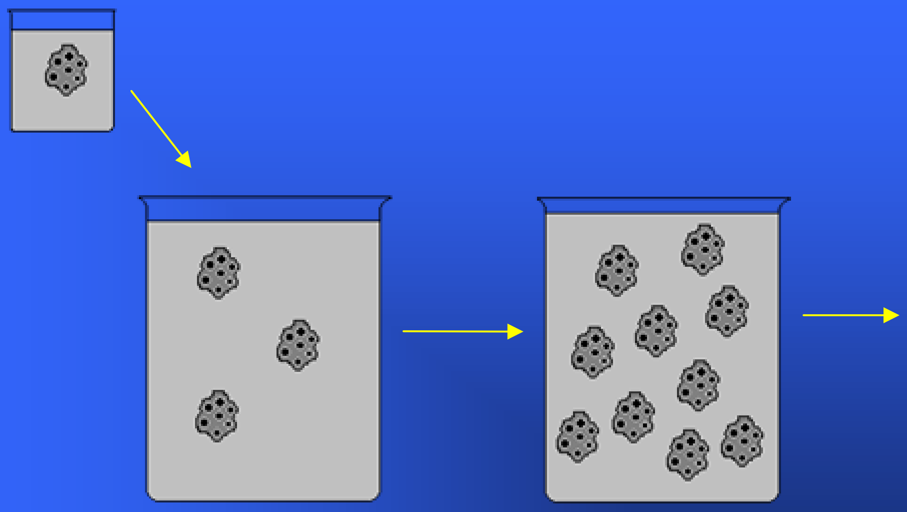
$$\frac{\eta'}{\eta} \equiv \frac{\eta+\Delta\eta}{\eta} = 1+\nu\left(\phi'-\phi\right)$$

$$= 1+\frac{\Delta\eta}{\eta} = 1+\nu\Delta\phi$$

$$\Delta\phi \approx \frac{d\phi}{(1-K\phi)} = \frac{\Delta V}{V_T} \approx \frac{dV}{V_T}$$

$$\int\frac{d\eta}{\eta} = \nu\int\frac{d\phi}{(1-K\phi)}$$

$$V_T = V_S + KV_i$$



$$\frac{\eta'}{\eta} \equiv \frac{\eta + \Delta\eta}{\eta} = 1 + \nu\left(\phi' - \phi\right)$$

$$= 1 + \frac{\Delta\eta}{\eta} = 1 + \nu\Delta\phi$$

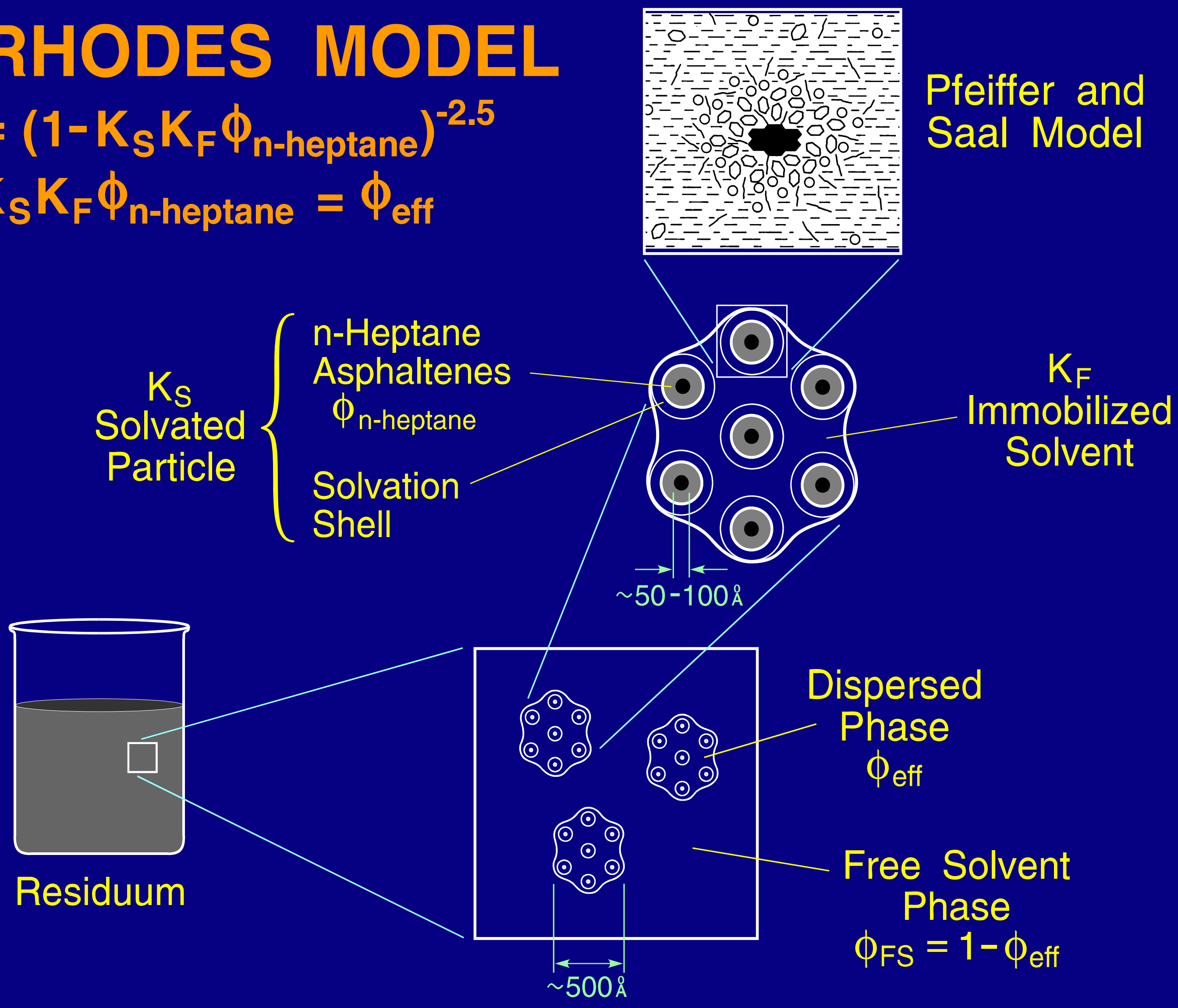
$$\int \frac{d\eta}{\eta} = \nu \int \frac{d\phi}{(1 - K\phi)} \longrightarrow \eta_r = (1 - K\phi)^{-\nu}$$

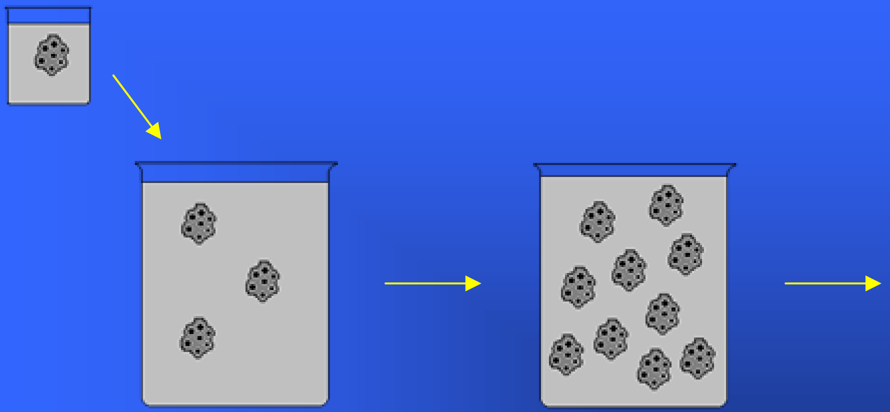
Pal-Rhodes Model

PAL-RHODES MODEL

$$\eta_{rel} = (1 - K_S K_F \phi_{n\text{-}heptane})^{-2.5}$$

$$K_S K_F \phi_{n\text{-}heptane} = \phi_{eff}$$





$$\frac{\eta'}{\eta} \equiv \frac{\eta + \Delta\eta}{\eta} = 1 + \nu(\phi' - \phi)$$

$$= 1 + \frac{\Delta\eta}{\eta} = 1 + \nu\Delta\phi$$

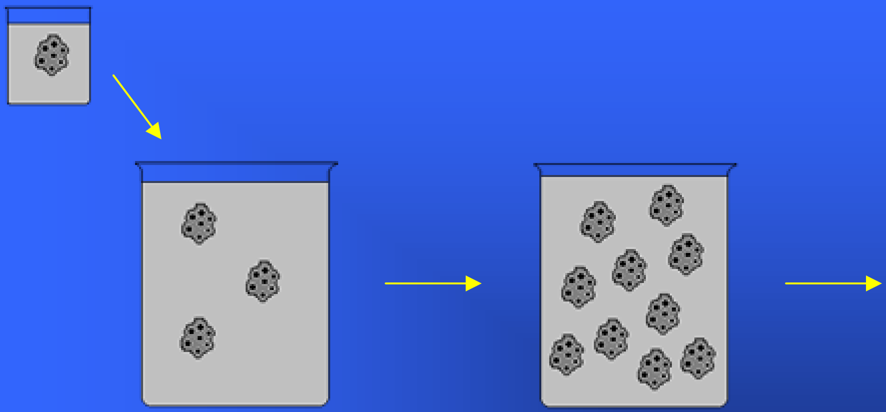
$$\frac{1}{\nu}\left[\frac{\eta - \eta_0}{\eta_0}\right] = \phi$$

Mean-Field Operator approach to derive the Pal-Rhodes Model

$$\lim_{\phi \to 0} \frac{1}{\phi}\left[\frac{\eta}{\eta_0} - 1\right] = \nu$$

ν: was defined by Einstein as the intrinsic viscosity, $[\eta]$, which is found to be equal to 5/2 for a dilute solution comprised of spherical particles

!



$$\frac{\eta'}{\eta} \equiv \frac{\eta + \Delta\eta}{\eta} = 1 + \nu(\phi' - \phi)$$

$$= 1 + \frac{\Delta\eta}{\eta} = 1 + \nu\Delta\phi$$

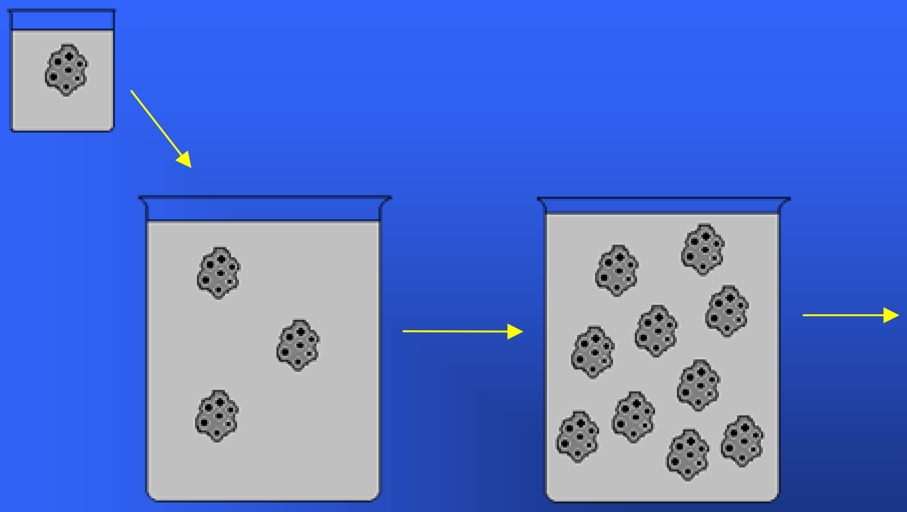
$$\frac{1}{\nu}\left[\frac{\eta - \eta_0}{\eta_0}\right] = \phi$$

$$\frac{1}{\nu}\int d\left[\frac{\eta - \eta_0}{\eta_0}\right] = \int d(\phi)$$

Mean-Field Operators

Dimensionless Quantities

$$\langle \eta \rangle = \langle \phi \rangle = \langle V \rangle$$



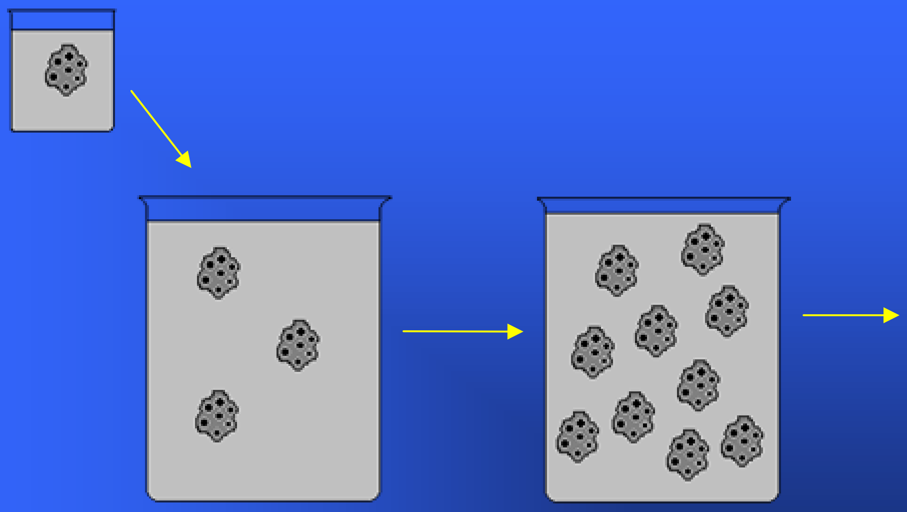
$$\frac{\eta'}{\eta} \equiv \frac{\eta + \Delta\eta}{\eta} = 1 + \nu(\phi' - \phi)$$

$$= 1 + \frac{\Delta\eta}{\eta} = 1 + \nu\Delta\phi$$

$$\eta' = \eta + \Delta\eta$$

$$\phi' = \phi + \Delta\phi$$

In effect, Pal and Rhodes suggested that a mean-field adjustment in the particle concentration, ϕ, resulted in a mean-field adjustment in the suspension viscosity, η.



$$\frac{\eta'}{\eta} \equiv \frac{\eta + \Delta\eta}{\eta} = 1 + \nu\left(\phi' - \phi\right)$$

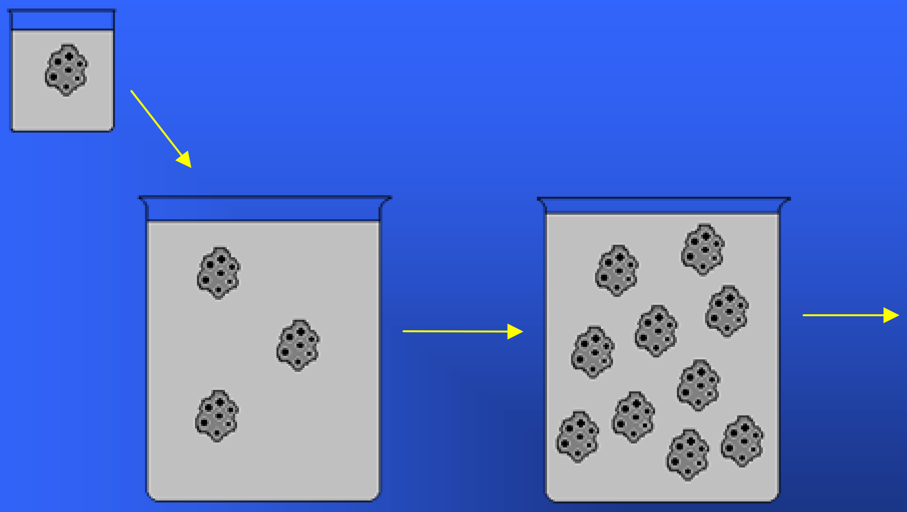
$$= 1 + \frac{\Delta\eta}{\eta} = 1 + \nu\Delta\phi$$

$$\eta' = \eta + \Delta\eta$$

$$\phi' = \phi + \Delta\phi$$

$$V' = V + \Delta V$$

This is actually accomplished by evaluating the mean-field adjustment in the particle volume, V.



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$$= 1 + \frac{\Delta\eta}{\eta} = 1 + \nu\Delta\phi$$

$$\eta' = \eta + \Delta\eta$$

$$\phi' = \phi + \Delta\phi$$

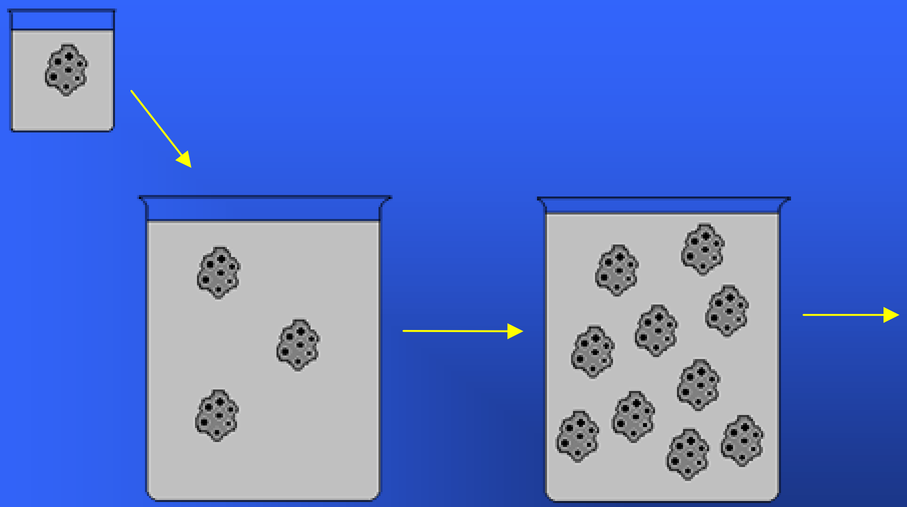
$$V' = V + \Delta V$$

Mean-Field Variables

$$\phi' = \phi + \Delta\phi$$

$$= \frac{V'}{V_T + (V' - V)}$$

$$= \frac{V + \Delta V}{V_T + \Delta V}$$



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$$\eta' = \eta + \Delta\eta$$

$$\phi' = \phi + \Delta\phi$$

$$V' = V + \Delta V$$

$$\phi' = \phi + \Delta\phi$$

$$= \frac{V'}{V_T + (V' - V)}$$

$$= \frac{V + \Delta V}{V_T + \Delta V}$$

Mean-Field Variables

$$\langle \eta \rangle \equiv \int f(\eta) d\eta$$
$$= \langle \phi \rangle \equiv \int g(\phi) d\phi$$
$$= \langle V \rangle \equiv \int h(V) dV$$

$\longrightarrow$

$$\langle \eta \rangle \equiv \int f(\eta) d\eta = \frac{1}{\nu} \ln(\eta)$$
$$\langle \phi \rangle \equiv \int g(\phi) d\phi = -\ln(1 - K\phi)$$
$$\langle V \rangle \equiv \int h(V) dV = \frac{1}{K} \ln(V_T)$$

Formal Solutions Derived for Mean-Field Operators

Dimensionless Quantities

$$\langle \eta \rangle \equiv \int f(\eta)d\eta$$

$$= \langle \phi \rangle \equiv \int g(\phi)d\phi$$

$$= \langle V \rangle \equiv \int h(V)dV$$

$$\langle \eta \rangle \equiv \int f(\eta)d\eta = \frac{1}{\nu}\ln(\eta)$$

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$$\langle V \rangle \equiv \int h(V)dV = \frac{1}{K}\ln(V_T)$$

$$\eta_r = (1-K\phi)^{-\nu}$$

$$\langle \eta \rangle \equiv \int f(\eta) d\eta$$

$$= \langle \phi \rangle \equiv \int g(\phi) d\phi$$

$$= \langle V \rangle \equiv \int h(V) dV$$

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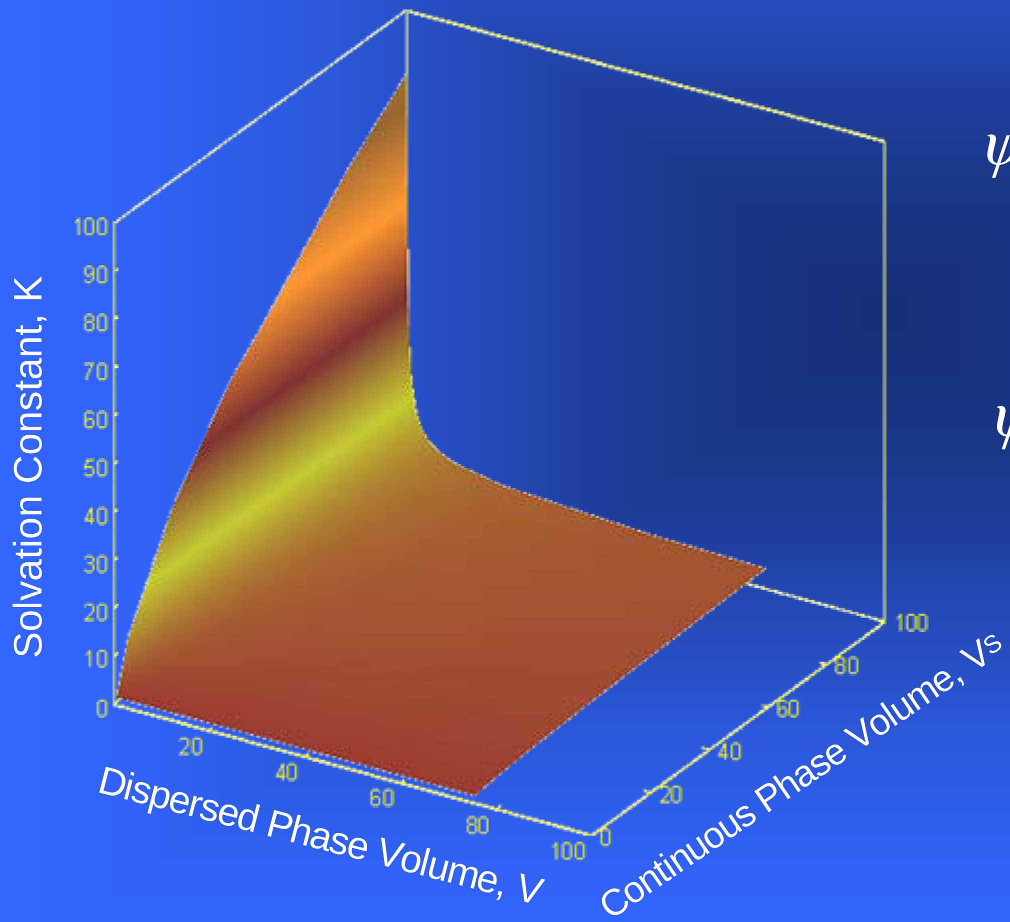
$$\langle V \rangle \equiv \int h(V) dV = \frac{1}{K} \ln(V_T)$$

$$\eta_r = (1 - K\phi)^{-\nu}$$

$$\frac{1}{1 - K\phi} = (V_T)^{1/K}$$

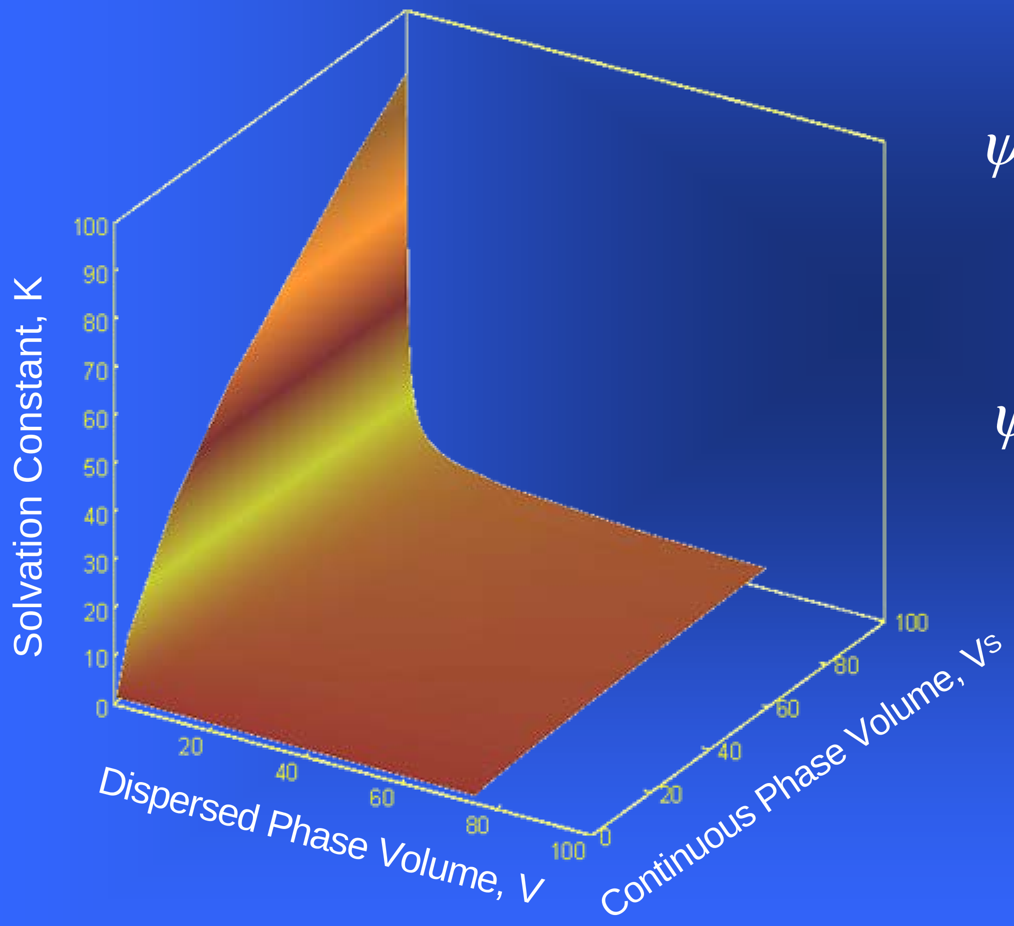
Solvation Shell "Phase Space"



$$\psi_1 = \frac{1}{1-K\phi} = 1 + \frac{KV}{V_S}$$

$$\psi_2 = (V_T)^{1/K} = (V_S + KV)^{1/K}$$

Solvation Shell "Phase Space"



Of Key Importance to calculating this surface is to minimize

$\Delta\psi = \psi_1 - \psi_2$ where

$$\psi_1 = \frac{1}{1 - K\phi} = 1 + \frac{KV}{V_S}$$

and

$$\psi_2 = (V_T)^{1/K} = (V_S + KV)^{1/K}$$

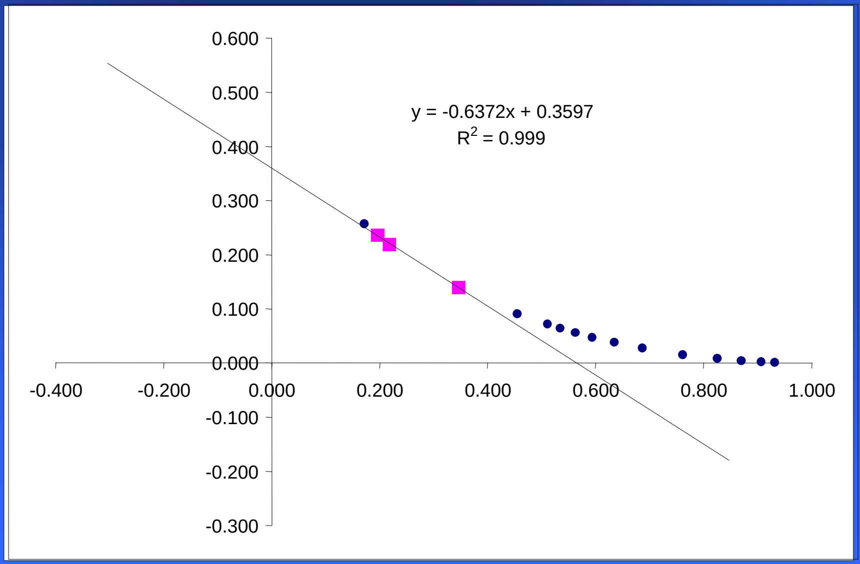
are referred to as "trial functions"

Working spreadsheet of an iterative calculation to determine stability parameters

V	V_S	K	ν	V_T	ϕ	ψ_1	ψ_2	dif	$(1/V_T)^{1/K}$	ψ^ν
0.0625	50	56	2.5	53.50	0.001	1.07	1.07	**-0.0037**	0.931	1.2
0.125	50	41	2.5	55.13	0.002	1.10	1.10	-0.0002	0.907	1.3
0.25	50	29	2.5	57.25	0.004	1.15	1.15	-0.0048	0.870	1.4
0.5	50	21.4	2.5	60.70	0.008	1.21	1.21	0.0025	0.825	1.6
1	50	15.3	2.5	65.30	0.015	1.31	1.31	-0.0081	0.761	1.9
2	50	11.4	2.5	72.80	0.027	1.46	1.46	-0.0006	0.687	2.6
3	50	9.6	2.5	78.80	0.038	1.58	1.58	0.0000	0.635	3.1
4	50	8.5	2.5	84.00	0.048	1.68	1.68	-0.0042	0.594	3.7
5	50	7.8	2.5	89.00	0.056	1.78	1.78	0.0020	0.562	4.2
6	50	7.25	2.5	93.50	0.064	1.87	1.87	0.0000	0.535	4.8
7	50	6.83	2.5	97.81	0.072	1.96	1.96	0.0000	0.511	5.4
10	50	5.965	2.5	109.65	0.091	2.19	2.20	-0.0048	0.455	7.1
20	**50**	**4.69**	2.5	**143.80**	**0.139**	**2.88**	**2.88**	**-0.0085**	**0.347**	**14.0**
50	**50**	**3.574**	2.5	**228.70**	**0.219**	**4.57**	**4.57**	**0.0019**	**0.219**	**44.7**
60	**50**	**3.405**	2.5	**254.30**	**0.236**	**5.09**	**5.09**	**-0.0005**	**0.197**	**58.3**
75	50	3.22	2.5	291.50	0.257	5.83	5.83	0.0034	0.172	82.1

y = -0.6372x + 0.3597
R2 = 0.999

c_{min}	-0.2292
m	-0.6372
ϕ_{max}	0.3597
α	**0.6403**
K_0	**1.2775**
K	**3.55157**



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20	**50**	**4.69**	2.5	**143.80**	**0.139**	**2.88**	**2.88**	**-0.0085**	**0.347**	**14.0**
50	**50**	**3.574**	2.5	**228.70**	**0.219**	**4.57**	**4.57**	**0.0019**	**0.219**	**44.7**
60	**50**	**3.405**	2.5	**254.30**	**0.236**	**5.09**	**5.09**	**-0.0005**	**0.197**	**58.3**
75	50	3.22	2.5	291.50	0.257	5.83	5.83	0.0034	0.172	82.1

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ϕ_{max}	0.3597
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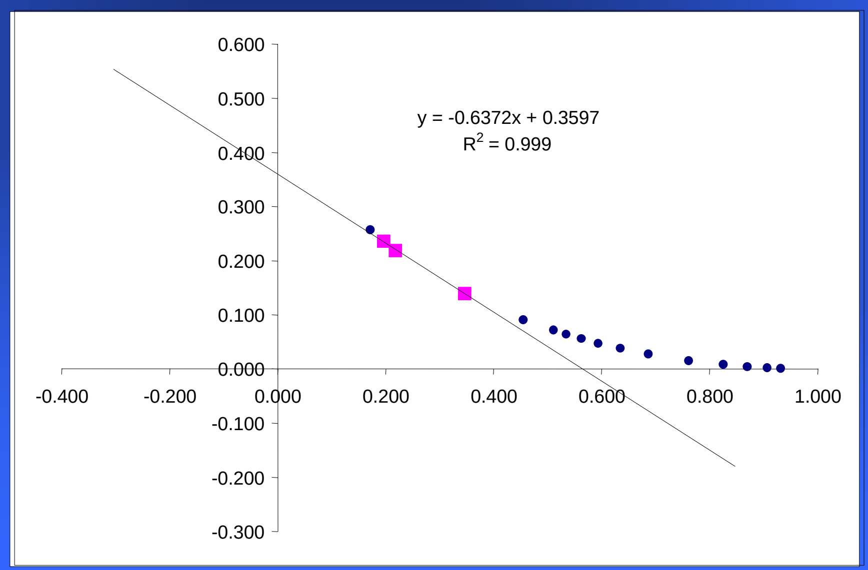
K_0	**1.2775**
K	**3.55157**



Working spreadsheet of an iterative calculation to determine stability parameters

V	V_S	K	ν	V_T	ϕ	ψ_1	ψ_2	dif	$(1/V_T)^{1/K}$	ψ^ν
0.0625	50	56	2.5	53.50	0.001	1.07	1.07	**-0.0037**	0.931	1.2
0.125	50	41	2.5	55.13	0.002	1.10	1.10	-0.0002	0.907	1.3
0.25	50	29	2.5	57.25	0.004	1.15	1.15	-0.0048	0.870	1.4
0.5	50	21.4	2.5	60.70	0.008	1.21	1.21	0.0025	0.825	1.6
1	50	15.3	2.5	65.30	0.015	1.31	1.31	-0.0081	0.761	1.9
2	50	11.4	2.5	72.80	0.027	1.46	1.46	-0.0006	0.687	2.6
3	50	9.6	2.5	78.80	0.038	1.58	1.58	0.0000	0.635	3.1
4	50	8.5	2.5	84.00	0.048	1.68	1.68	-0.0042	0.594	3.7
5	50	7.8	2.5	89.00	0.056	1.78	1.78	0.0020	0.562	4.2
6	50	7.25	2.5	93.50	0.064	1.87	1.87	0.0000	0.535	4.8
7	50	6.83	2.5	97.81	0.072	1.96	1.96	0.0000	0.511	5.4
10	50	5.965	2.5	109.65	0.091	2.19	2.20	-0.0048	0.455	7.1
20	**50**	**4.69**	2.5	**143.80**	**0.139**	**2.88**	**2.88**	**-0.0085**	**0.347**	**14.0**
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75	50	3.22	2.5	291.50	0.257	5.83	5.83	0.0034	0.172	82.1

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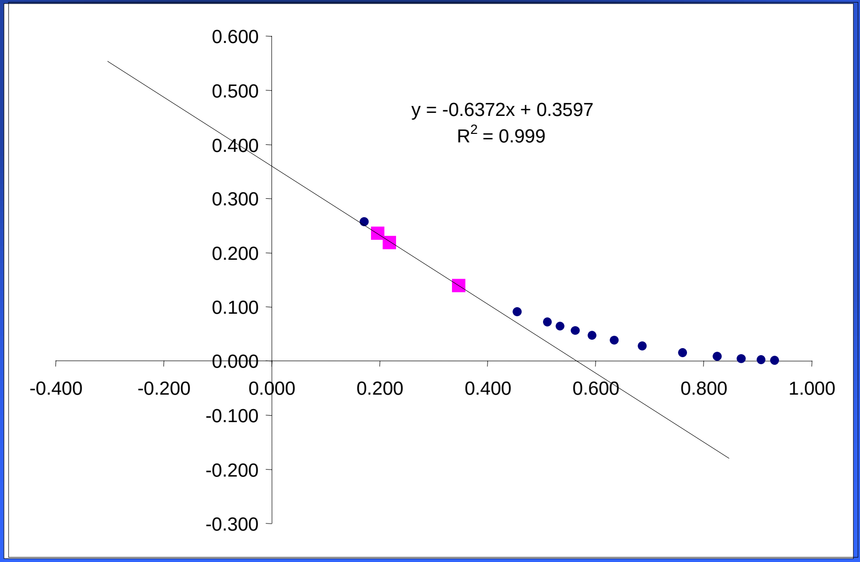

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0.25	50	29	2.5	57.25	0.004	1.15	1.15	-0.0048	0.870	1.4
0.5	50	21.4	2.5	60.70	0.008	1.21	1.21	0.0025	0.825	1.6
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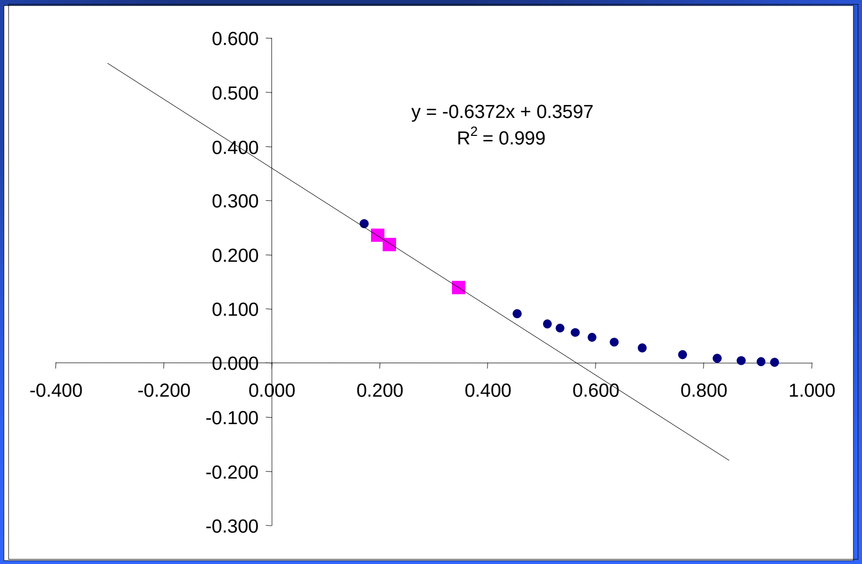

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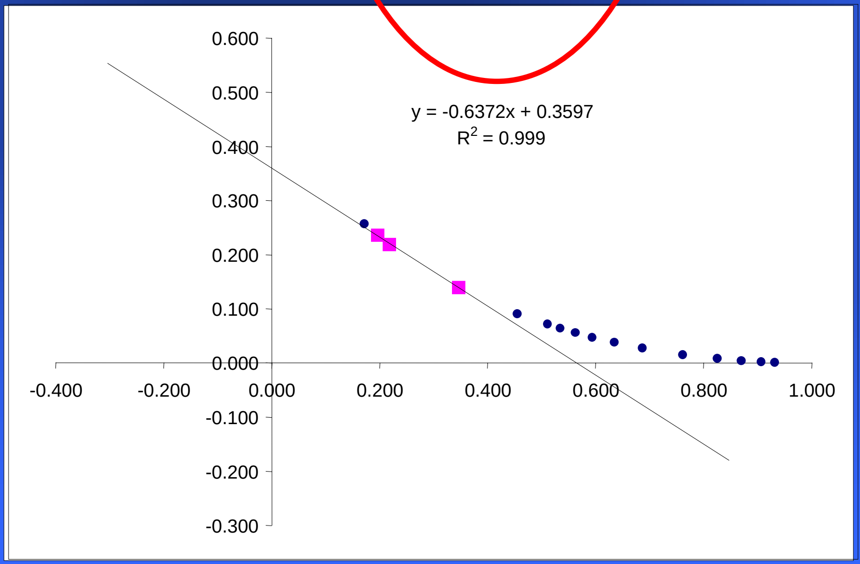


Towards a Unified Physico-Chemical Model of Asphalt Binder

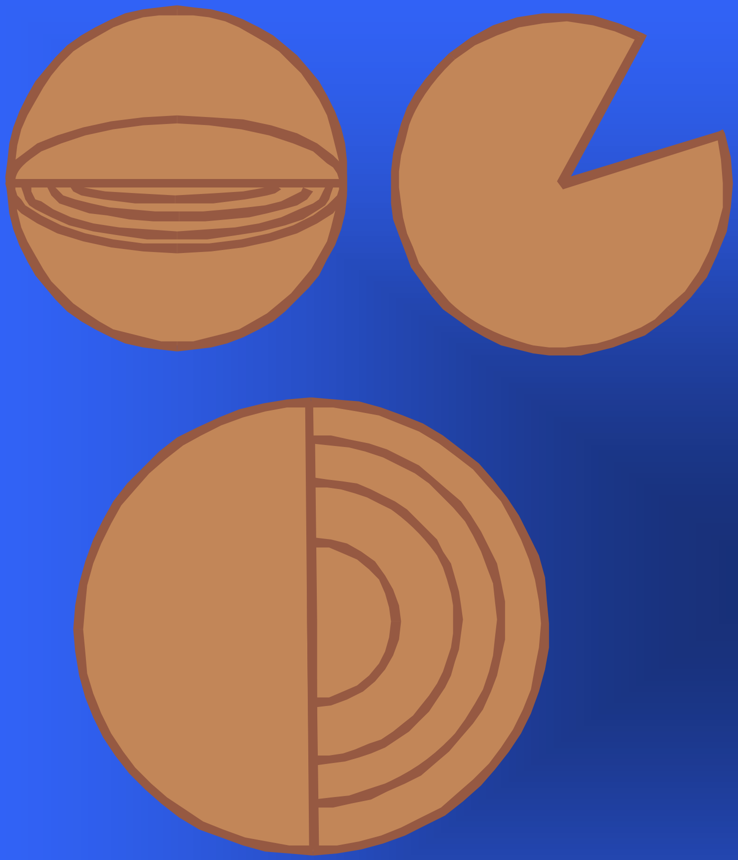
Asphalt Microstructure Model

- Introduction to micro-Emulsion Colloid Mechanics
- The Onion Model and Colligative Properties
- Equilibrium Thermodynamics in micro-Emulsion Colloid Mechanics
- Kinetics in micro-Emulsion Colloid Mechanics

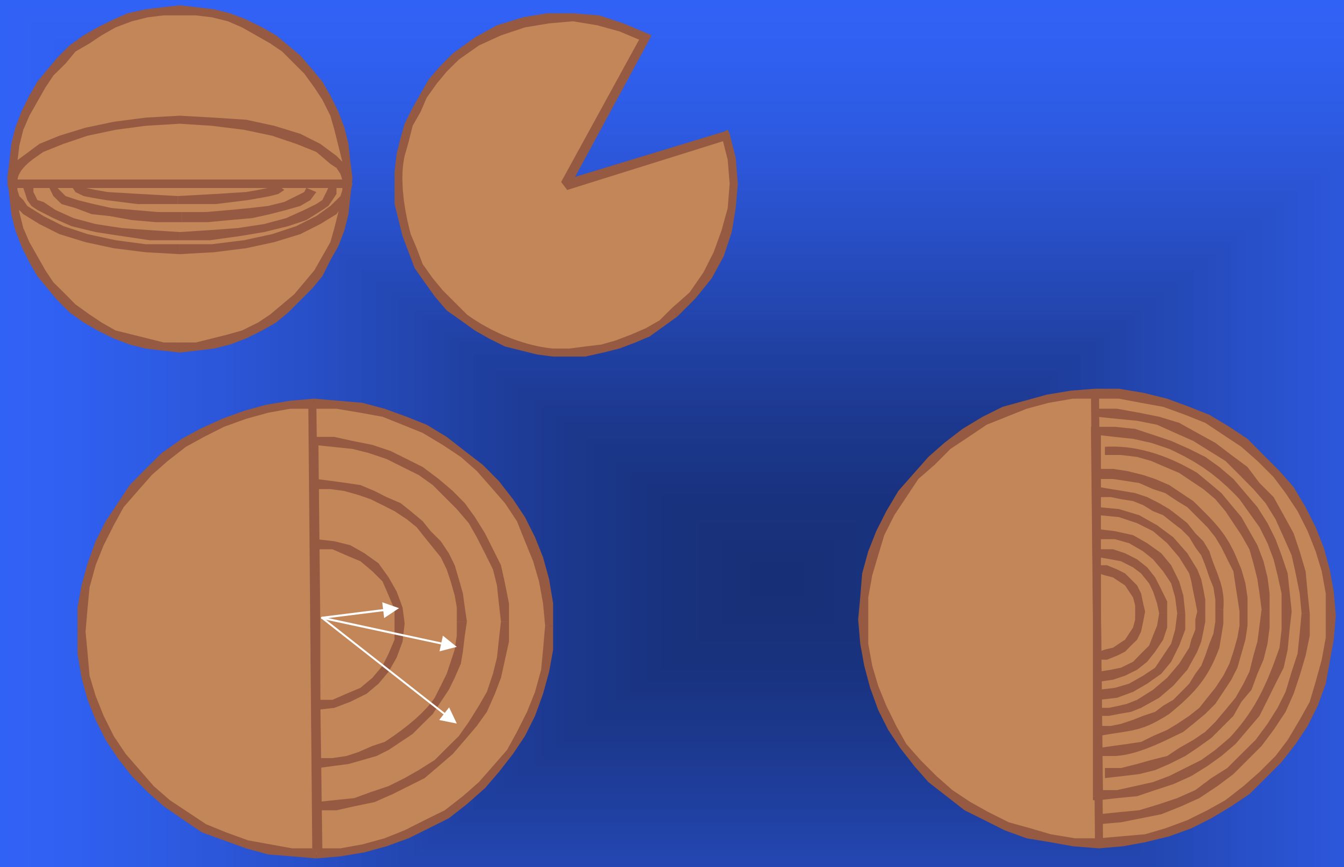
Asphalt Solidification Model

- Equilibrium Thermodynamics of Surfaces and Interfaces
- Phase Transformations and Colligative Properties
- non-Equilibrium Thermodynamics of Surface micro-Structuring
- Dissipative Structure Theory
- Application to Fracture Mechanics

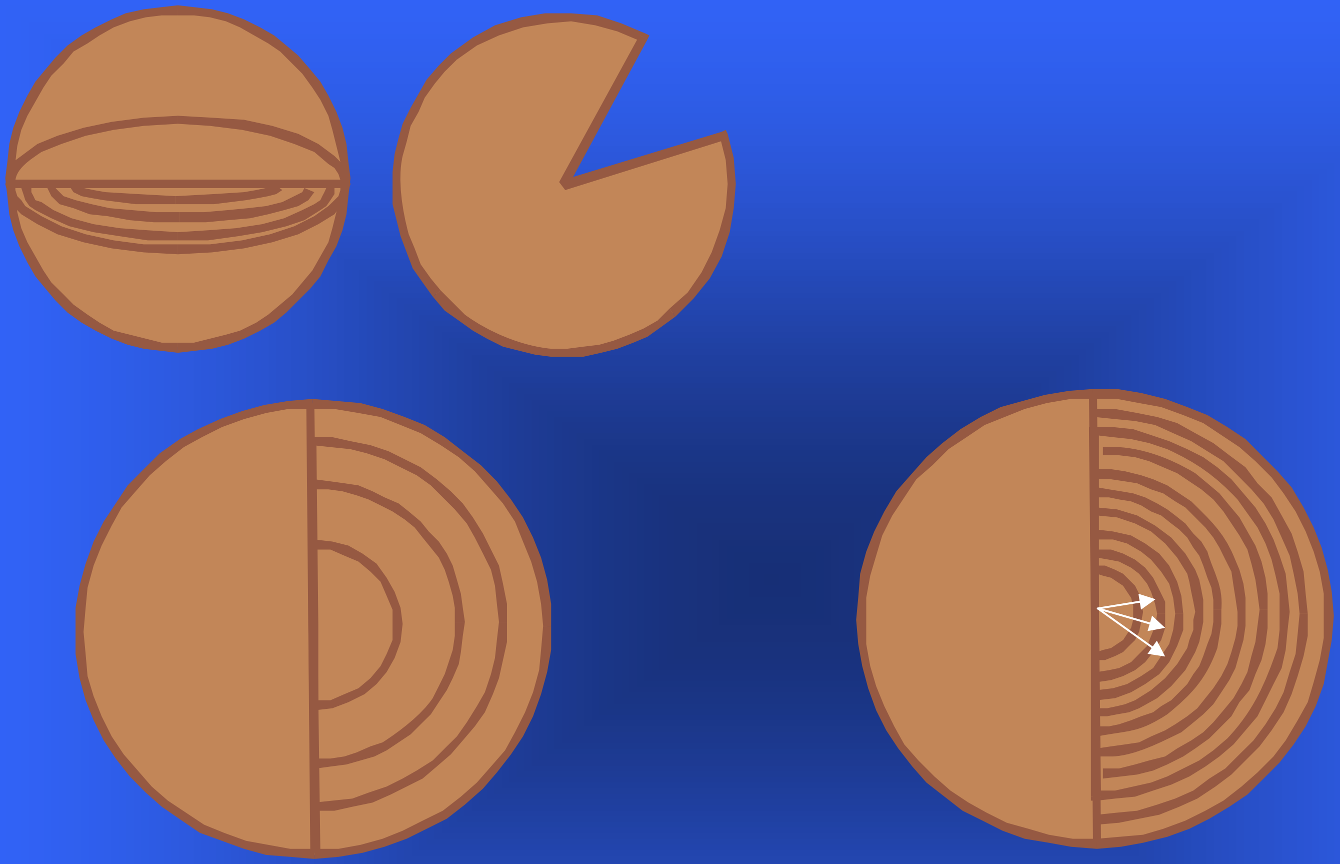
Further Thoughts on Fatigue and Moisture Damage, Rutting, and Thermal Cracking



If you're going to make
an asphalt stew, you first
better slice up some onion



Some onions may have
thick layers



Some onions may have thick layers

While other onions will have thin layers

Working spreadsheet of an iterative calculation to determine stability parameters

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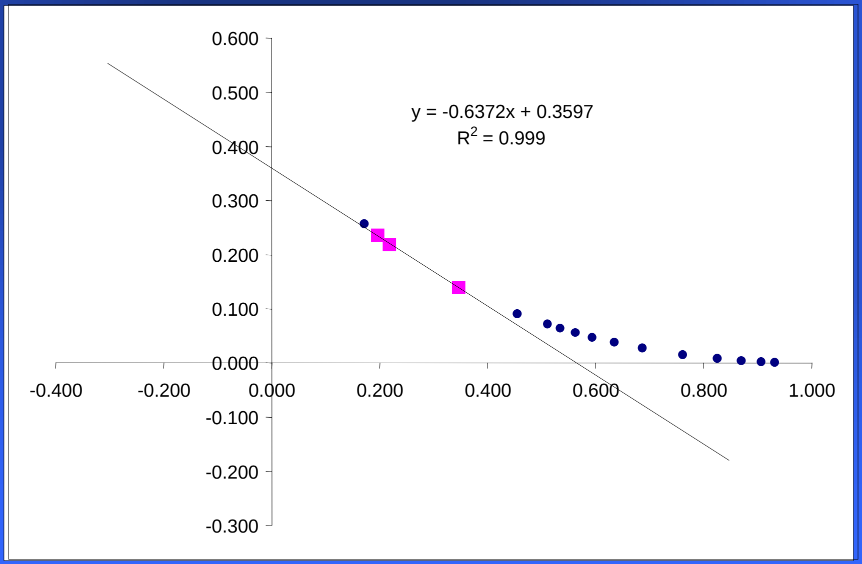

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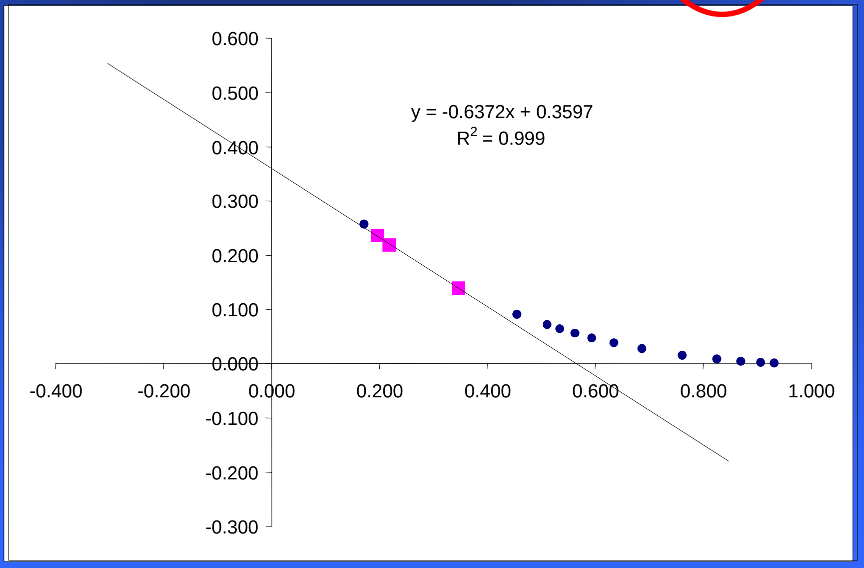

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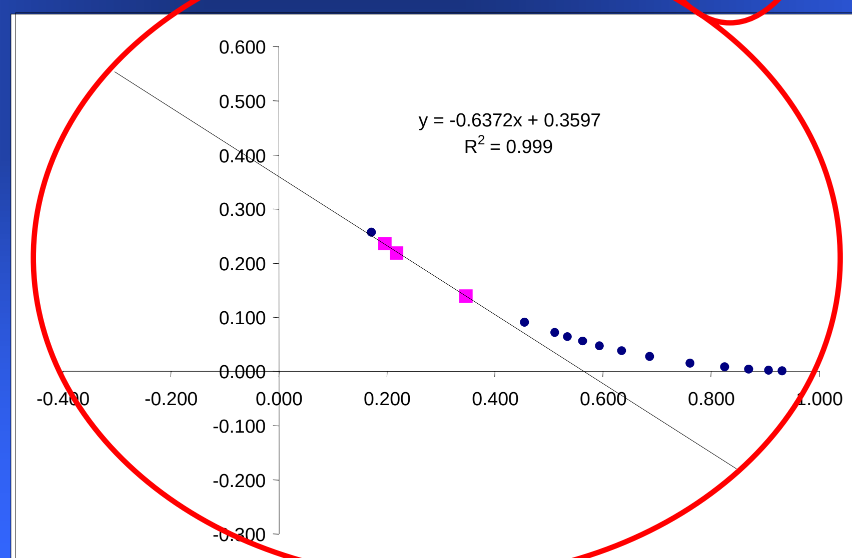
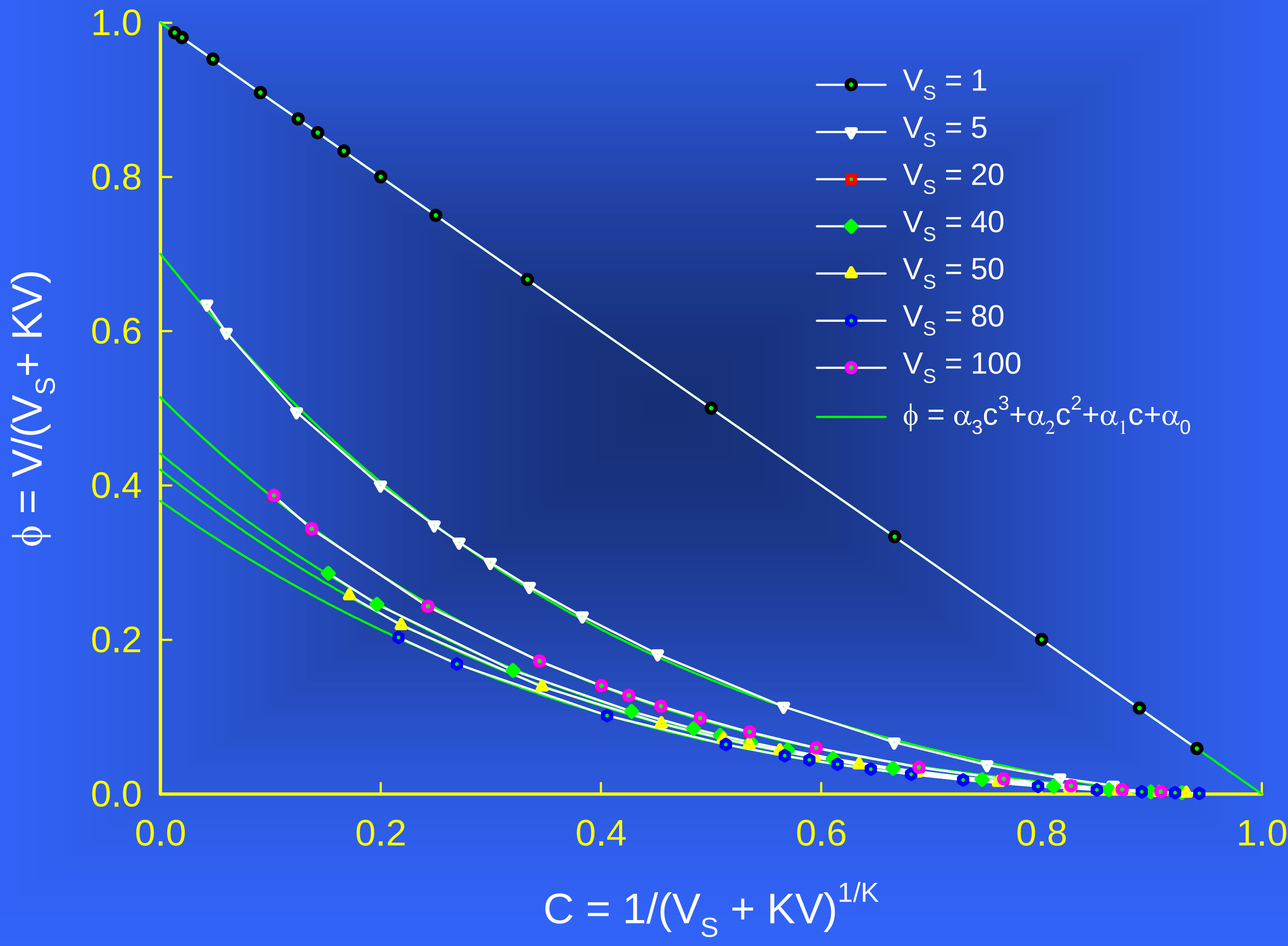
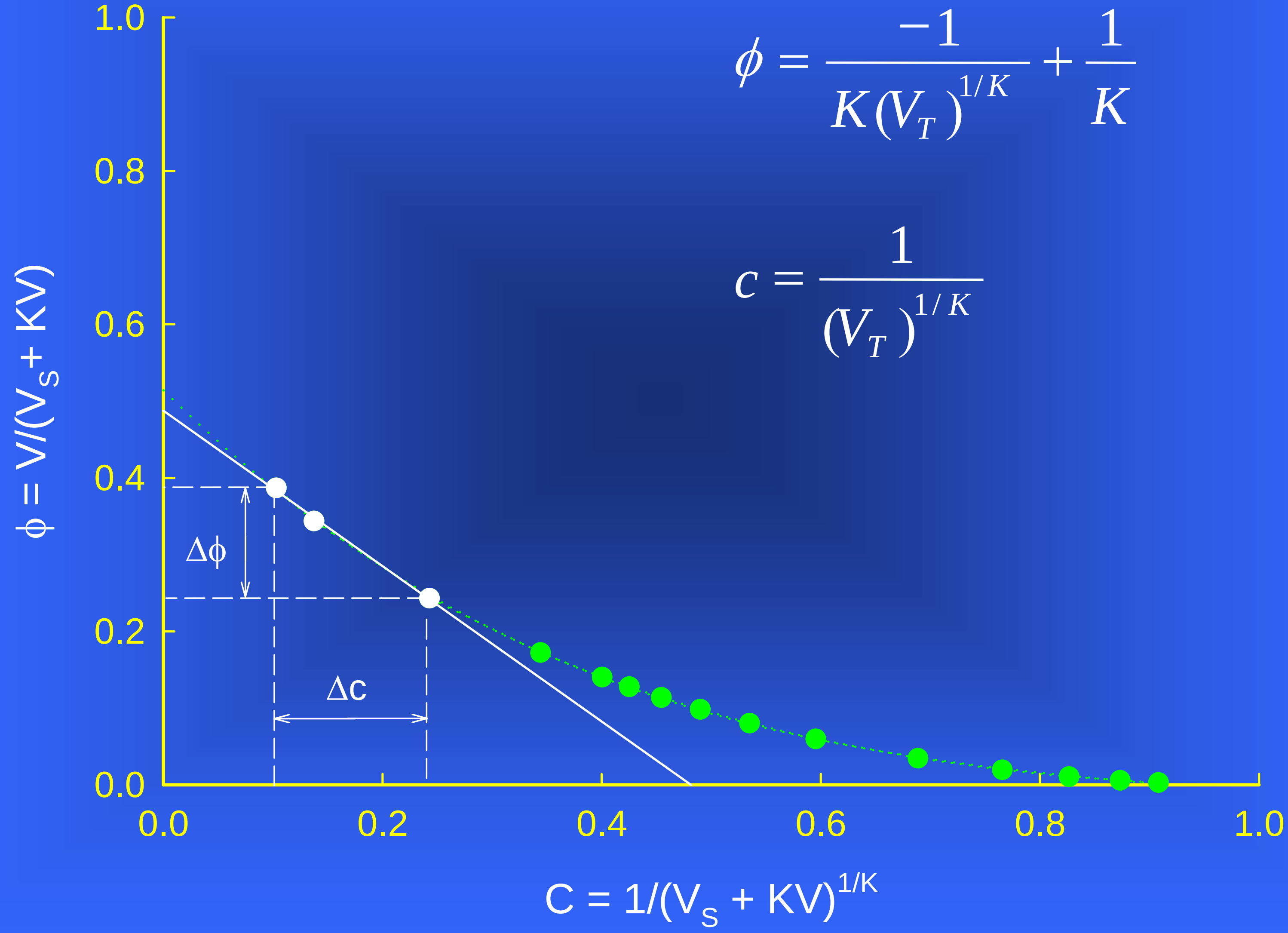


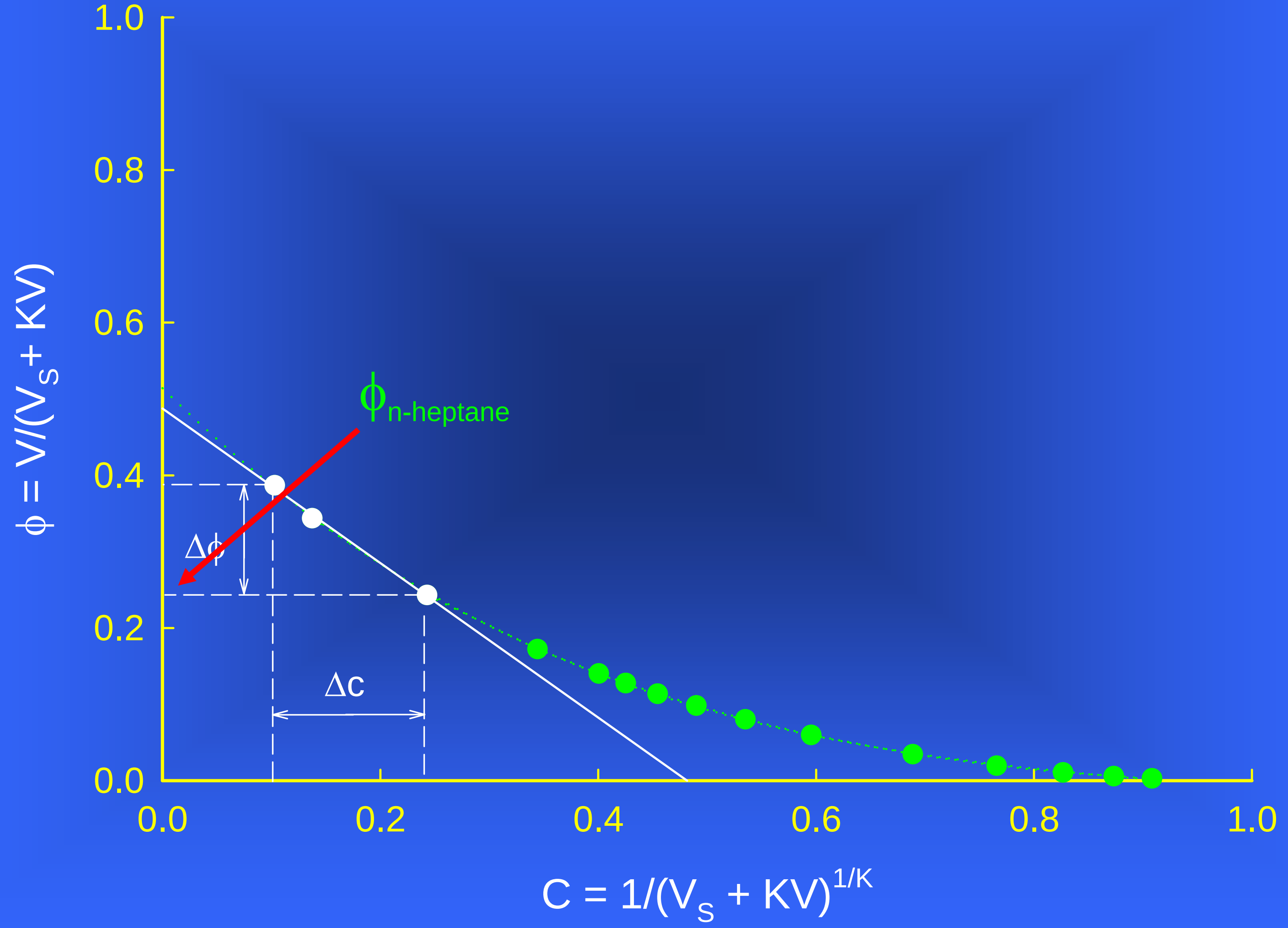
Derivation of Theoretical "State of Dispersion" Stability Parameters



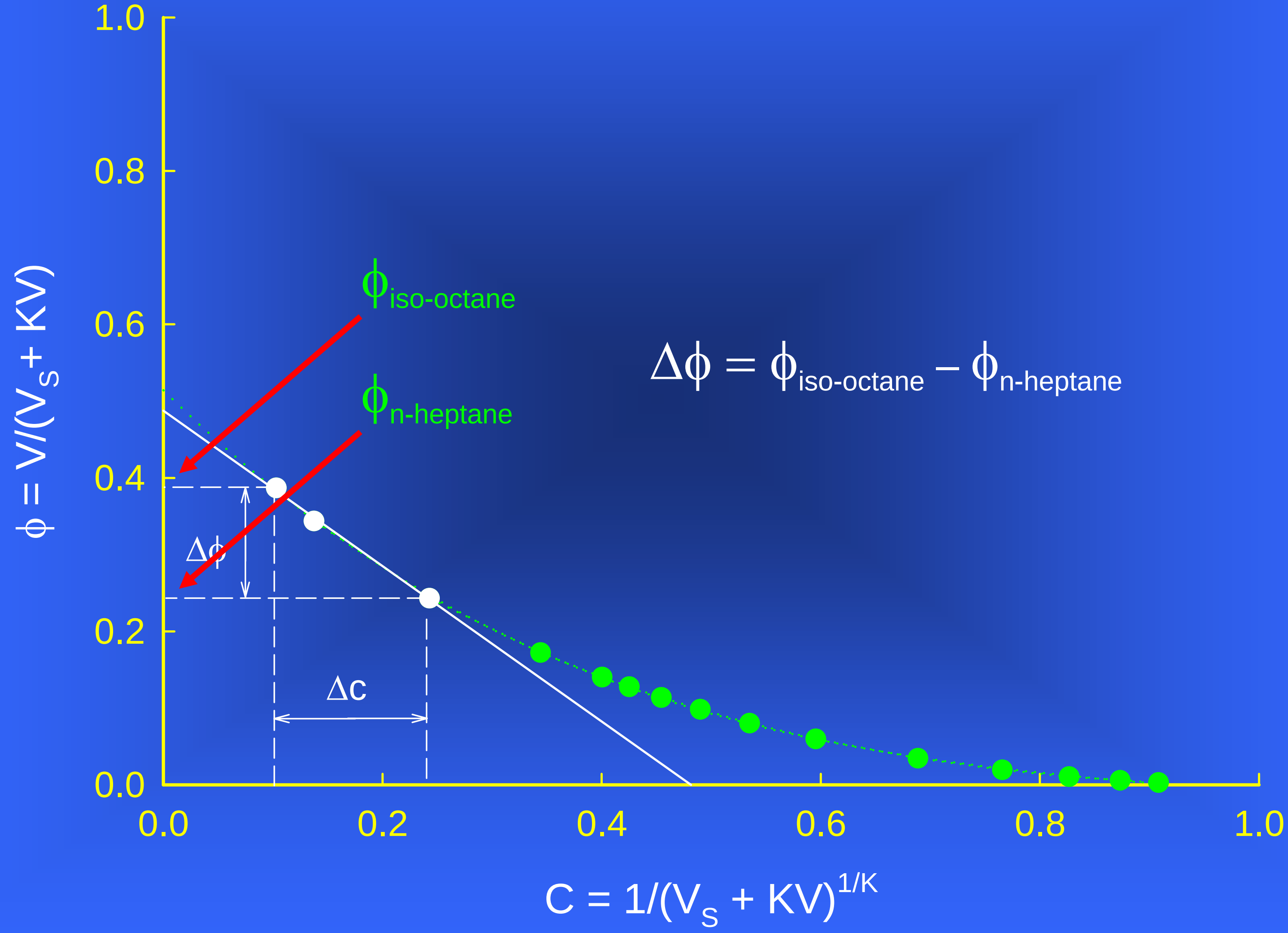


$$\phi = \frac{-1}{K(V_T)^{1/K}} + \frac{1}{K}$$

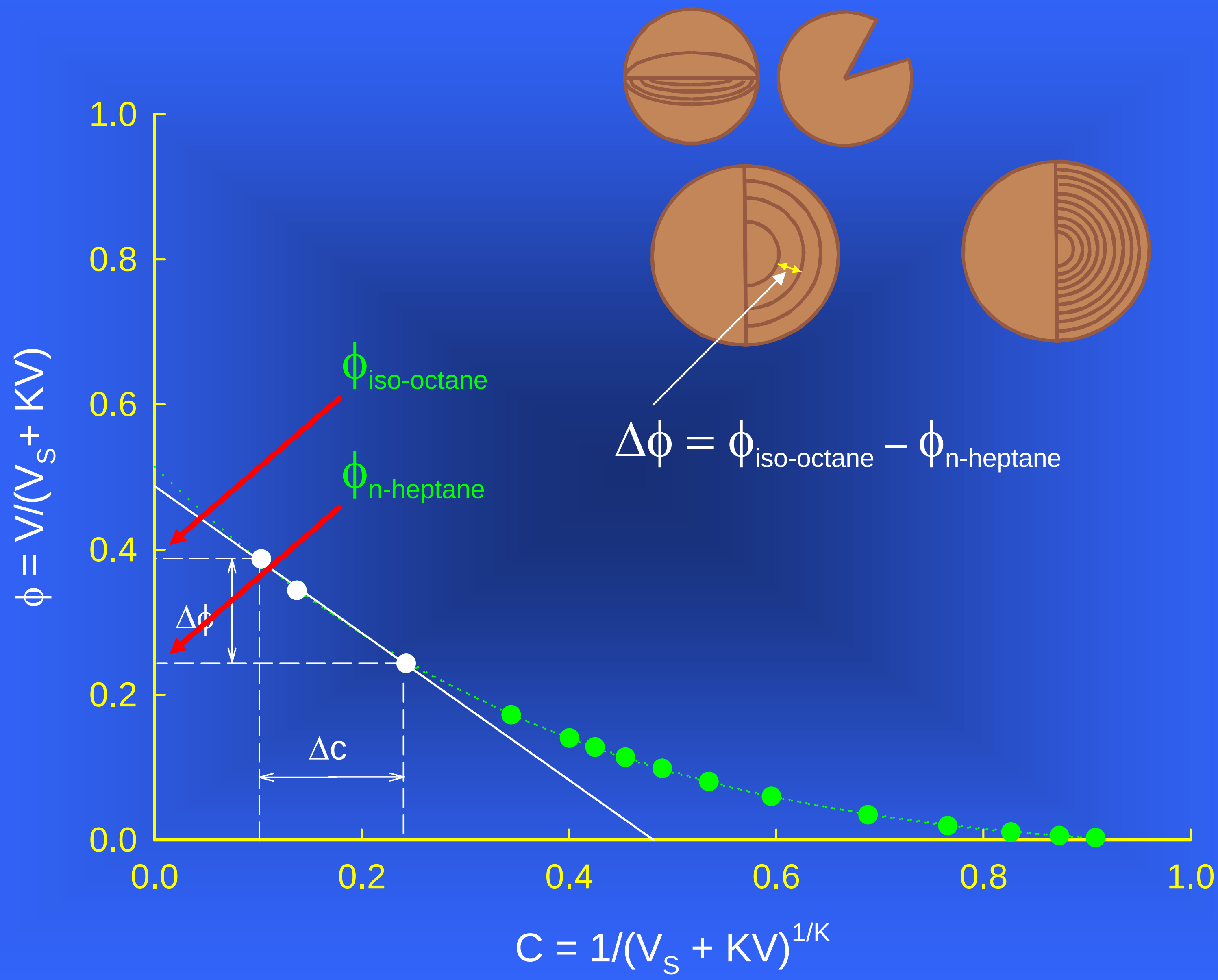
$$c = \frac{1}{(V_T)^{1/K}}$$



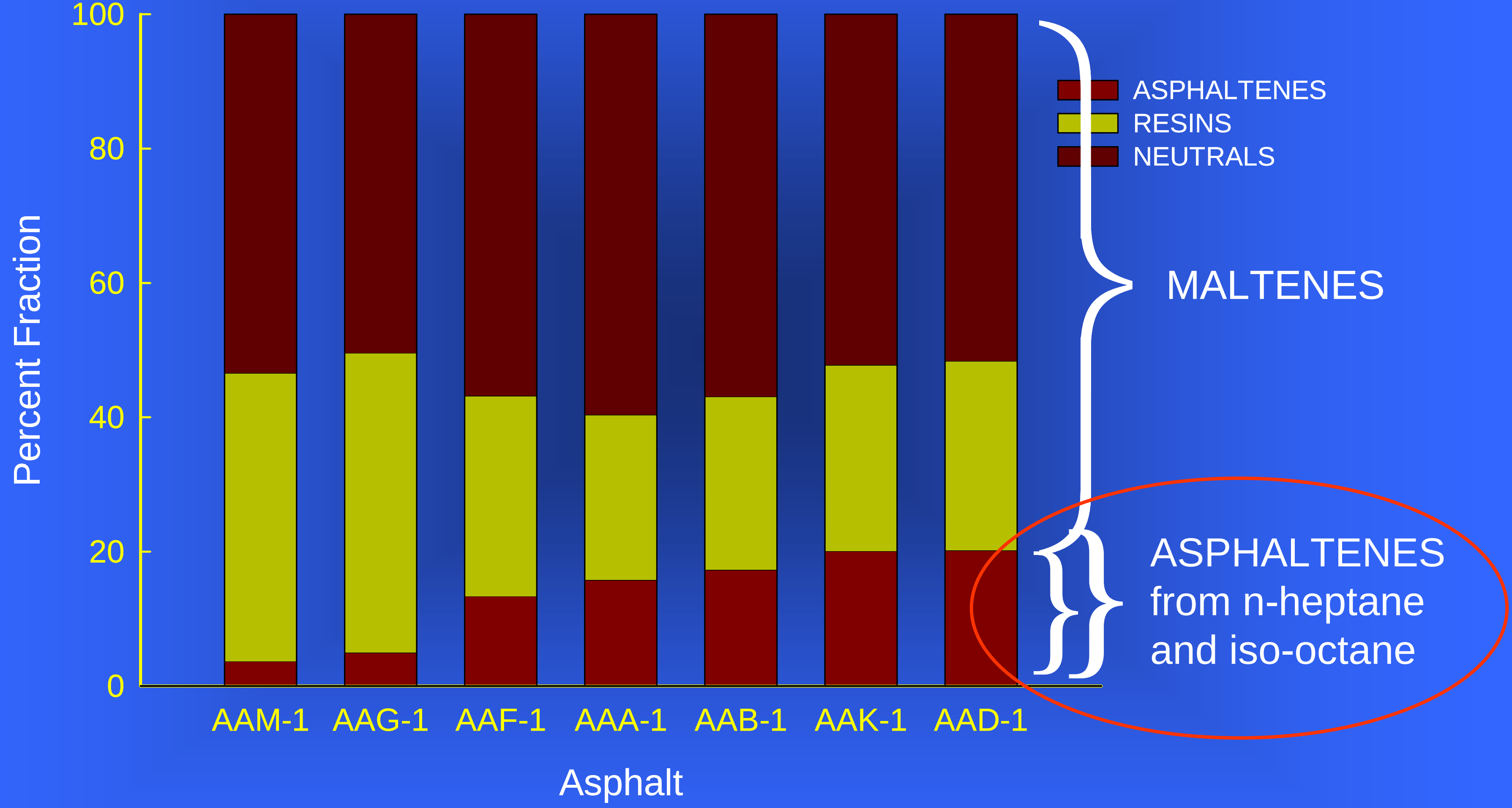
1.0
0.8
0.6
0.4
0.2
0.0
$\phi = V/(V_S + KV)$
$\phi_{n\text{-heptane}}$
$\Delta\phi$
Δc
0.0
0.2
0.4
0.6
0.8
1.0
$C = 1/(V_S + KV)^{1/K}$



1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
ϕ = V/(V_S + KV)
C = 1/(V_S + KV)^1/K
ϕ_iso-octane
ϕ_n-heptane
Δϕ = ϕ_iso-octane − ϕ_n-heptane
Δϕ
Δc



φ = V/(V_S + KV)
1.0
0.8
0.6
0.4
0.2
0.0
φ iso-octane
φ n-heptane
Δφ
Δc
Δφ = φ iso-octane − φ n-heptane
0.0
0.2
0.4
0.6
0.8
1.0
C = 1/(V_S + KV)^1/K


100
80
60
40
20
0
Percent Fraction
ASPHALTENES
RESINS
NEUTRALS
MALTENES
ASPHALTENES
from n-heptane
and iso-octane
AAM-1
AAG-1
AAF-1
AAA-1
AAB-1
AAK-1
AAD-1
Asphalt

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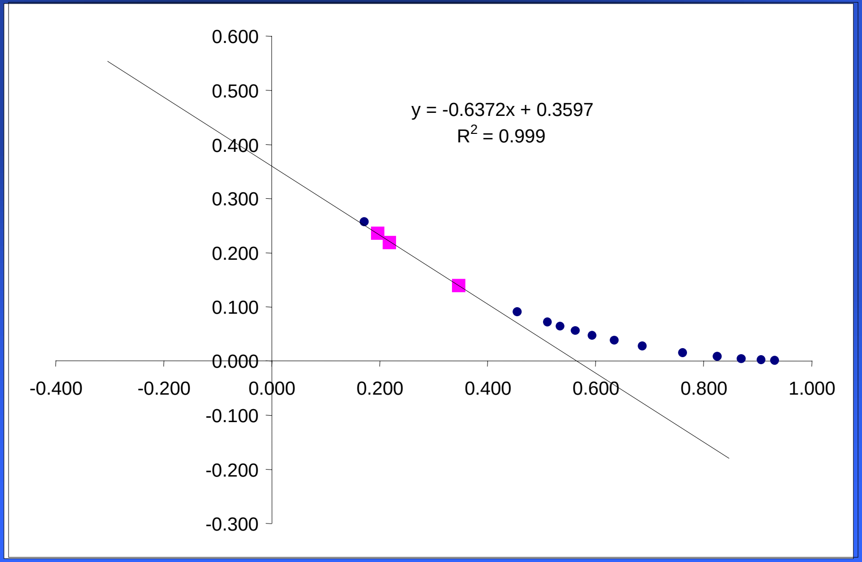
0.125	50	41	2.5	55.13	0.002	1.10	1.10	-0.0002	0.907	1.3
0.25	50	29	2.5	57.25	0.004	1.15	1.15	-0.0048	0.870	1.4
0.5	50	21.4	2.5	60.70	0.008	1.21	1.21	0.0025	0.825	1.6
1	50	15.3	2.5	65.30	0.015	1.31	1.31	-0.0081	0.761	1.9
2	50	11.4	2.5	72.80	0.027	1.46	1.46	-0.0006	0.687	2.6
3	50	9.6	2.5	78.80	0.038	1.58	1.58	0.0000	0.635	3.1
4	50	8.5	2.5	84.00	0.048	1.68	1.68	-0.0042	0.594	3.7
5	50	7.8	2.5	89.00	0.056	1.78	1.78	0.0020	0.562	4.2
6	50	7.25	2.5	93.50	0.064	1.87	1.87	0.0000	0.535	4.8
7	50	6.83	2.5	97.31	0.072	1.96	1.96	0.0000	0.511	5.4
10	50	5.965	2.5	109.65	0.091	2.19	2.20	-0.0048	0.455	7.1
20	**50**	**4.69**	2.5	**143.80**	**0.139**	**2.88**	**2.88**	**-0.0085**	**0.347**	**14.0**
50	**50**	**3.574**	2.5	**228.70**	**0.219**	**4.57**	**4.57**	**0.0019**	**0.219**	**44.7**
60	**50**	**3.405**	2.5	**254.30**	**0.236**	**5.09**	**5.09**	**-0.0005**	**0.197**	**58.3**
75	50	3.22	2.5	291.50	0.257	5.83	5.83	0.0034	0.172	82.1

y = -0.6372x + 0.3597
R2 = 0.999

c_{min}	-0.2292
m	-0.6372
ϕ_{max}	0.3597
α	**0.6403**
K_0	**1.2775**
K	**3.55157**



$$\begin{bmatrix} (c_i)_{V_S} & 1 \\ (c_{i+1})_{V_S} & 1 \\ \vdots & \vdots \\ (c_n)_{V_S} & 1 \end{bmatrix} \begin{bmatrix} m \\ (\phi)_{max} \end{bmatrix} = \begin{bmatrix} (\phi_i)_{V_S} \\ (\phi_{i+1})_{V_S} \\ \vdots \\ (\phi_n)_{V_S} \end{bmatrix}$$

$$\mathbf{x} = \begin{bmatrix} m \\ (\phi)_{max} \end{bmatrix} = \left(A^T A\right)^{-1} A^T \mathbf{y}$$

$$\phi(@\, c = 0) = (\phi)_{max}$$

$(\phi)_{max}$: Theoretical Maximum Flocculation Ratio

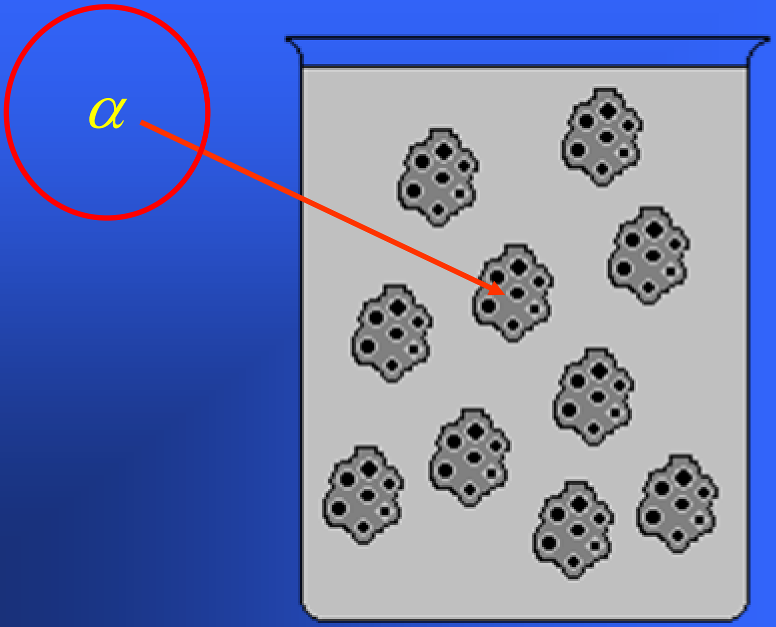
$$m(@\, \phi = 0) = \frac{-c_{min}}{(\phi)_{max}}$$

c_{min}: Theoretical Minimum Dilution Concentration

$$\alpha = 1 - (\phi)_{max}$$

α: Volume Fraction of Trapped Solvent per Floc

$$\begin{bmatrix} (c_i)_{V_S} & 1 \\ (c_{i+1})_{V_S} & 1 \\ \vdots & \vdots \\ (c_n)_{V_S} & 1 \end{bmatrix} \begin{bmatrix} m \\ (\phi)_{max} \end{bmatrix} = \begin{bmatrix} (\phi_i)_{V_S} \\ (\phi_{i+1})_{V_S} \\ \vdots \\ (\phi_n)_{V_S} \end{bmatrix}$$



$$\mathbf{x} = \begin{bmatrix} m \\ (\phi)_{max} \end{bmatrix} = \left(A^T A\right)^{-1} A^T \mathbf{y}$$

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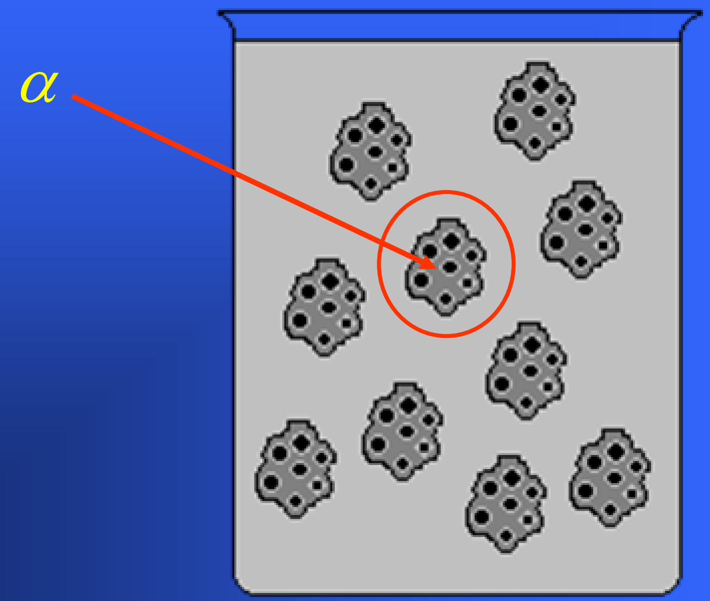
$$
\begin{bmatrix} (c_i)_{V_S} & 1 \\ (c_{i+1})_{V_S} & 1 \\ \vdots & \vdots \\ (c_n)_{V_S} & 1 \end{bmatrix} \begin{bmatrix} m \\ (\phi)_{max} \end{bmatrix} = \begin{bmatrix} (\phi_i)_{V_S} \\ (\phi_{i+1})_{V_S} \\ \vdots \\ (\phi_n)_{V_S} \end{bmatrix}
$$



$$
\mathbf{x} = \begin{bmatrix} m \\ (\phi)_{max} \end{bmatrix} = \left(A^T A\right)^{-1} A^T \mathbf{y}
$$

$$
\phi(@\, c = 0) = (\phi)_{max}
$$

$(\phi)_{max}$: Theoretical Maximum Flocculation Ratio

$$
m(@\, \phi = 0) = \frac{-c_{min}}{(\phi)_{max}}
$$

c_{min}: Theoretical Minimum Dilution Concentration

$$
\alpha = 1 - (\phi)_{max}
$$

α: Volume Fraction of Trapped Solvent per Floc

V	V_0	K	[illegible]	V_T	φ	[illegible]	[illegible]	dif	$(1/V_r)^{[illegible]}$	[illegible]
0.0625	50	58	2.5	53.50	0.001	1.07	1.07	-0.0037	0.931	1.2
0.125	60	41	2.6	66.13	0.002	1.10	1.10	-0.0002	0.907	1.3
0.25	60	29	2.6	67.25	0.004	1.16	1.16	-0.0048	0.870	1.4
0.5	60	21.4	2.6	60.70	0.008	1.21	1.21	0.0025	0.825	1.6
1	60	16.3	2.6	66.30	0.016	1.31	1.31	-0.0081	0.761	1.9
2	60	11.4	2.6	72.90	0.027	1.48	1.48	-0.0006	0.697	2.6
3	60	9.8	2.6	78.90	0.038	1.69	1.69	0.0000	0.636	3.1
4	60	8.6	2.6	84.00	0.048	1.88	1.88	-0.0042	0.594	3.7
6	60	7.8	2.6	89.00	0.068	1.78	1.78	0.0020	0.562	4.2
8	60	7.25	2.6	93.60	0.084	1.87	1.87	0.0000	0.536	4.8
7	60	6.83	2.6	97.91	0.072	1.99	1.99	0.0000	0.511	6.4
10	60	6.986	2.6	109.06	0.091	2.10	2.20	-0.0048	0.466	7.1
20	60	4.69	2.6	143.80	0.139	2.88	2.88	-0.0086	0.347	14.0
60	60	3.674	2.6	228.70	0.210	4.67	4.67	0.0010	0.210	44.7
80	60	3.406	2.6	264.30	0.236	6.09	6.09	-0.0006	0.197	68.9
75	60	3.22	2.6	291.60	0.267	6.83	6.83	0.0034	0.172	82.1

$y = -0.6372x + 0.3597$
R2 = 0.999

c_{min}	-0.2292
m	-0.6372
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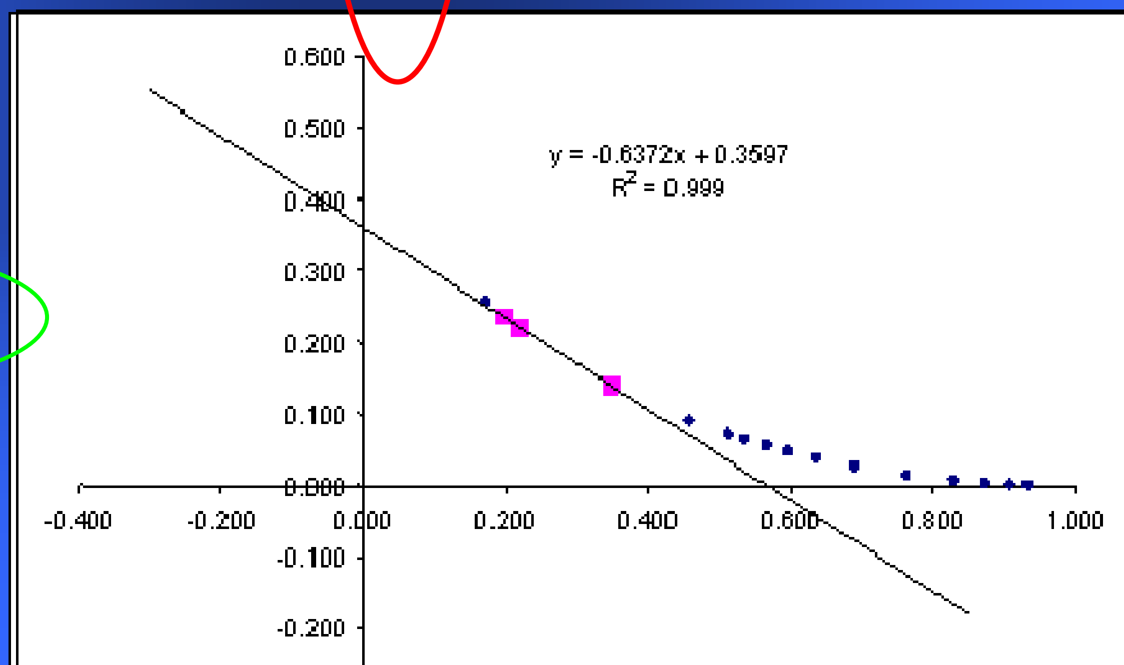


Theoretical Colloidal Stability Parameters

$$K_0 = 1 - (\phi)_{max} - m = \alpha - m$$

$$= 1 - (\phi)_{max} + \frac{c_{min}}{(\phi)_{max}}$$

$$= \alpha + \frac{c_{min}}{1-\alpha}$$

$$= \alpha + c_{min} K_\alpha$$

$$K = K_0 K_\alpha$$

$$= \frac{K_0}{1-\alpha}$$

$$= \frac{\alpha}{1-\alpha} + \frac{c_{min} K_\alpha}{1-\alpha}$$

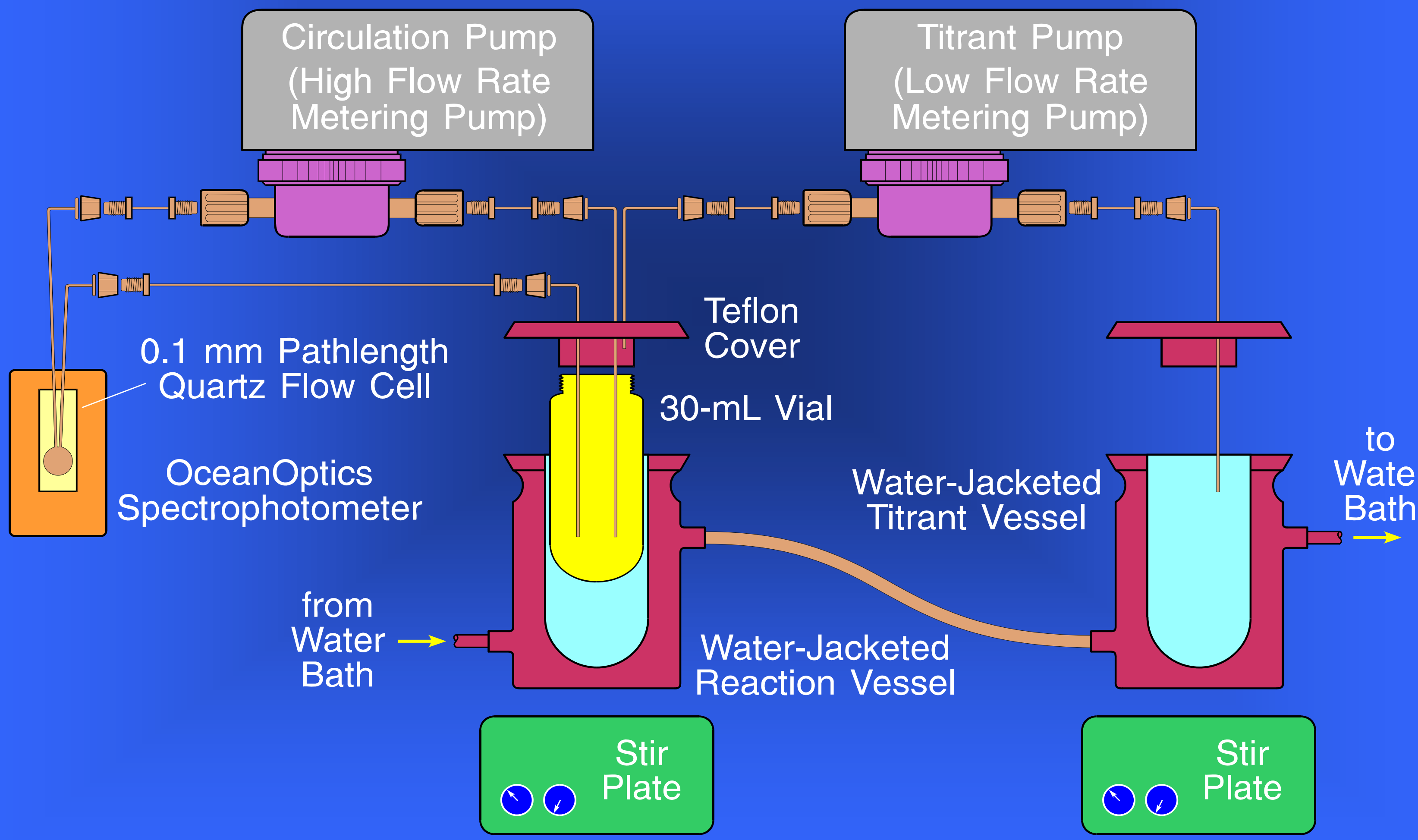
$$= \alpha K_\alpha + c_{min} K_\alpha^{\,2}$$

$$= K_\alpha \left(\alpha + c_{min} K_\alpha \right)$$

$$= K_\alpha K_0$$

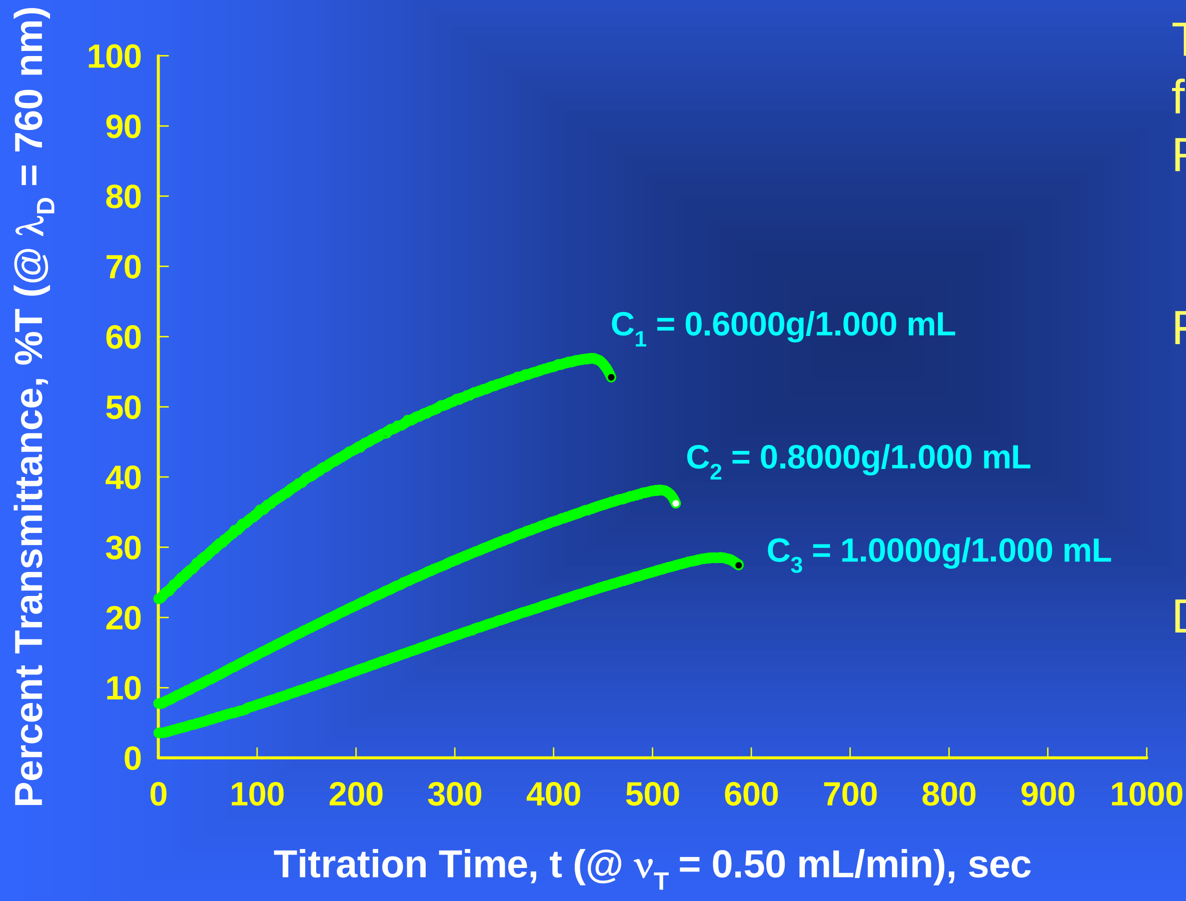
Automated Flocculation Titrimeter

Schematic of Instrument



Automated Flocculation Titrimeter, available from Koehler Instruments

ASTM “Standard D6703-01” Measurement of Heithaus Compatibility Parameters



Titrant Volume (mL) as a function of Titrant Flow Rate (mL/min) and Time:

$$V_T = t_f \upsilon_T$$

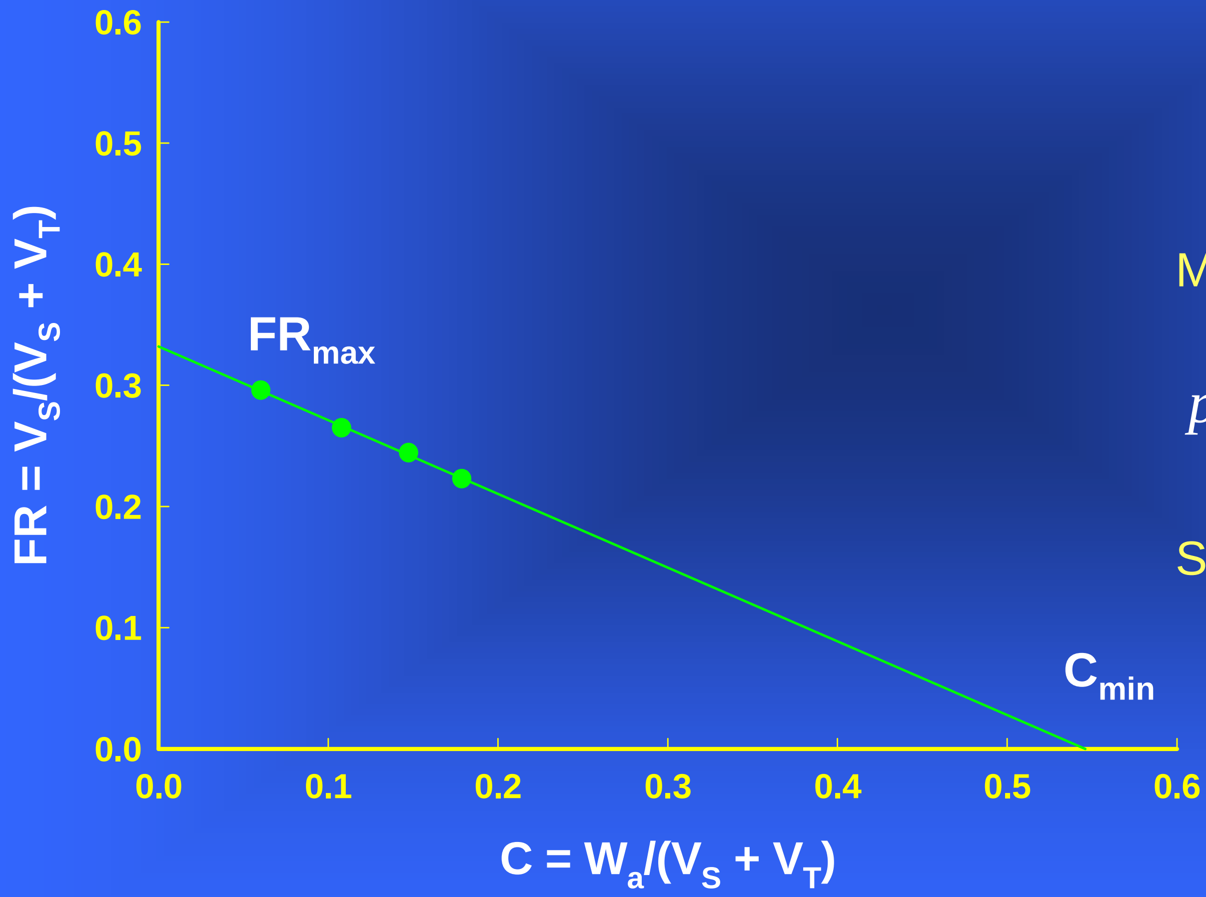
Flocculation Ratio:

$$FR = \frac{V_S}{V_S + V_T}$$

Dilution Concentration:

$$C = \frac{W_a}{V_S + V_T}$$

Determination of Heithaus Compatibility Parameters from *FR-vs-C* Plots



Asphaltene Peptizability:

$$p_a = 1 - FR_{\max}$$

Maltene Peptizing Power:

$$p_o = FR_{\max}\left[\left(\frac{1}{C_{\min}}\right)+1\right]$$

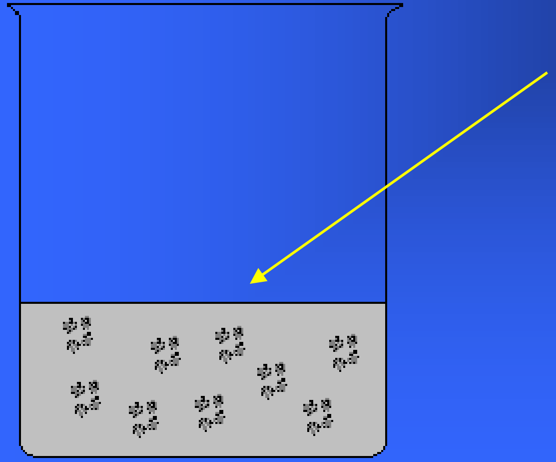
State of Peptization:

$$P = \frac{p_o}{1 - p_a}$$

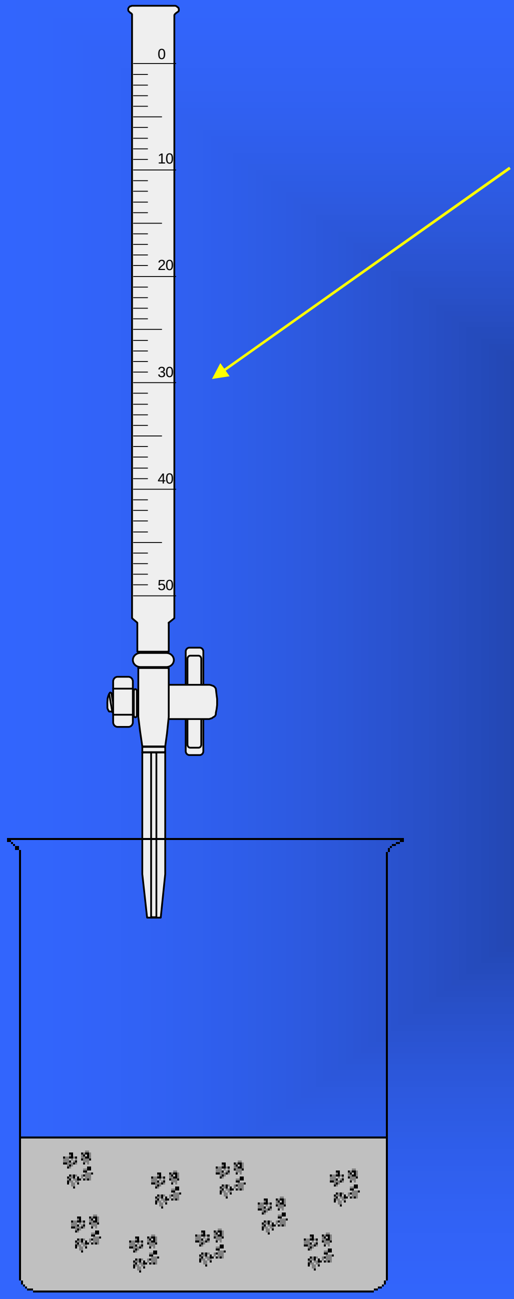
Reversible Flocculation Titrimetry

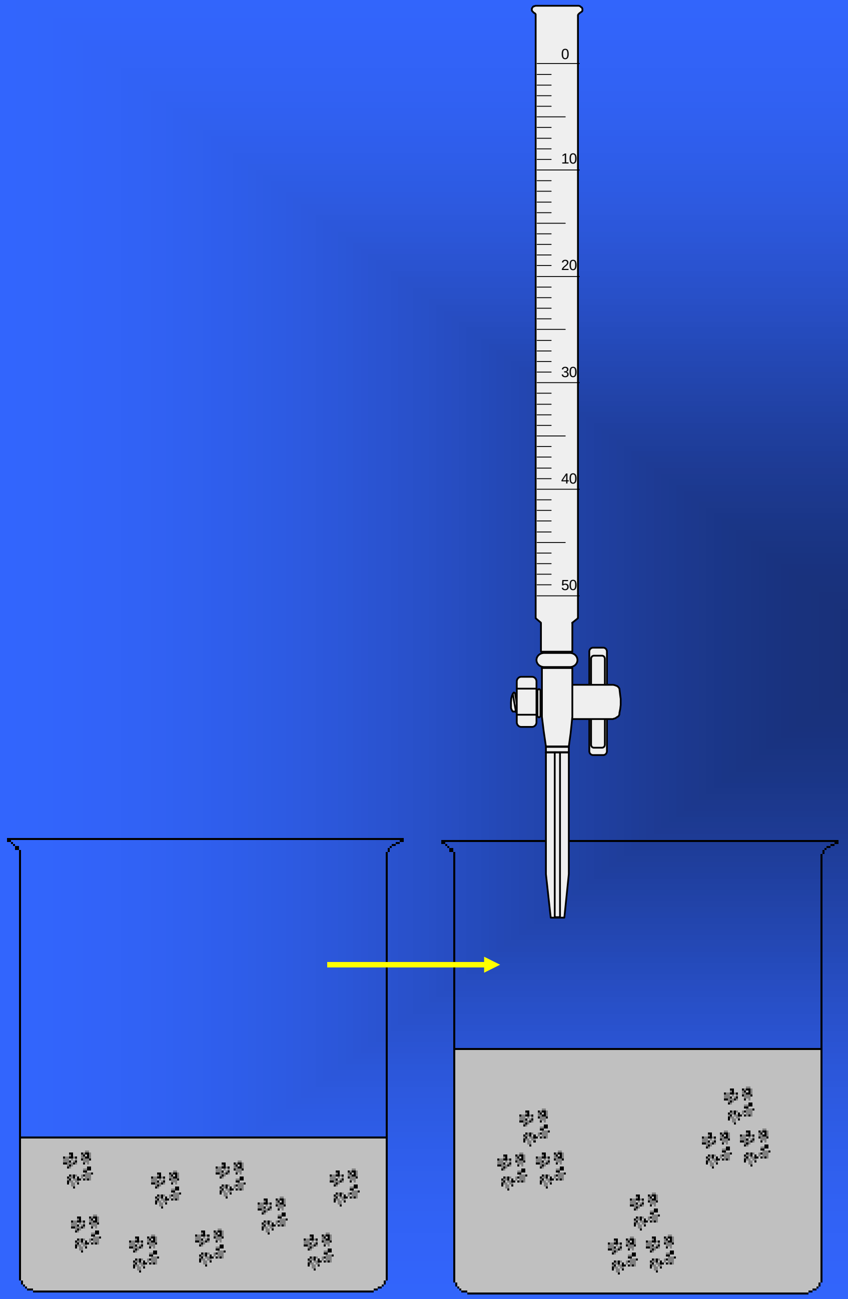
Methodology:

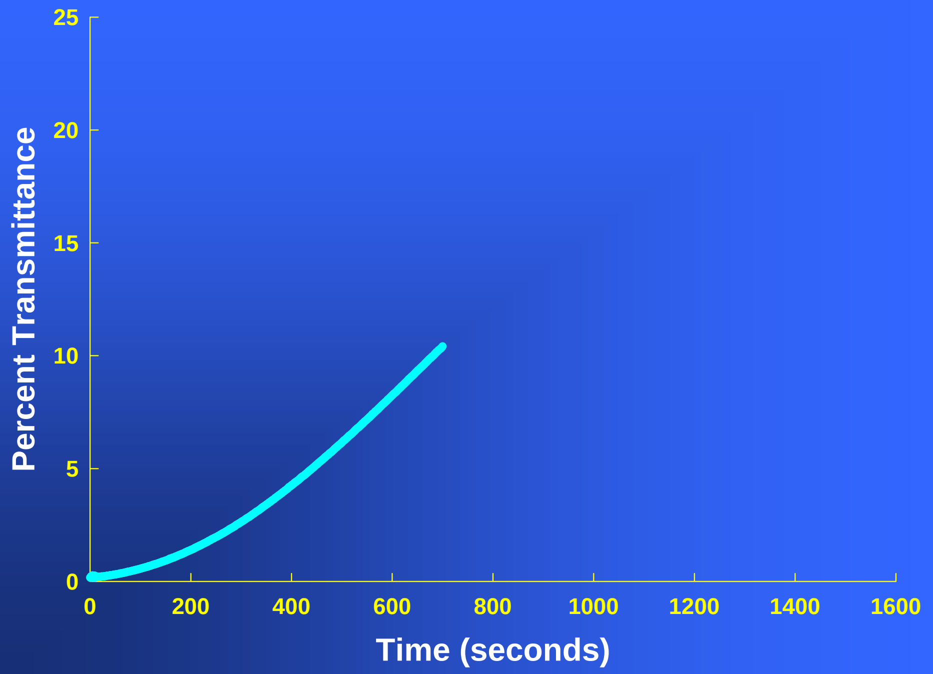
Periodic Back-Titration of Toluene-Sample Solution with Toluene at Successive Flocculation Onset Points, While Continually Titrated with iso-Octane

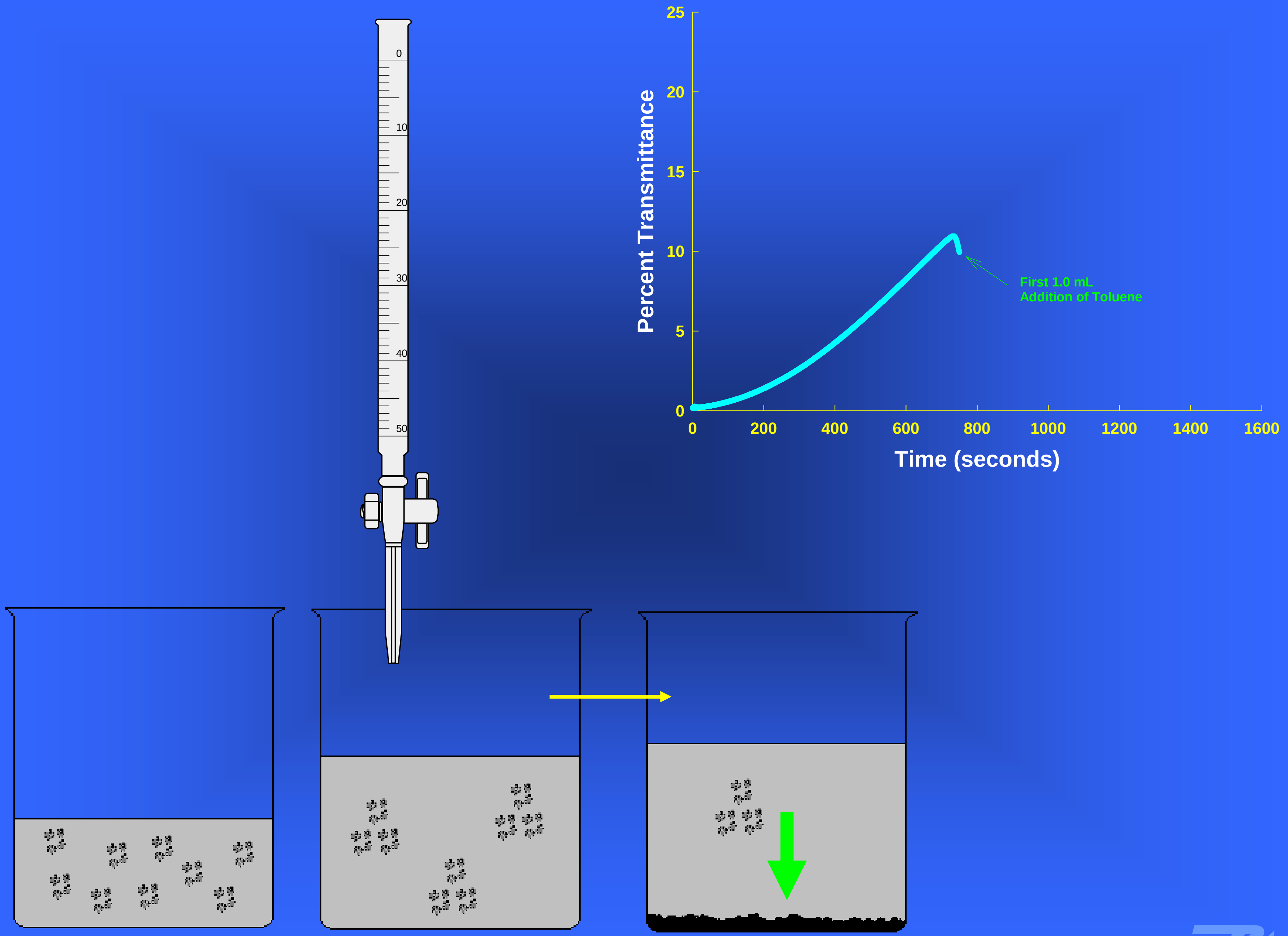


Prepare an asphalt solution dissolved in toluene at a single concentration (1.0g/3.0mL) followed by titration of this solution with iso-octane (2,2,4-trimethyl pentane)

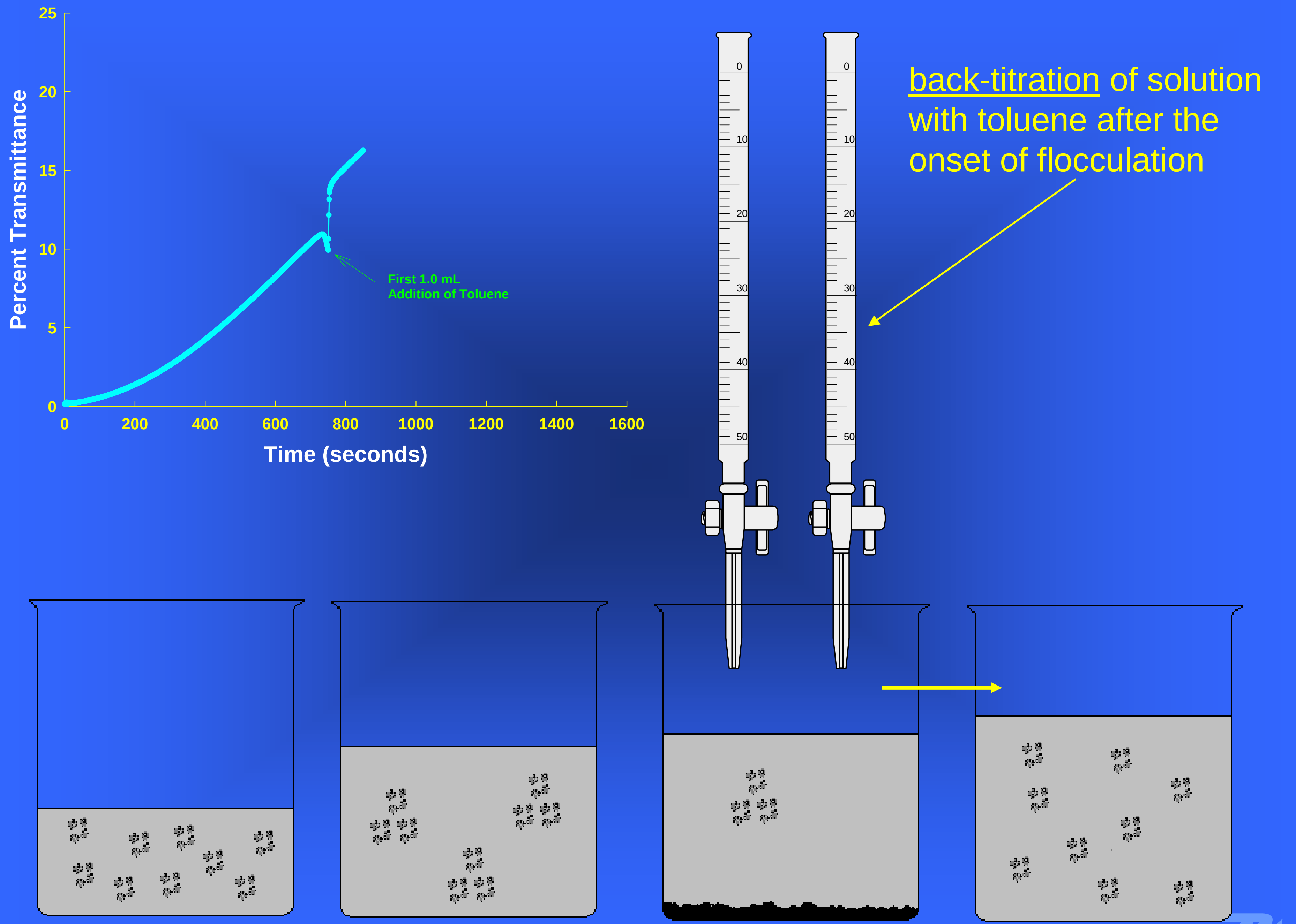



0
10
20
30
40
50


Percent Transmittance
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Time (seconds)

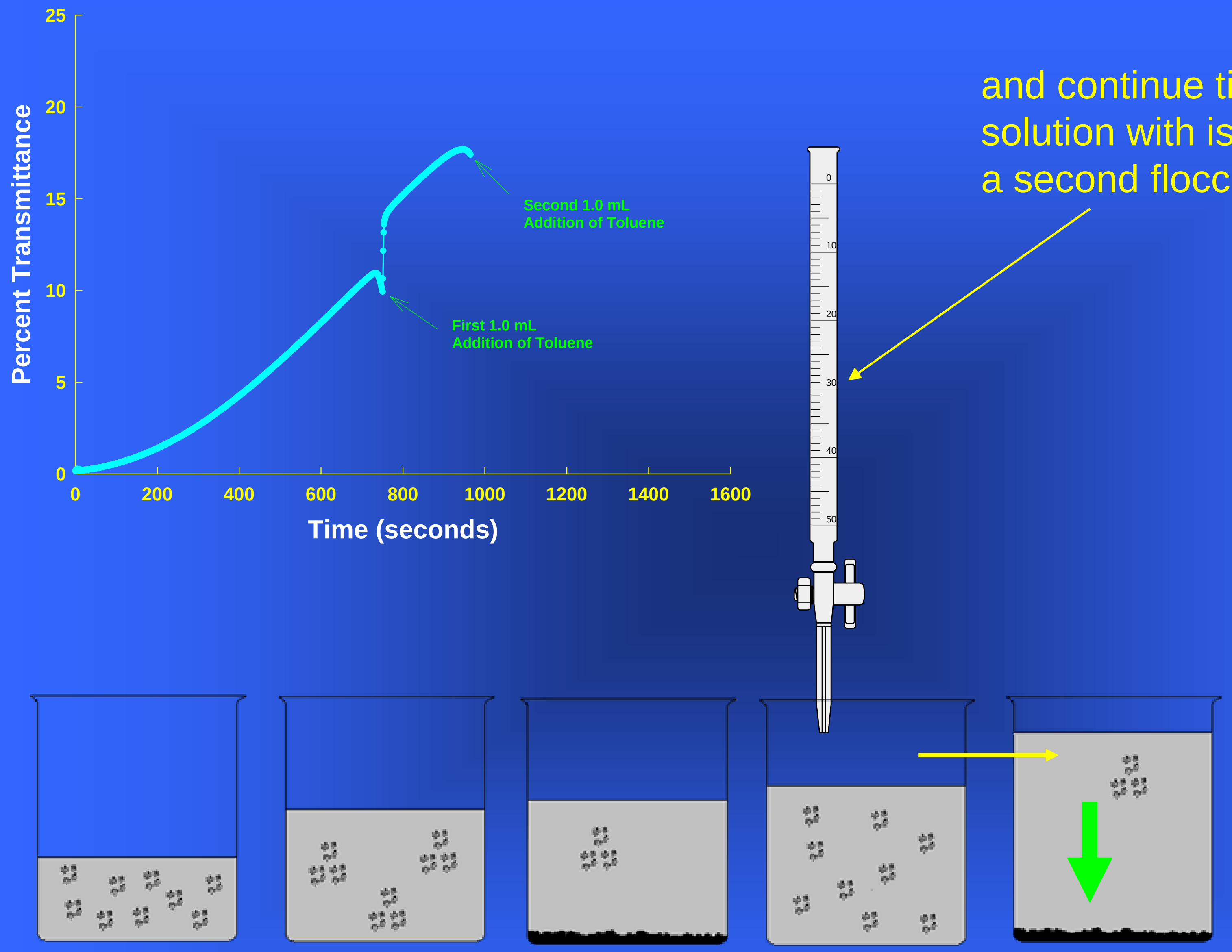


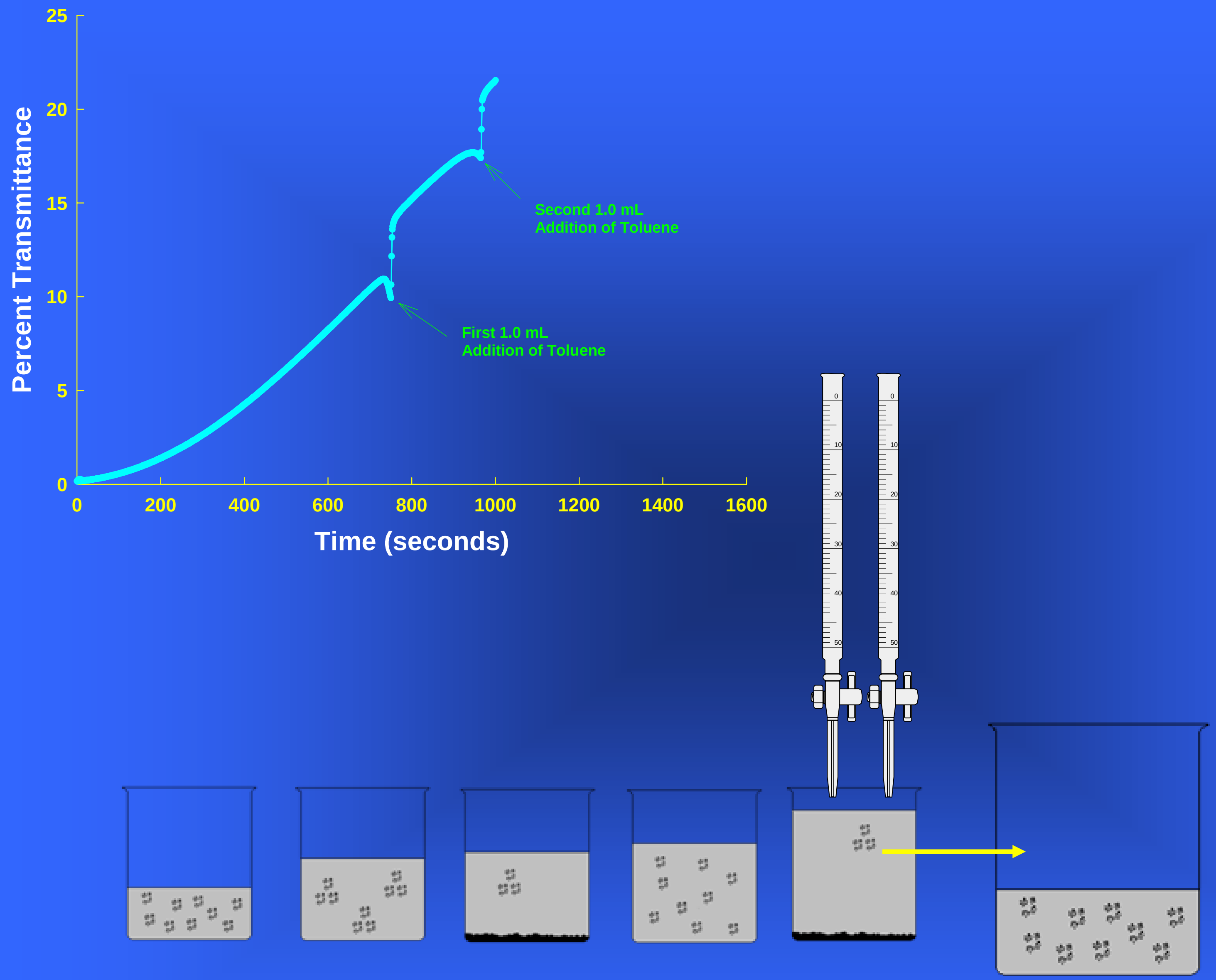
Percent Transmittance
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Time (seconds)
First 1.0 mL
Addition of Toluene
0
10
20
30
40
50



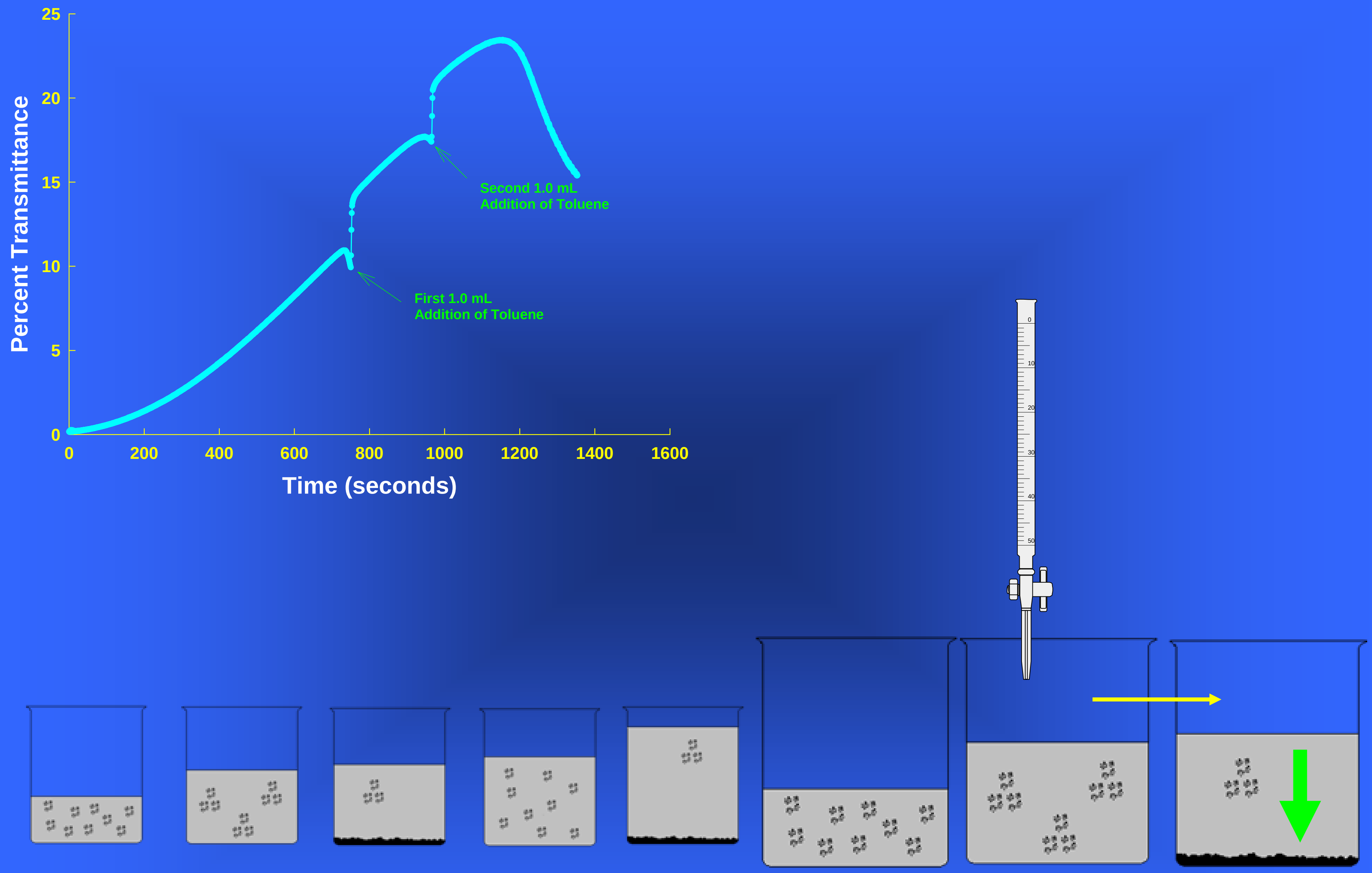
Percent Transmittance
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Time (seconds)
First 1.0 mL
Addition of Toluene
back-titration of solution with toluene after the onset of flocculation

and continue titration of the solution with iso-octane to a second flocculation point





Percent Transmittance
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Time (seconds)
Second 1.0 mL
Addition of Toluene
First 1.0 mL
Addition of Toluene



Percent Transmittance
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Time (seconds)
Second 1.0 mL
Addition of Toluene
First 1.0 mL
Addition of Toluene

Reversible Flocculation Titrimetry
Experimental Approach cont:

$$V_{T,i}^{rev} = t_{f,i}^{rev} \upsilon_T$$

Titrant volume related to rate of addition and time of experiment

$$V_S = V_S(0)$$

$$V_S(1) = V_S(0) + V_{S,1}$$

$$V_S(2) = V_S(0) + V_{S,1} + V_{S,2}$$

.

.

.

$$V_S(i) = V_S(0) + \sum_{i=1}^{n} V_{S,i}$$

Reversible Flocculation Titrimetry Experimental Approach cont:

$$V_{T,i}^{rev} = t_{f,i}^{rev} \upsilon_T$$

Titrant volume related to rate of addition and time of experiment

Back-titrant volume related to periodic after Flocculation onset

$$V_S = V_S(0)$$

$$V_S(1) = V_S(0) + V_{S,1}$$

$$V_S(2) = V_S(0) + V_{S,1} + V_{S,2}$$

$$\vdots$$

$$V_S(i) = V_S(0) + \sum_{i=1}^{n} V_{S,i}$$

Reversible Flocculation Titrimetry Experimental Approach cont:

Calculation of Reversible Flocculation Ratio and Dilution Concentration

$$FR^{rev} = \frac{V_S \ldots V_S(i)}{V_{T,i}^{\ rev} + V_S \ldots V_S(i)}$$

$$C^{rev} = \frac{W_a}{V_{T,i}^{\ rev} + V_S \ldots V_S(i)}$$

$$\begin{bmatrix} C^{rev}(0) & 1 \\ C^{rev}(1) & 1 \\ \vdots & \vdots \\ C^{rev}(n) & 1 \end{bmatrix} \begin{bmatrix} m \\ \left(FR^{rev}\right)_{\max} \end{bmatrix} = \begin{bmatrix} FR^{rev}(0) \\ FR^{rev}(1) \\ \vdots \\ FR^{rev}(n) \end{bmatrix}$$

$$\mathbf{x} = \begin{bmatrix} m \\ \left(FR^{rev}\right)_{max} \end{bmatrix} = \left(A^T A\right)^{-1} A^T \mathbf{y}$$

$$FR^{rev} = mC^{rev} + \left(FR^{rev}\right)_0$$

$$FR^{rev}\left(@\, C^{rev} = 0\right) = \left(FR^{rev}\right)_{max}$$

$$m\left(@\, FR^{rev} = 0\right) = \frac{-\left(C^{rev}\right)_{min}}{\left(FR^{rev}\right)_{max}}$$

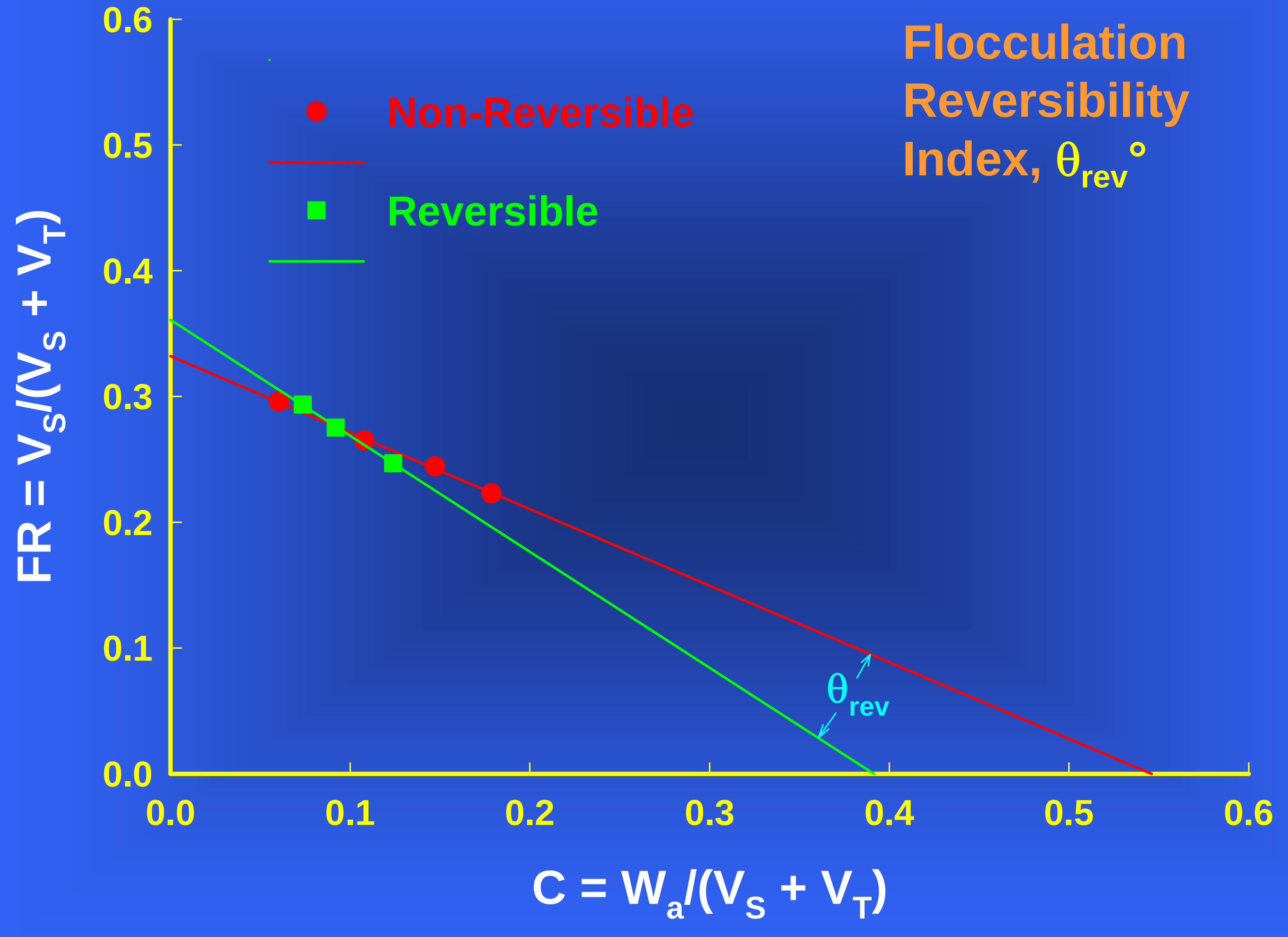
$$FR^{rev}\left(@\,C^{rev}=0\right)=\left(FR^{rev}\right)_{max}$$

$$m\left(@\,FR^{rev}=0\right)=\frac{-\left(C^{rev}\right)_{min}}{\left(FR^{rev}\right)_{max}}$$

$$p_a{}^{rev}=1-\left(FR^{rev}\right)_{max}$$

$$p_o{}^{rev}=\left(FR^{rev}\right)_{\max}-m=\left(FR^{rev}\right)_{\max}\left[\frac{1}{\left(C^{rev}\right)_{\min}}+1\right]$$

$$P_{rev}=\frac{p_o{}^{rev}}{1-p_a{}^{rev}}$$



Flocculation Reversibility Index, θ_{rev}°
Non-Reversible
Reversible
θ_{rev}
0.0
0.1
0.2
0.3
0.4
0.5
0.6
$FR = V_S/(V_S + V_T)$
$C = W_a/(V_S + V_T)$

Reversible Flocculation Titrimetry Experimental Approach cont:

Flocculation Reversibility Index, $\theta_{rev}°$

$$m = 1 - p_a - p_o$$

$$m_{rev} = 1 - p_a^{rev} - p_o^{rev}$$

$$\theta_{rev}^{\circ} = \tan^{-1}\left(\frac{m_{rev} - m}{1 + m_{rev} m}\right)$$

So,

Basically the whole point of this exercise is to show

$$K_0 = 1 - (\phi)_{max} - m = \alpha - m$$

$$= 1 - (\phi)_{max} + \frac{c_{min}}{(\phi)_{max}}$$

$$= \alpha + \frac{c_{min}}{1 - \alpha}$$

$$= \alpha + c_{min} K_\alpha$$

$$K = K_0 K_\alpha$$

$$= \frac{K_0}{1 - \alpha}$$

$$= \frac{\alpha}{1 - \alpha} + \frac{c_{min} K_\alpha}{1 - \alpha}$$

$$= \alpha K_\alpha + c_{min} K_\alpha^{\ 2}$$

$$= K_\alpha (\alpha + c_{min} K_\alpha)$$

$$= K_\alpha K_0$$

→

$$p_a^{rev} = 1 - (FR^{rev})_{max}$$

$$p_o^{rev} = (FR^{rev})_{\max} - m = (FR^{rev})_{\max} \left[\frac{1}{(C^{rev})_{\min}} + 1 \right]$$

$$P_{rev} = \frac{p_o^{rev}}{1 - p_a^{rev}}$$

$$K_0 = 1 - (\phi)_{max} - m = \alpha - m$$

$$= 1 - (\phi)_{max} + \frac{c_{min}}{(\phi)_{max}}$$

$$= \alpha + \frac{c_{min}}{1 - \alpha}$$

$$= \alpha + c_{min} K_\alpha$$

$$K = K_0 K_\alpha$$

$$= \frac{K_0}{1 - \alpha}$$

$$= \frac{\alpha}{1 - \alpha} + \frac{c_{min} K_\alpha}{1 - \alpha}$$

$$= \alpha K_\alpha + c_{min} K_\alpha^{\ 2}$$

$$= K_\alpha (\alpha + c_{min} K_\alpha)$$

$$= K_\alpha K_0$$

$$p_a^{\ rev} = 1 - \left(FR^{rev}\right)_{max}$$

$$p_o^{\ rev} = \left(FR^{rev}\right)_{\max} - m = \left(FR^{rev}\right)_{\max} \left[\frac{1}{\left(C^{rev}\right)_{\min}} + 1\right]$$

$$P_{rev} = \frac{p_o^{\ rev}}{1 - p_a^{\ rev}}$$

$$K_0 = 1 - (\phi)_{max} - m = \alpha - m$$

$$= 1 - (\phi)_{max} + \frac{c_{min}}{(\phi)_{max}}$$

$$= \alpha + \frac{c_{min}}{1-\alpha}$$

$$= \alpha + c_{min} K_\alpha$$

$$K = K_0 K_\alpha$$

$$= \frac{K_0}{1-\alpha}$$

$$= \frac{\alpha}{1-\alpha} + \frac{c_{min} K_\alpha}{1-\alpha}$$

$$= \alpha K_\alpha + c_{min} K_\alpha^{\ 2}$$

$$= K_\alpha (\alpha + c_{min} K_\alpha)$$

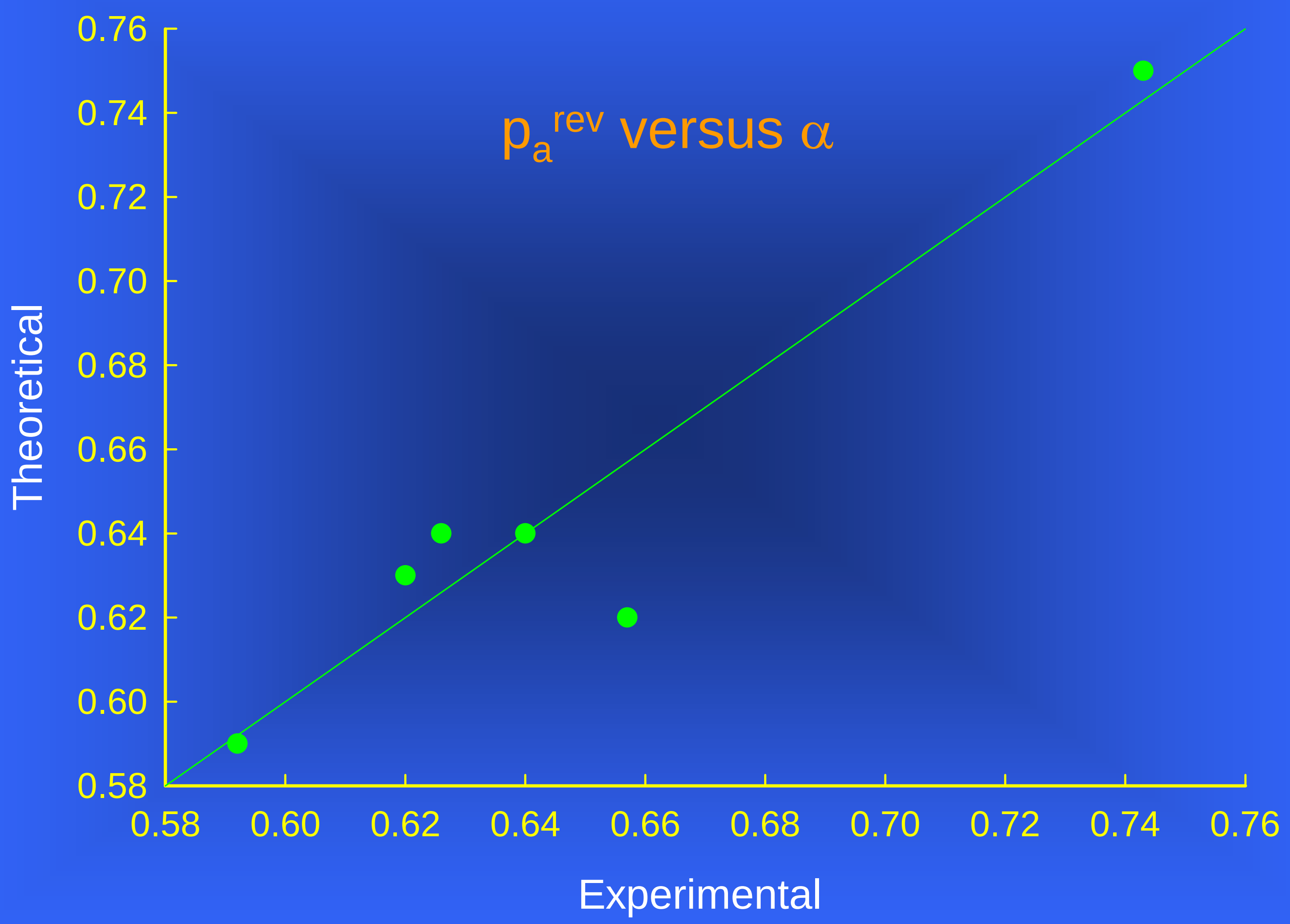
$$= K_\alpha K_0$$

→

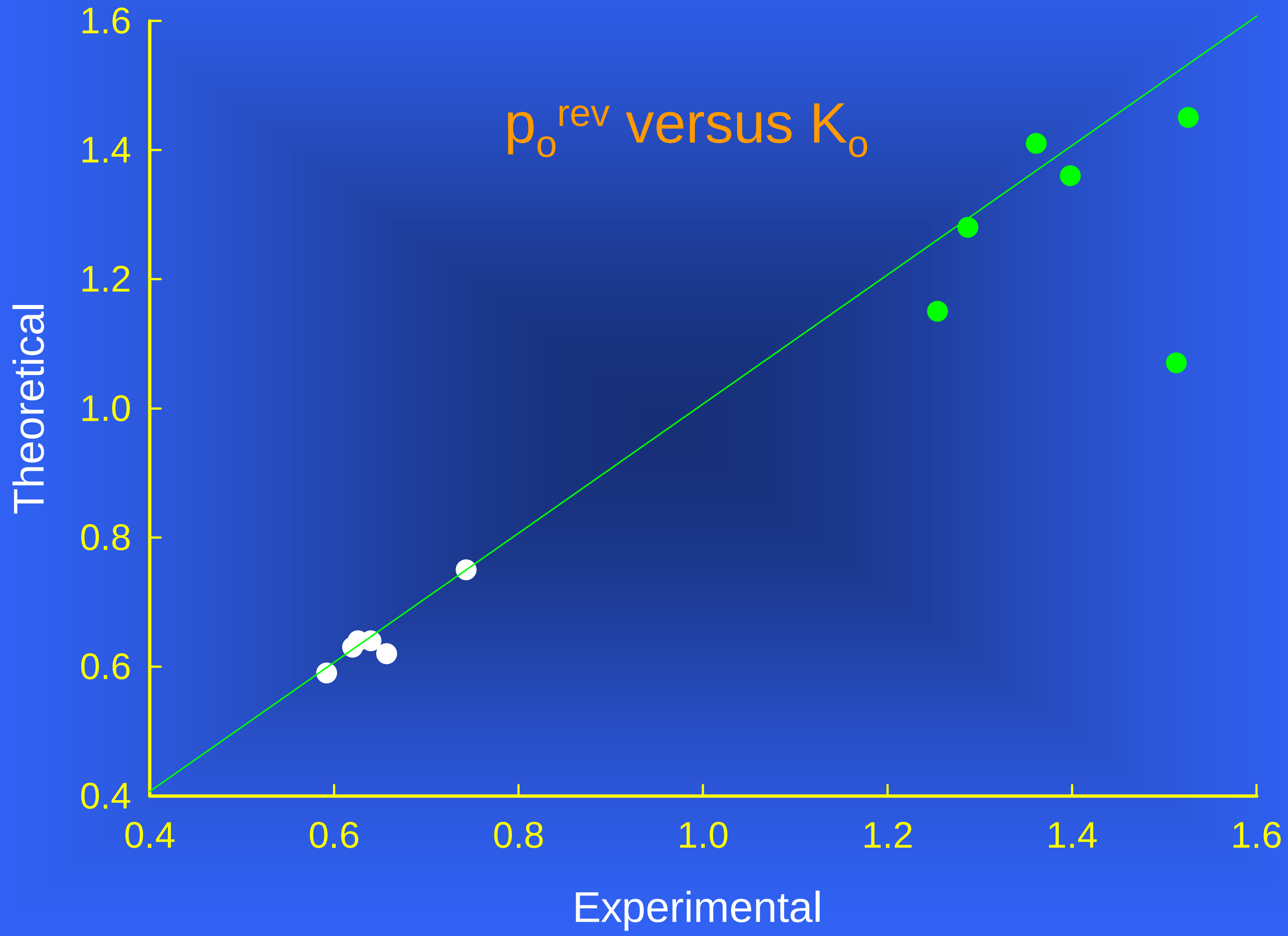
$$p_a^{\ rev} = 1 - \left(FR^{rev}\right)_{max}$$

$$p_o^{\ rev} = \left(FR^{rev}\right)_{\max} - m = \left(FR^{rev}\right)_{\max} \left[\frac{1}{\left(C^{rev}\right)_{\min}} + 1 \right]$$

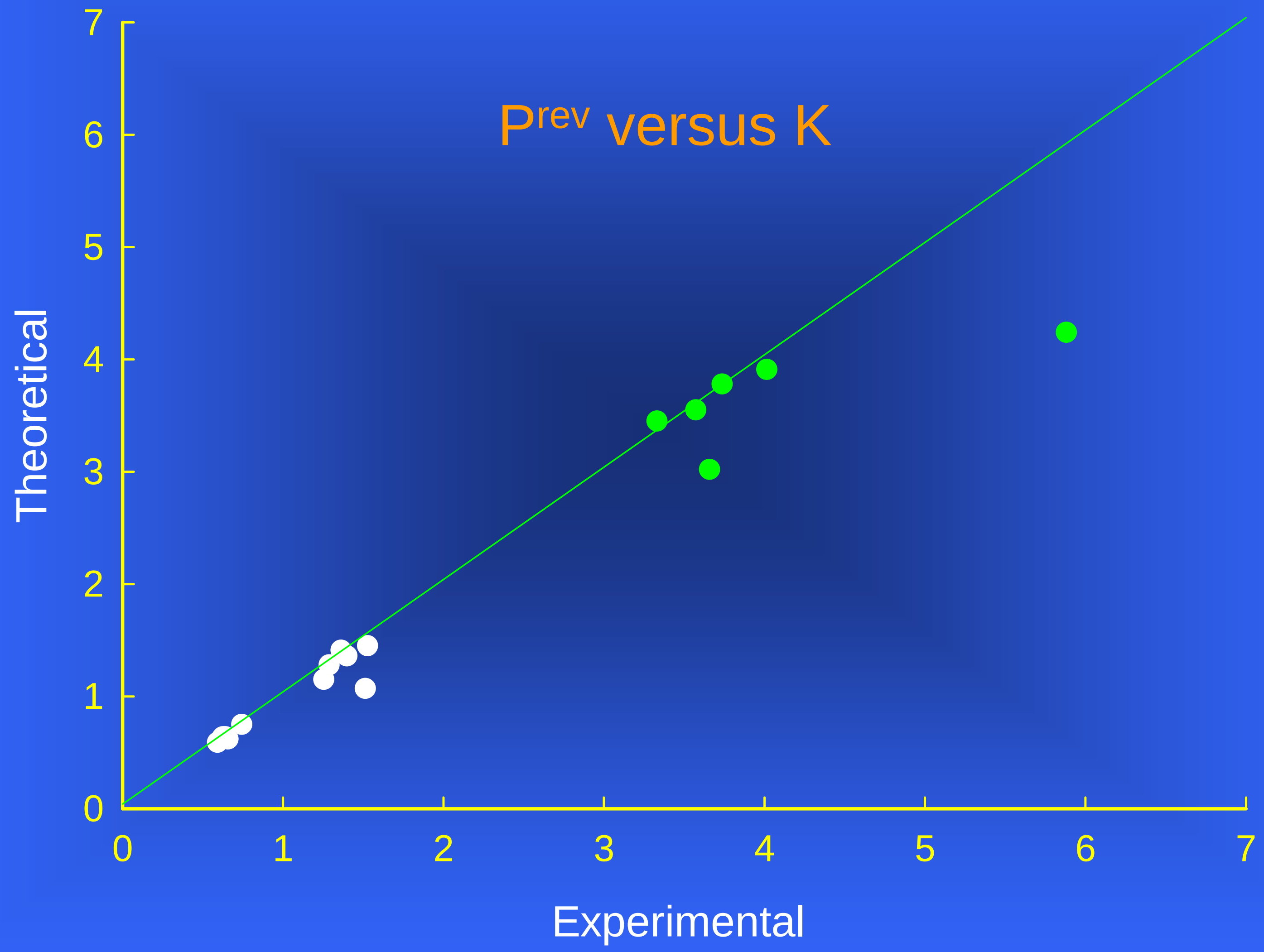
$$P_{rev} = \frac{p_o^{\ rev}}{1 - p_a^{\ rev}}$$



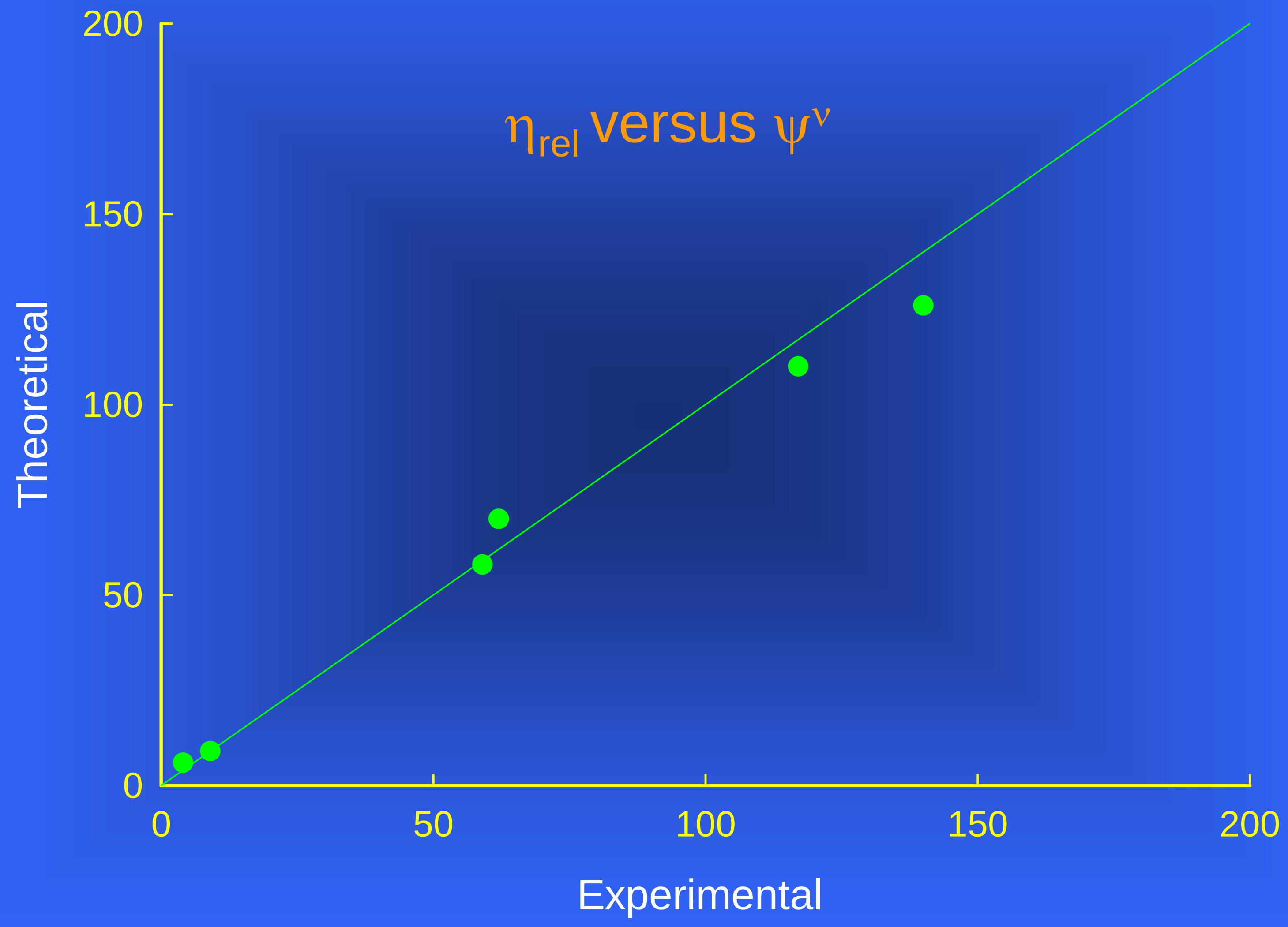
p_a^{rev} versus α
Theoretical
Experimental
0.58
0.60
0.62
0.64
0.66
0.68
0.70
0.72
0.74
0.76



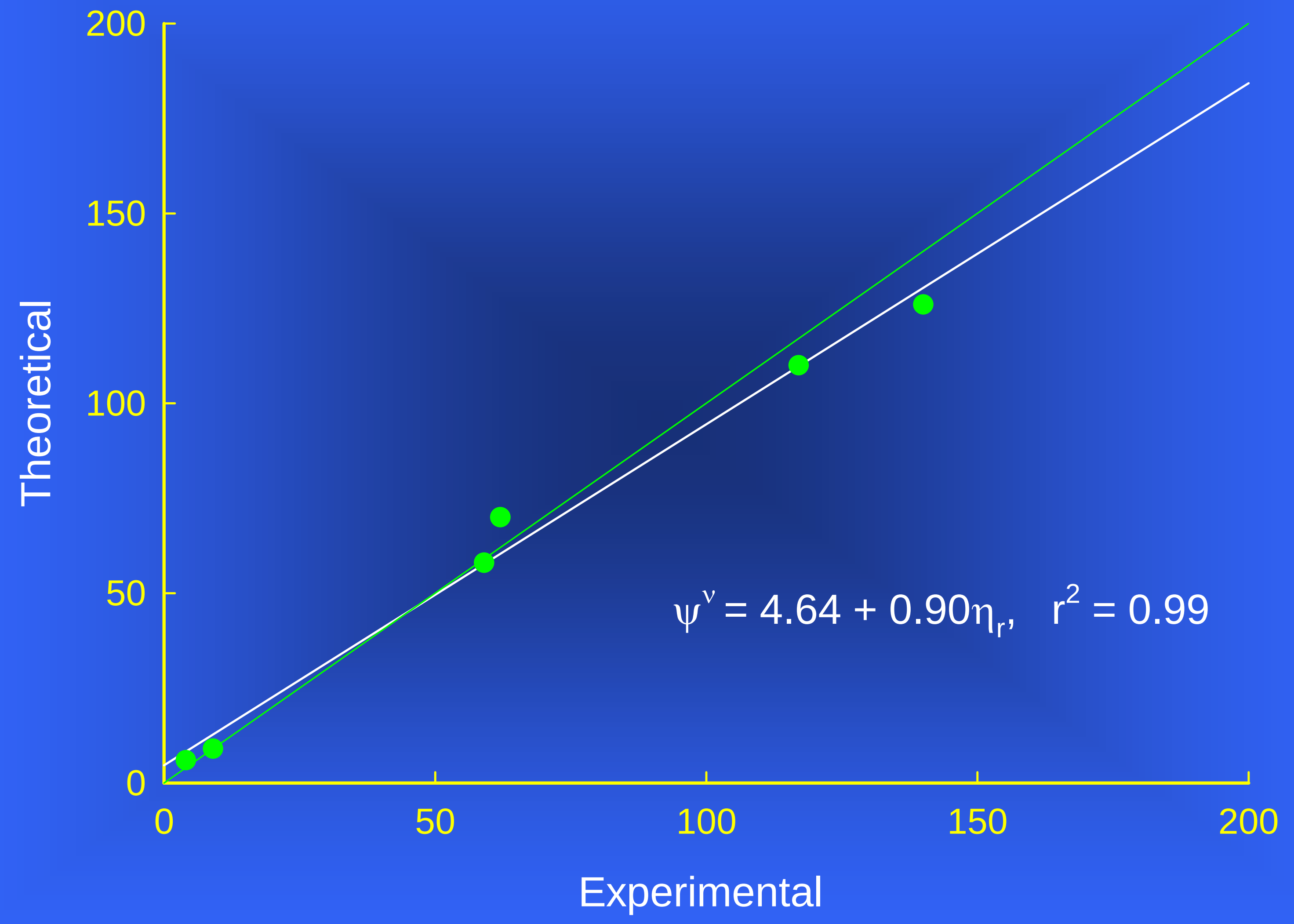
p_o^{rev} versus K_o
Theoretical
Experimental
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.4
0.6
0.8
1.0
1.2
1.4
1.6



P^{rev} versus K
Theoretical
Experimental
0
1
2
3
4
5
6
7



η_{rel} versus ψ^{ν}
Theoretical
Experimental
0
50
100
150
200
0
50
100
150
200



Theoretical
Experimental
0
50
100
150
200
0
50
100
150
200
$\psi^{\nu} = 4.64 + 0.90\eta_r, \quad r^2 = 0.99$

Towards a Unified Physico-Chemical Model of Asphalt Binder

Asphalt Microstructure Model

- Introduction to micro-Emulsion Colloid Mechanics
- The Onion Model and Colligative Properties
- Equilibrium Thermodynamics in micro-Emulsion Colloid Mechanics
- Kinetics in micro-Emulsion Colloid Mechanics

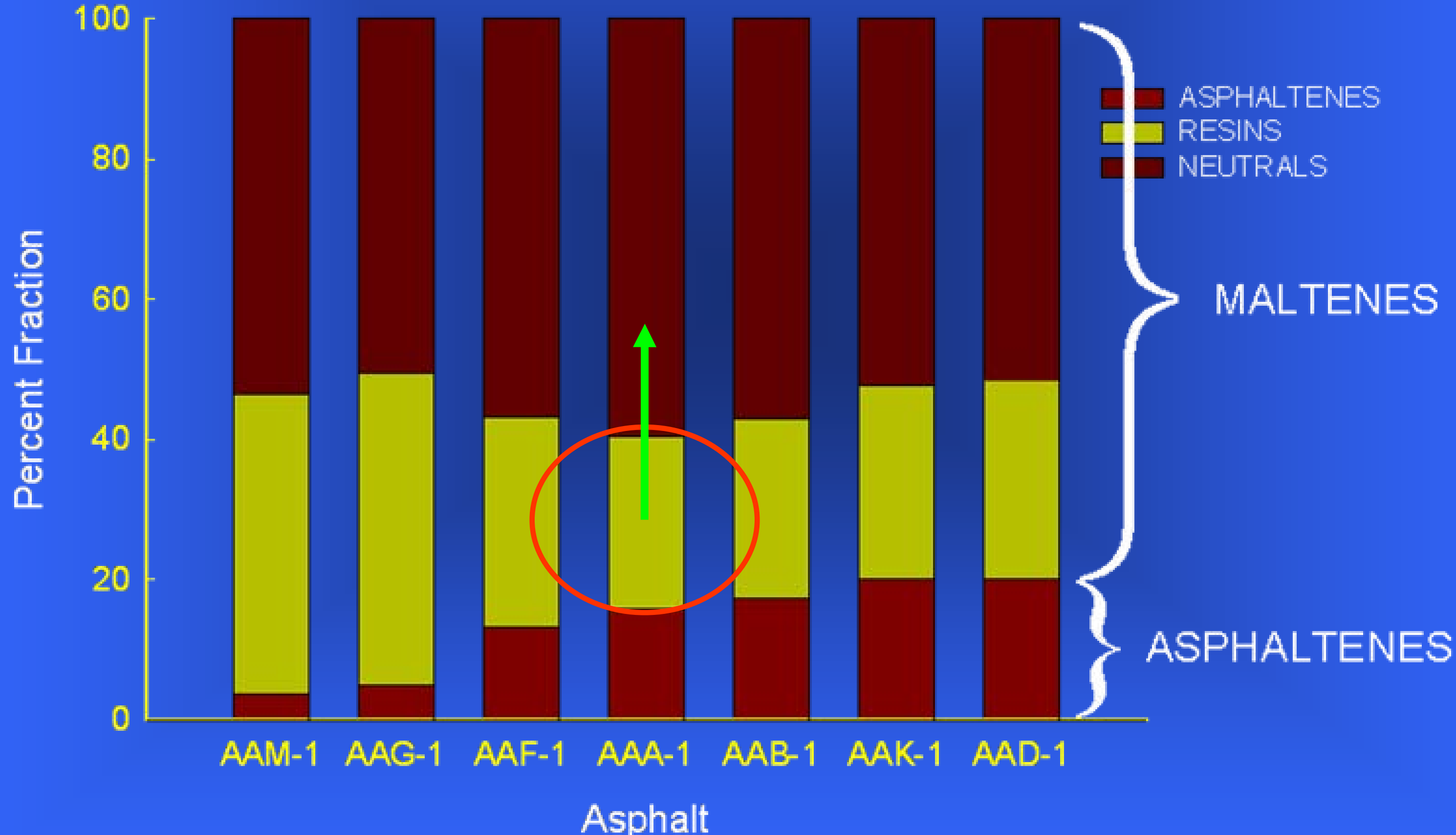
Asphalt Solidification Model

- Equilibrium Thermodynamics of Surfaces and Interfaces
- Phase Transformations and Colligative Properties
- non-Equilibrium Thermodynamics of Surface micro-Structuring
- Dissipative Structure Theory
- Application to Fracture Mechanics

Further Thoughts on Fatigue and Moisture Damage, Rutting, and Thermal Cracking

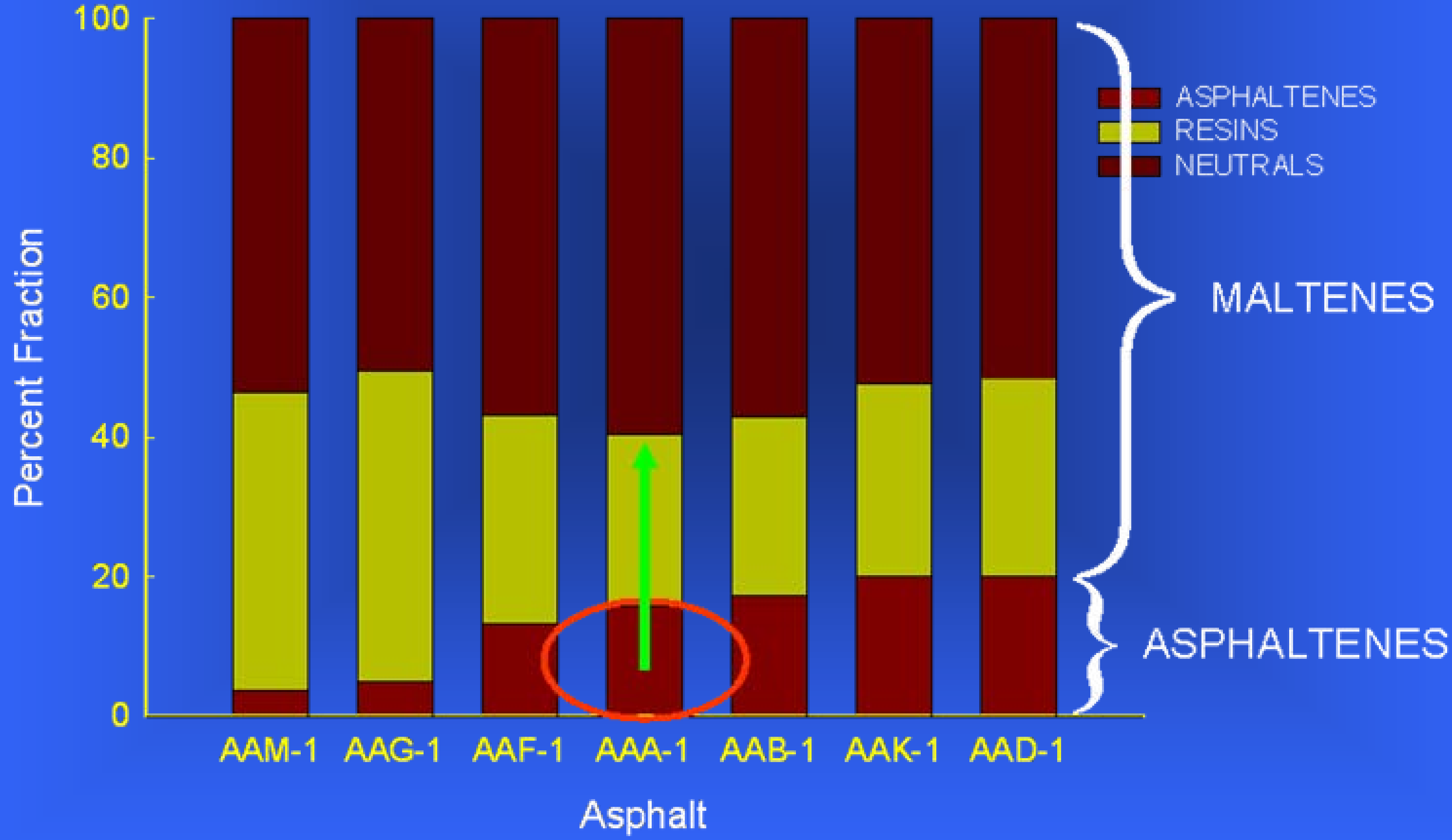
Effect of adding resins to neutrals

$$\Delta T = \frac{x_r R T^{*2}}{\Delta H_f}$$



Effect of adding asphaltenes to maltenes

$$\Delta T = \frac{x_a R T^{*2}}{\Delta H_f}$$



$$\eta = \eta_0 (\phi_{FS})^{-\nu}$$

Pal-Rhodes Model as defined by the volume fraction of free solvent, ϕ_{FS}

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$$\eta = Ae^{E_a / RT}$$

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When Combined with Eyring's Definition of Viscosity

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$$\ln(\eta) - \ln(\eta_0) = \nu \ln\left(\frac{1}{\phi_{FS}}\right)$$

Which may be expressed as

$$\frac{E_a}{RT} - \frac{E_a{}^0}{RT} = \nu \ln\left(\frac{1}{\phi_{FS}}\right) + \ln(A_0) - \ln(A)$$

$$\Delta U_{vap} = nE_a$$

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$$\Delta H_{dis} - T\left[n\,\nu R\, ln\left(\frac{1}{\phi_{FS}}\right) + nR\, ln(A_0) - nR\, ln(A) + R\right] = 0$$

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But this is simply the “free energy of dispersion” expressed as

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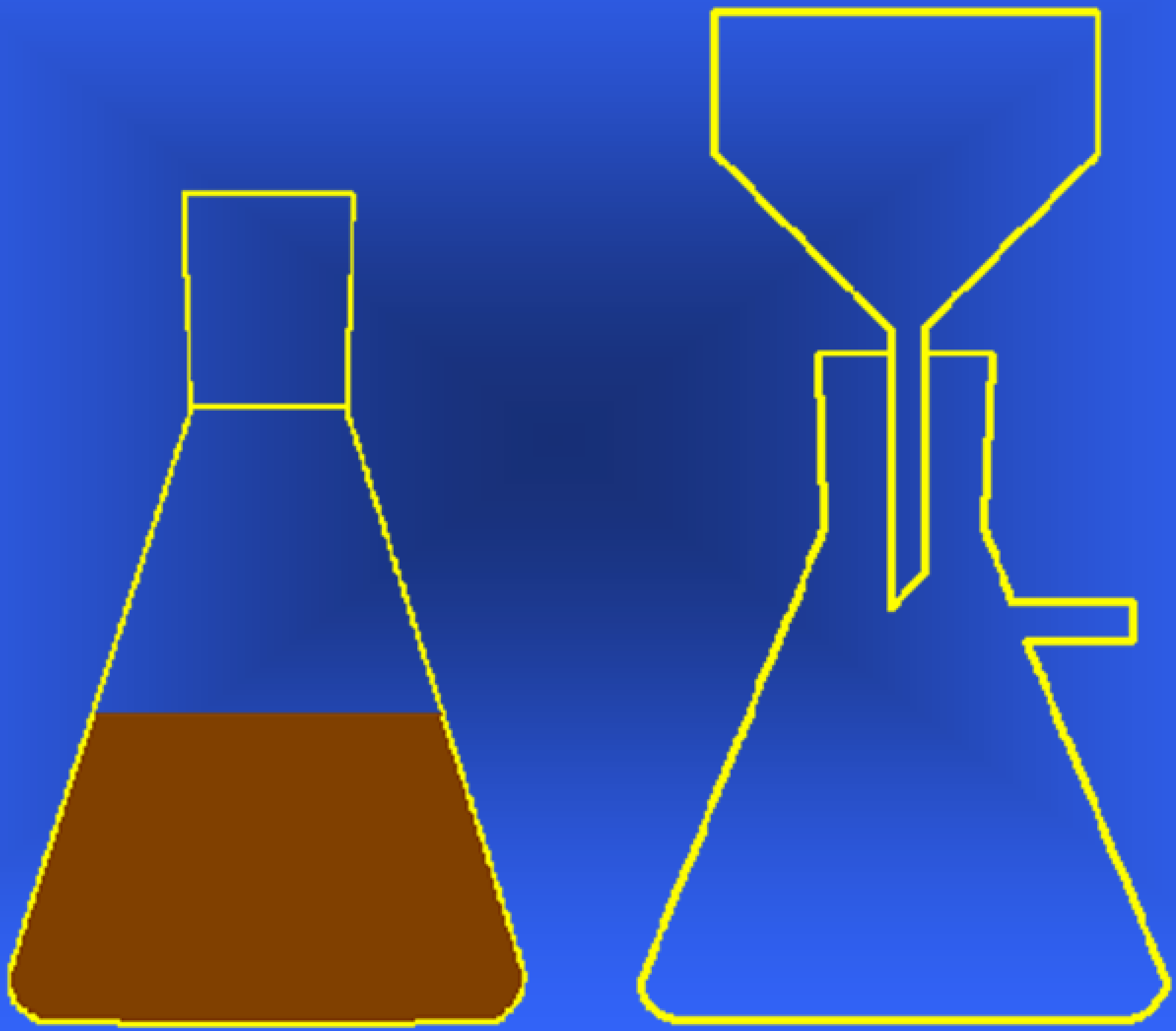
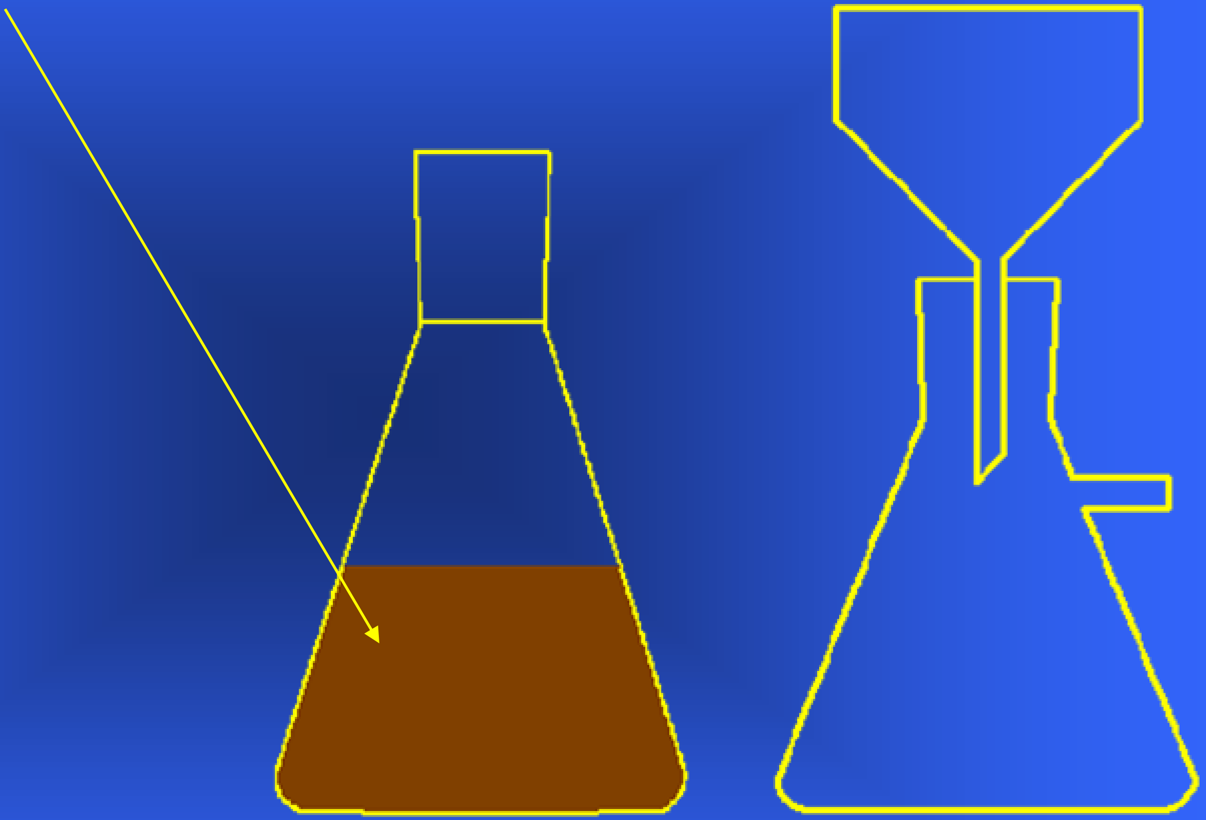
So that the "entropy of dispersion" is finally expressed as

$$\Delta S_{dis} \equiv R\left[\left(n\,\nu\, ln\left(\frac{1}{\phi_{FS}}\right) + n\, ln(A_0)\right) - n\, ln(A) + 1\right]$$

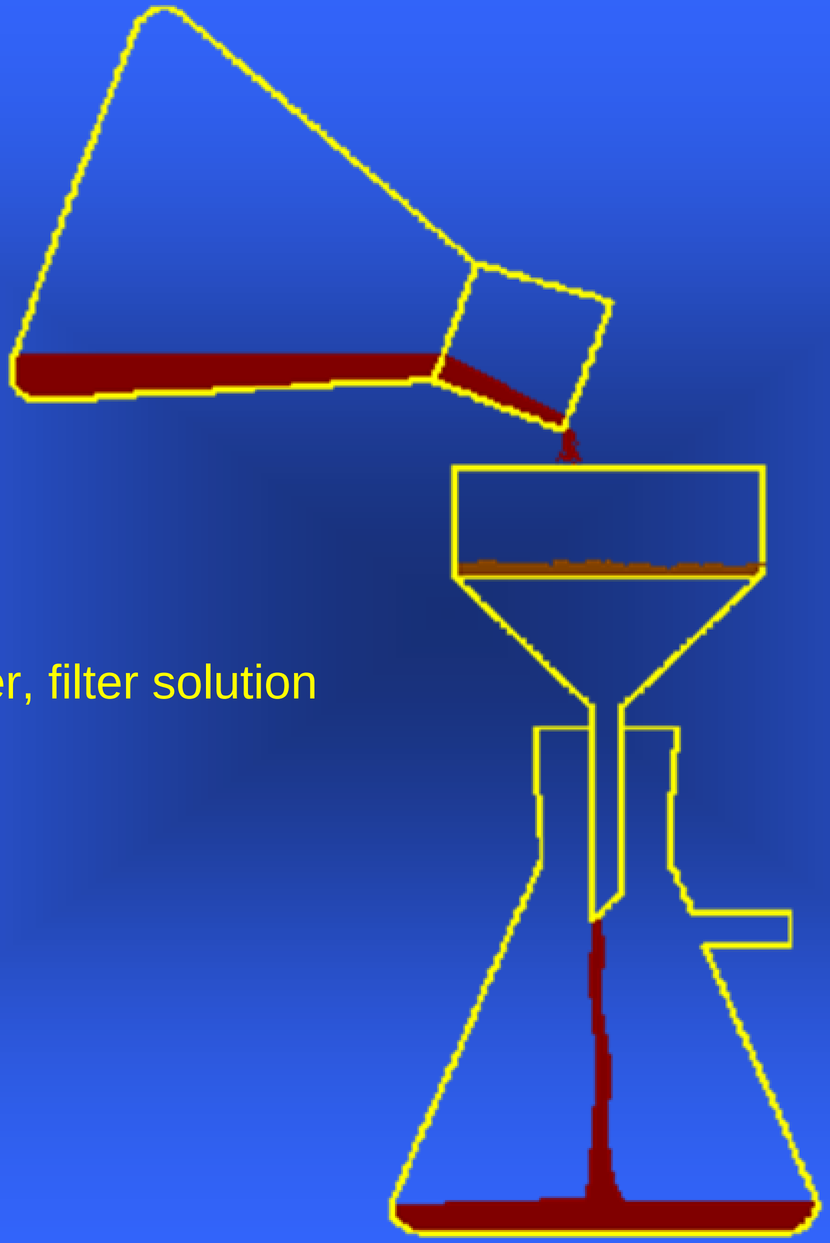
Common procedure for preparing asphaltenes

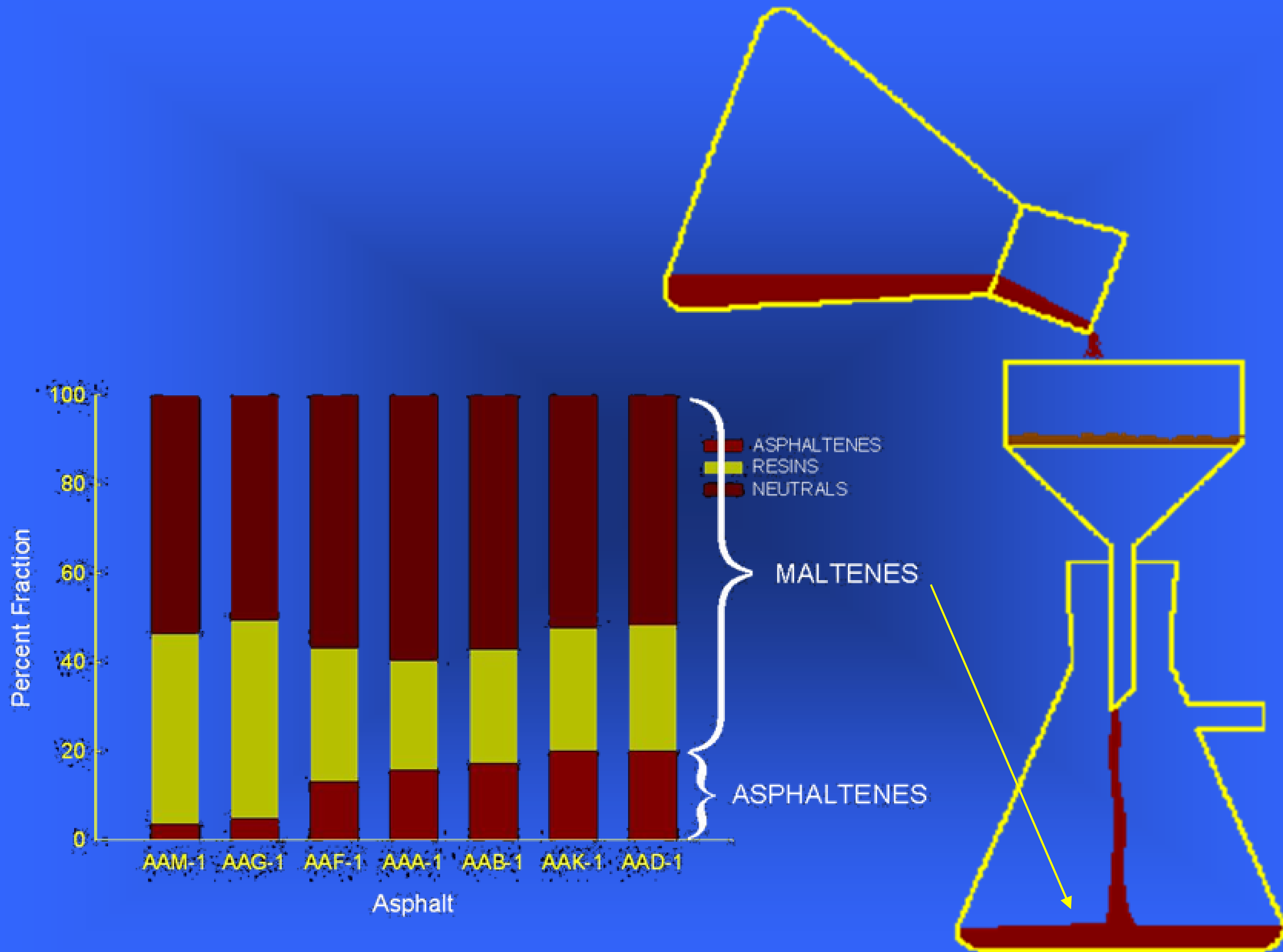


Asphalt dissolved in n-heptane in a 1:40 dilution ratio
(i.e., 1.0g of asphalt per 40.0 mL of “non-solvent”)

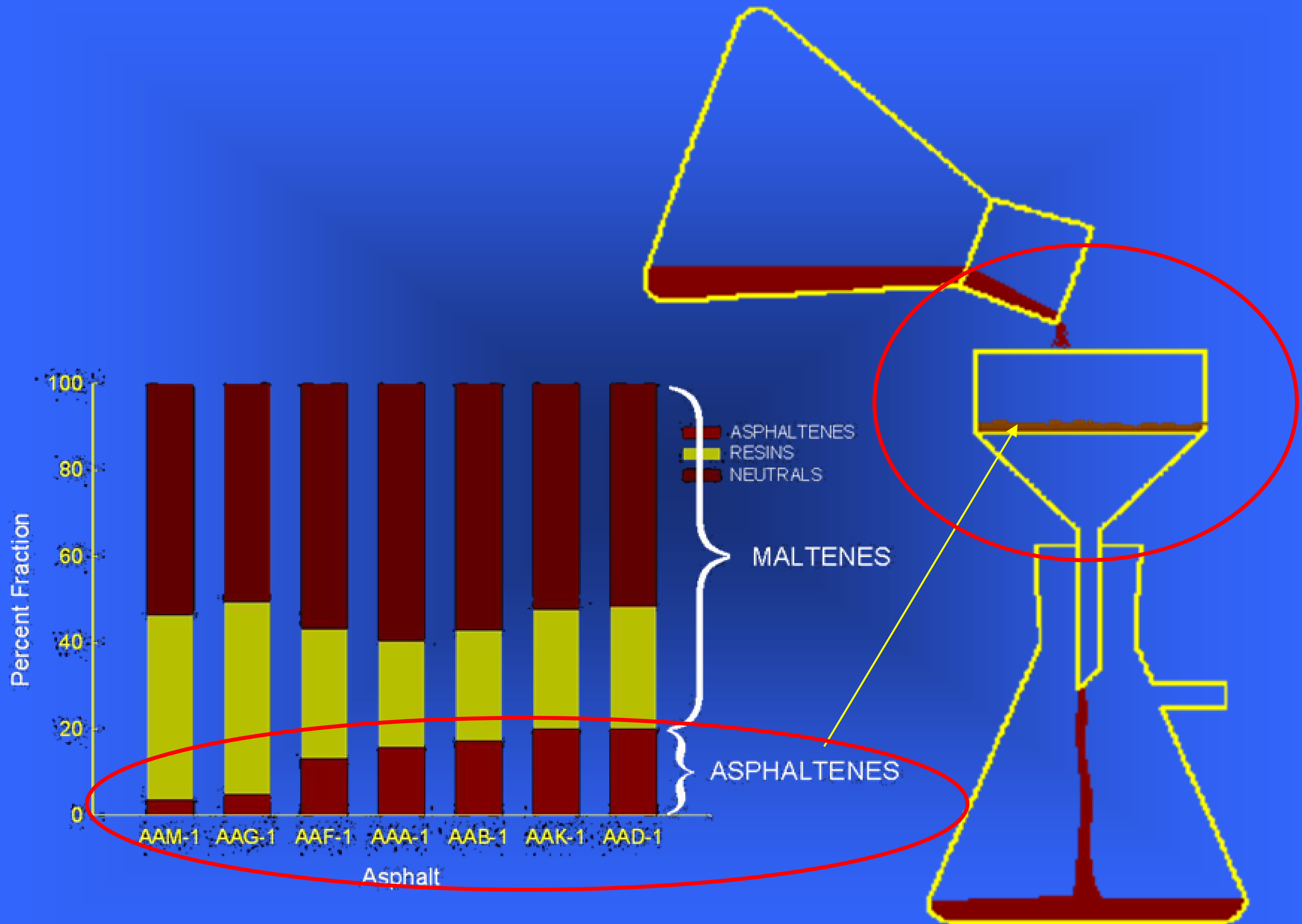


24 hours later, filter solution





Percent Fraction
100
80
60
40
20
0
AAM-1
AAG-1
AAF-1
AAA-1
AAB-1
AAK-1
AAD-1
Asphalt
ASPHALTENES
RESINS
NEUTRALS
MALTENES
ASPHALTENES


100
80
60
40
20
0
Percent Fraction
AAM-1
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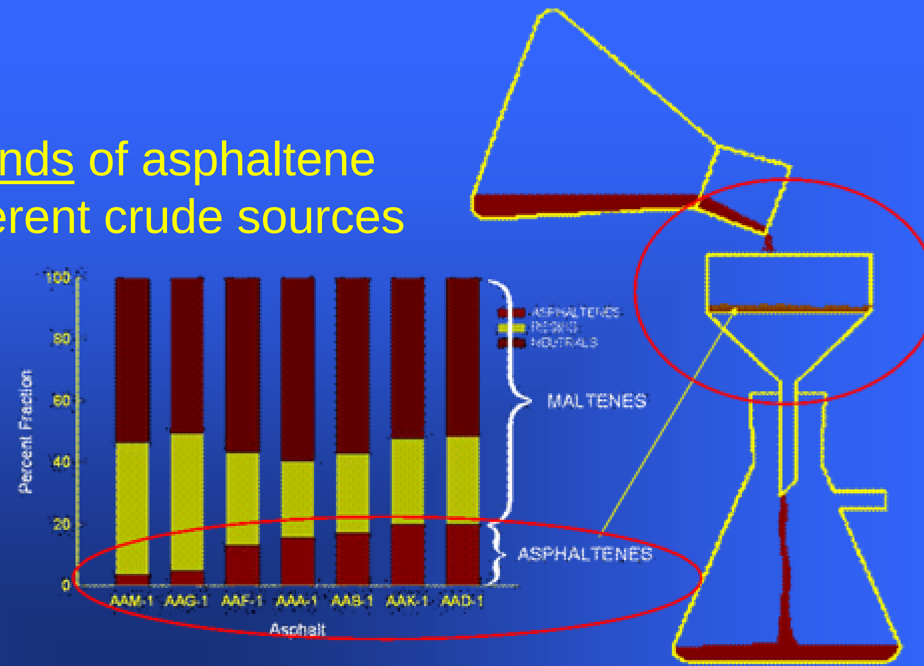
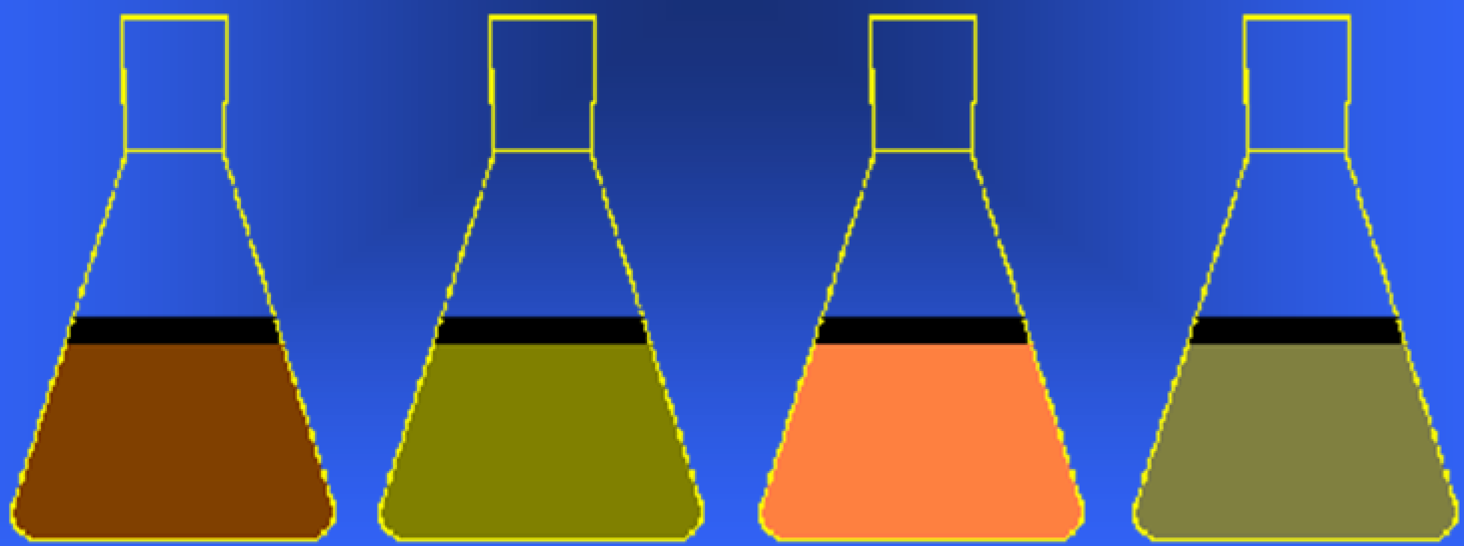
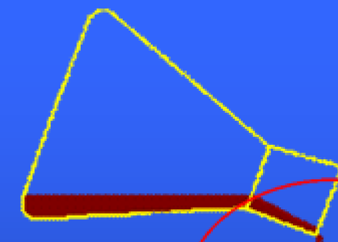
AAF-1
AAA-1
AAB-1
AAK-1
AAD-1
Asphalt
ASPHALTENES
RESINS
NEUTRALS
MALTENES
ASPHALTENES

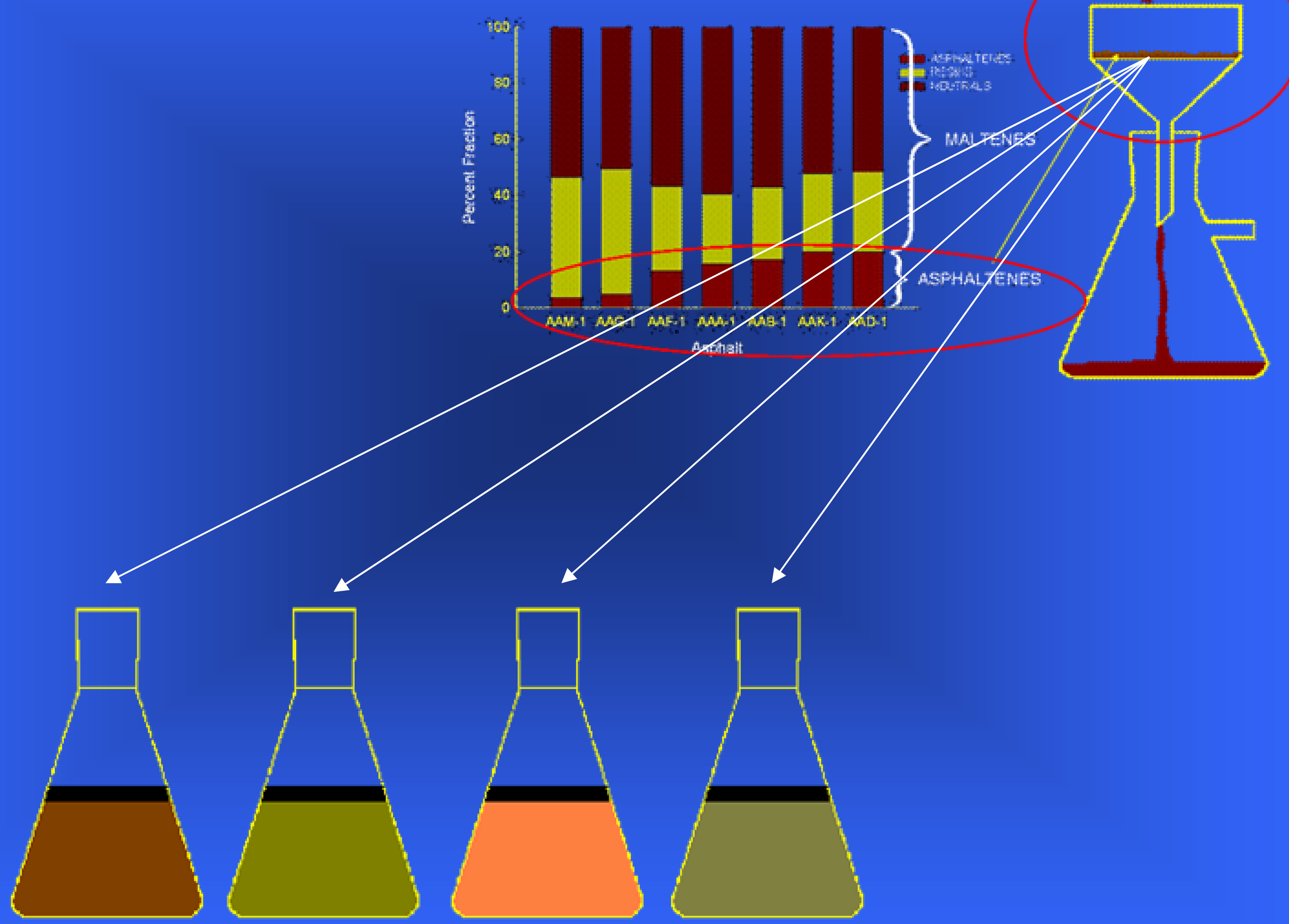
Prepare synthetic asphalt blends of asphaltene in maltenes derived from different crude sources





20% asphaltene in four “types” of maltenes derived from AAA-1, AAB-1, AAC-1, and AAD-1

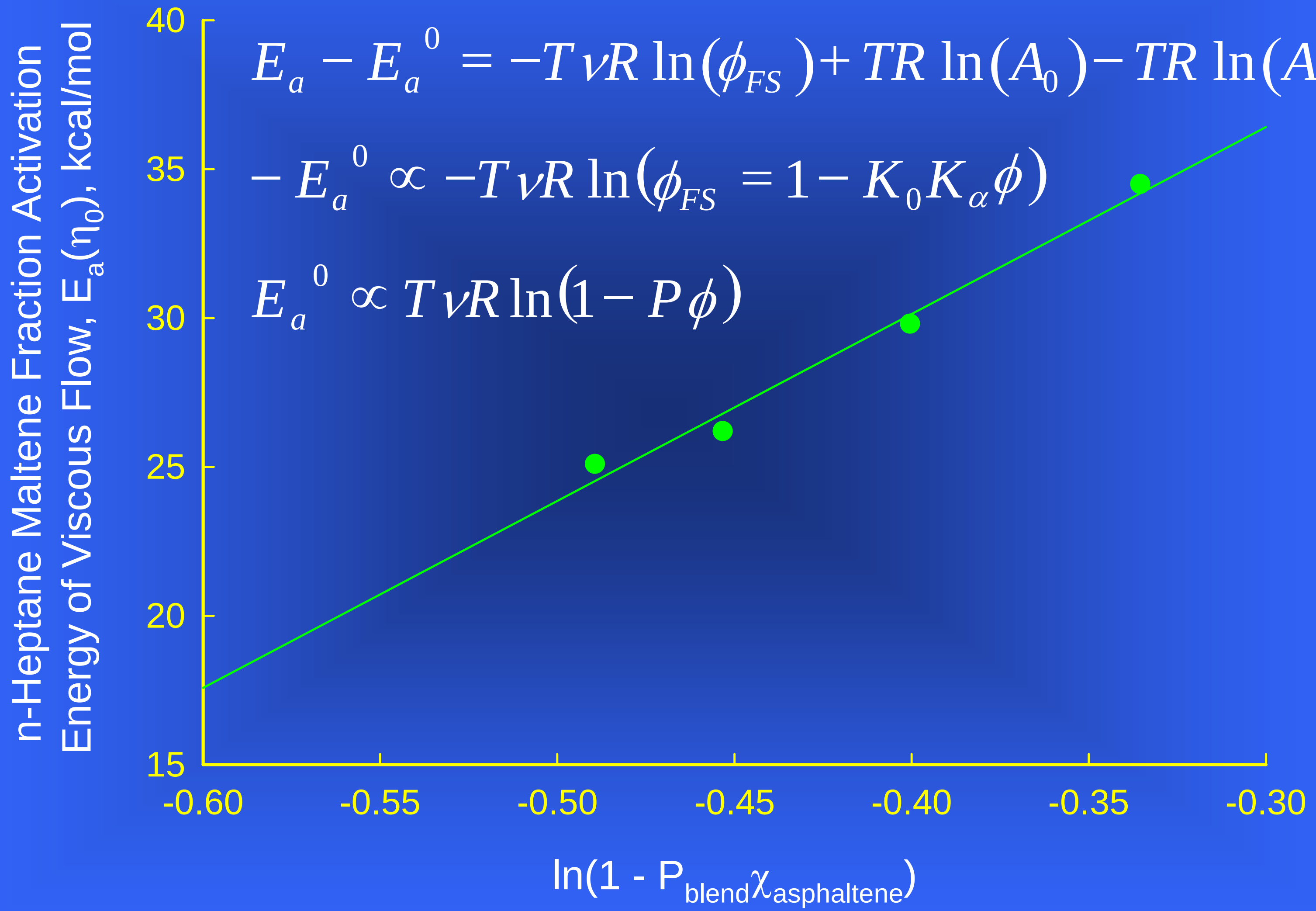




$$E_a - E_a^{\,0} = -T\nu R\ln(\phi_{FS}) + TR\ln(A_0) - TR\ln(A)$$

$$-E_a^{\,0} \propto -T\nu R\ln(\phi_{FS} = 1 - K_0 K_\alpha \phi)$$

$$E_a^{\,0} \propto T\nu R\ln(1 - P\phi)$$



Towards a Unified Physico-Chemical Model of Asphalt Binder

Asphalt Microstructure Model

- Introduction to micro-Emulsion Colloid Mechanics
- The Onion Model and Colligative Properties
- Equilibrium Thermodynamics in micro-Emulsion Colloid Mechanics
- Kinetics in micro-Emulsion Colloid Mechanics

Asphalt Solidification Model

- Equilibrium Thermodynamics of Surfaces and Interfaces
- Phase Transformations and Colligative Properties
- non-Equilibrium Thermodynamics of Surface micro-Structuring
- Dissipative Structure Theory
- Application to Fracture Mechanics

Further Thoughts on Fatigue and Moisture Damage, Rutting, and Thermal Cracking

Asphaltene Flocculation Kinetics

By Automated Flocculation Titrimetry

Methodology:

Titration of toluene-sample solution with iso-octane to flocculation onset,

Followed by stopping of titrant flow
and continued monitoring of flocculation kinetics process

Flocculation Kinetics Model of the Formation Process: n_j-Asphaltene Clusters, $\sum n_1 n_j$ interacting with n_1-Monomer Particles

Smoluchowski Equation

Mass Flux

$$j_n = \frac{dn}{dt}$$

Non-Reversible Rate Equation:

$$\frac{dn_i}{dt} = -k_i \sum_{i=1}^{\infty} n_i n_j$$

Reversible Rate Equation:

$$\frac{dn_k}{dt} = \sum_{i+j=k} K_{i+j} n_i n_j - n_k \sum_{i}^{\infty} K_{k-i} n_i$$

Relationship Between Solution Viscosity and the Rate Constant for a Diffusion-Limited Reaction

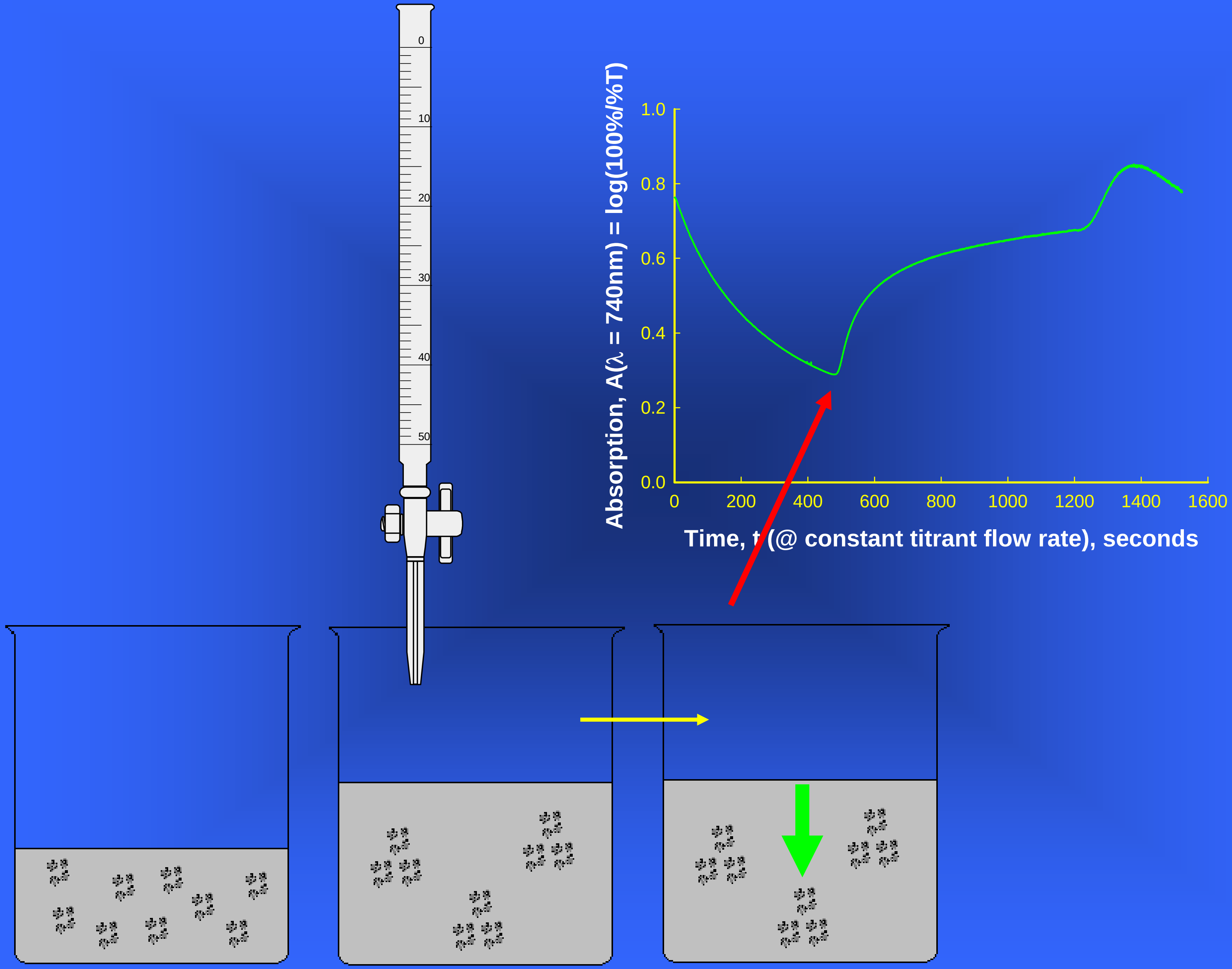
Stoke-Einstein Diffusion Equation:

$$D_{si}^{\infty} = \frac{k_b T}{6\pi \eta_s r_j}$$

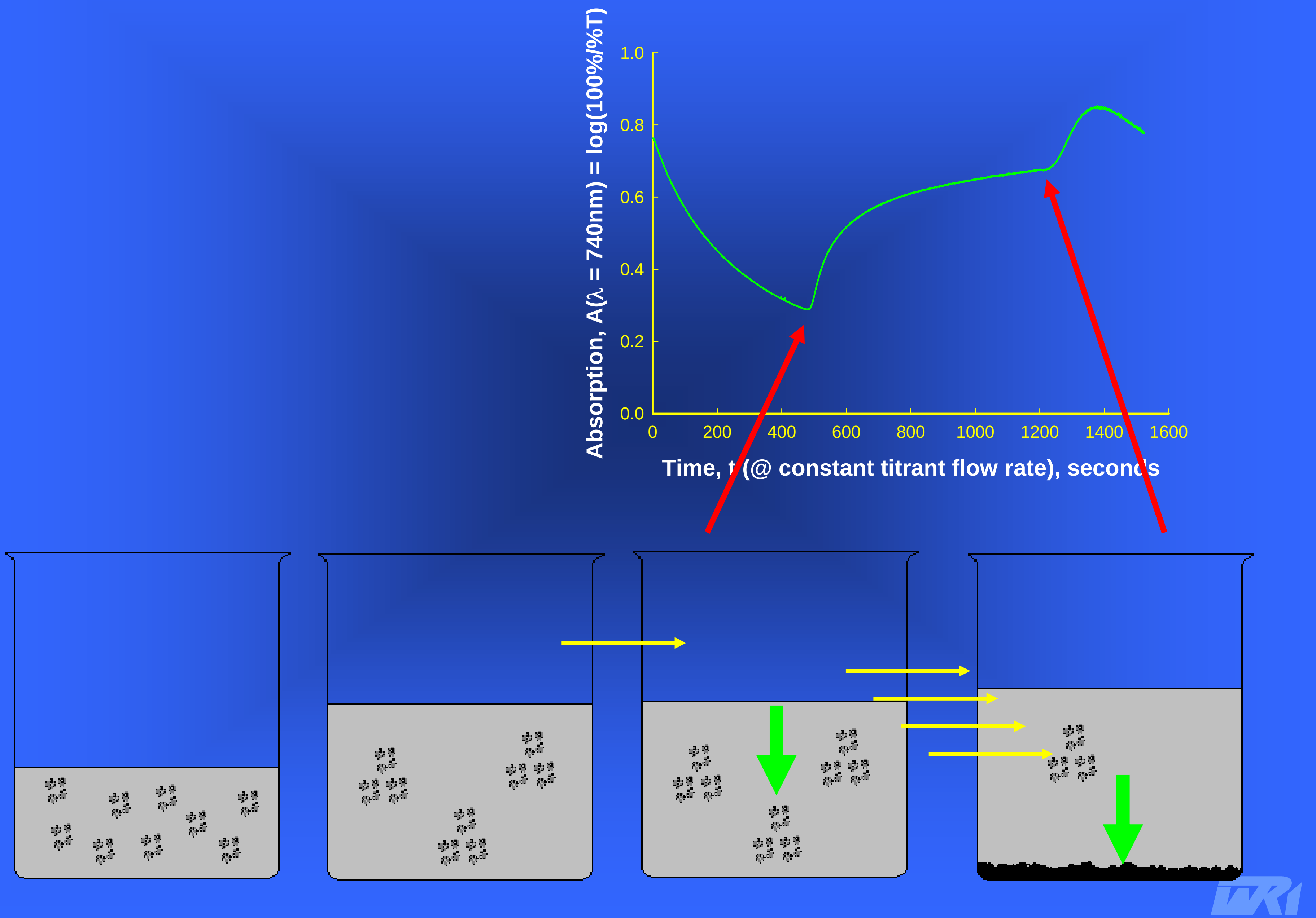
Inverse Proportionality of η to k:

$$4\pi N_A R_{ji}\left(\frac{k_b T}{3\pi\eta_s R_{ji}} + \frac{k_b T}{3\pi\eta_s R_{ji}}\right) = \boxed{\frac{8RT}{3\eta_s} = k_{diff} \quad !}$$

$$N_A k_b = R$$



0
10
20
30
40
50
Absorption, A(λ = 740nm) = log(100%/%T)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
Time, t (@ constant titrant flow rate), seconds



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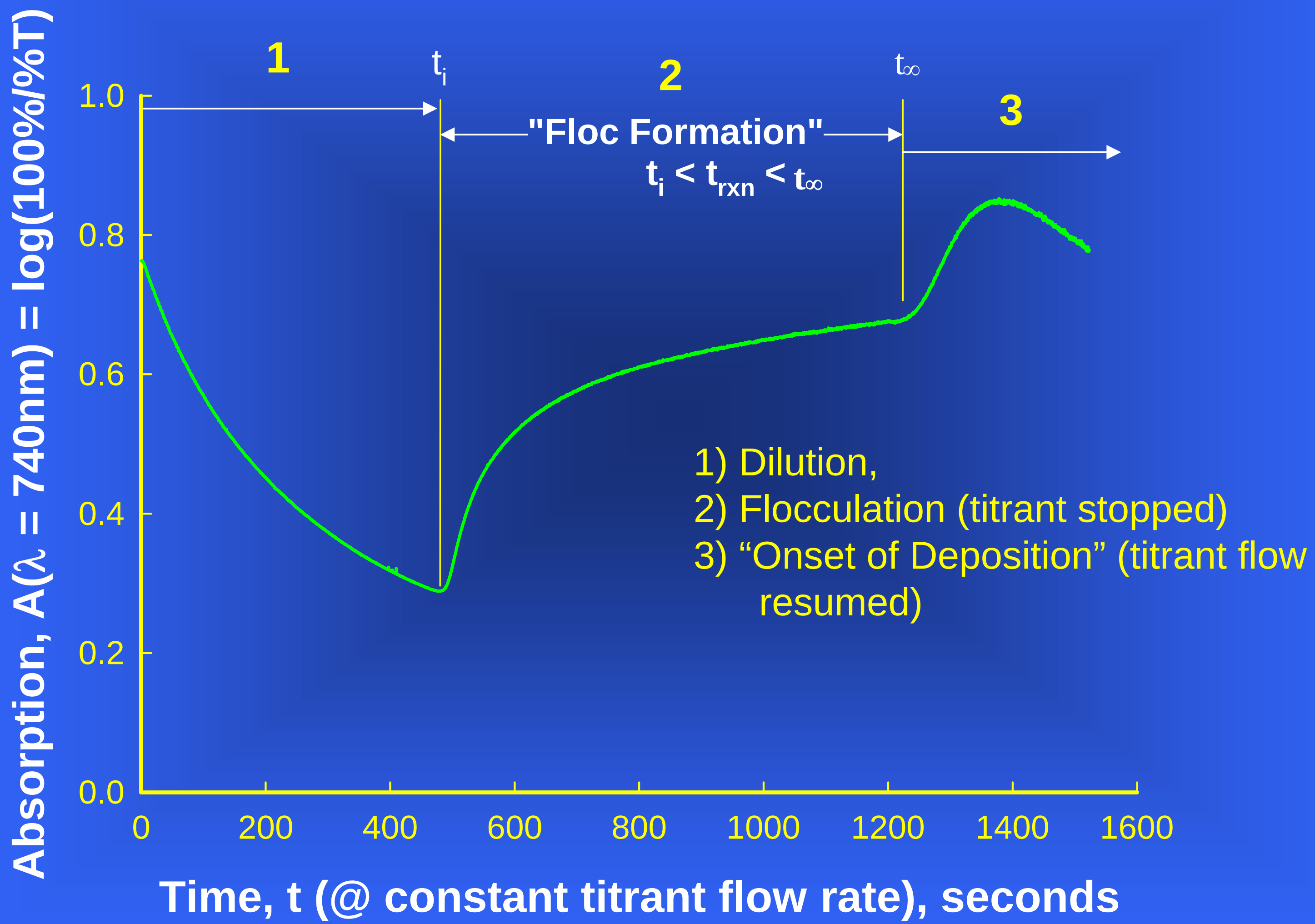
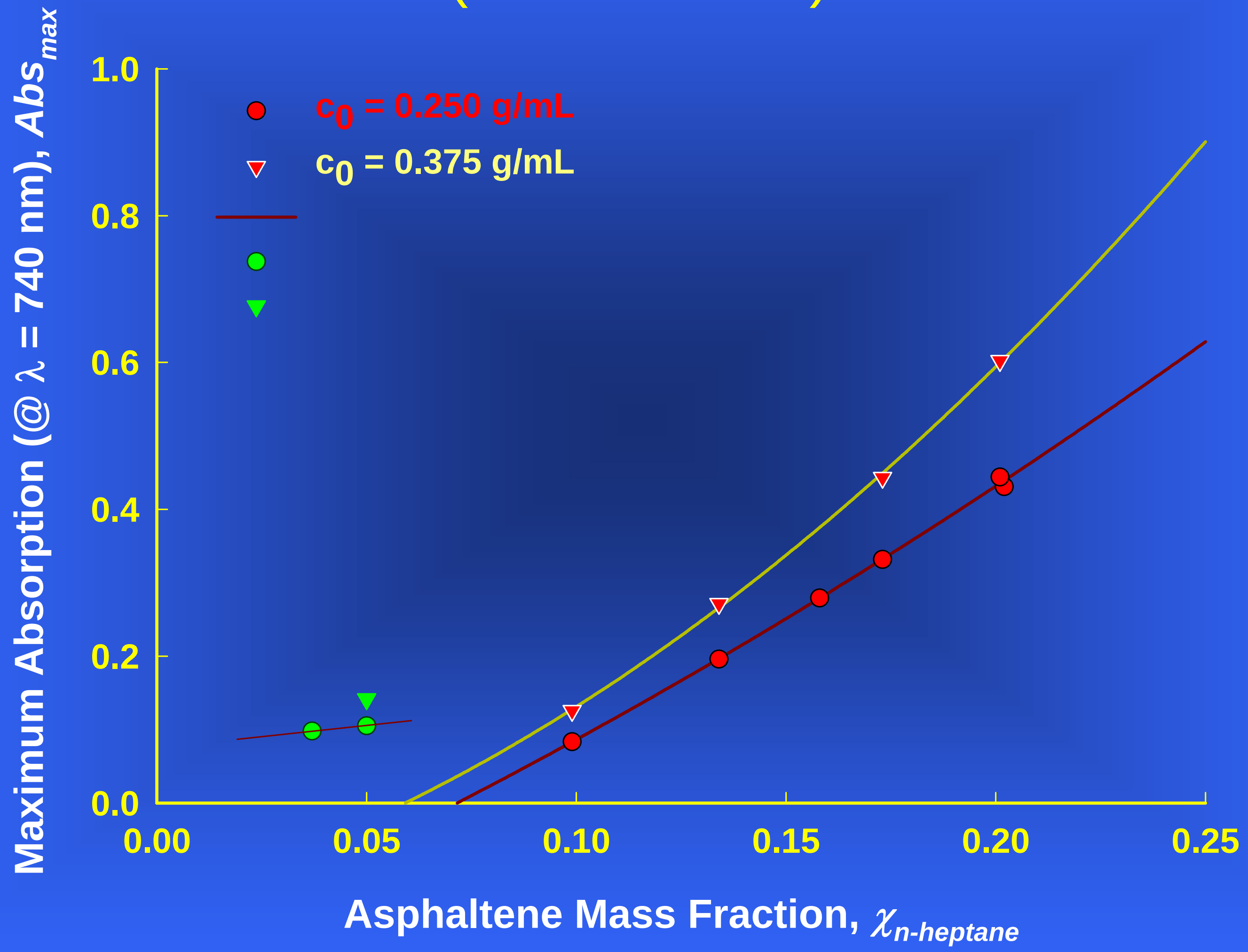
0
200
400
600
800
1000
1200
1400
1600
Time, t (@ constant titrant flow rate), seconds

Absorption-versus-Time (sec)

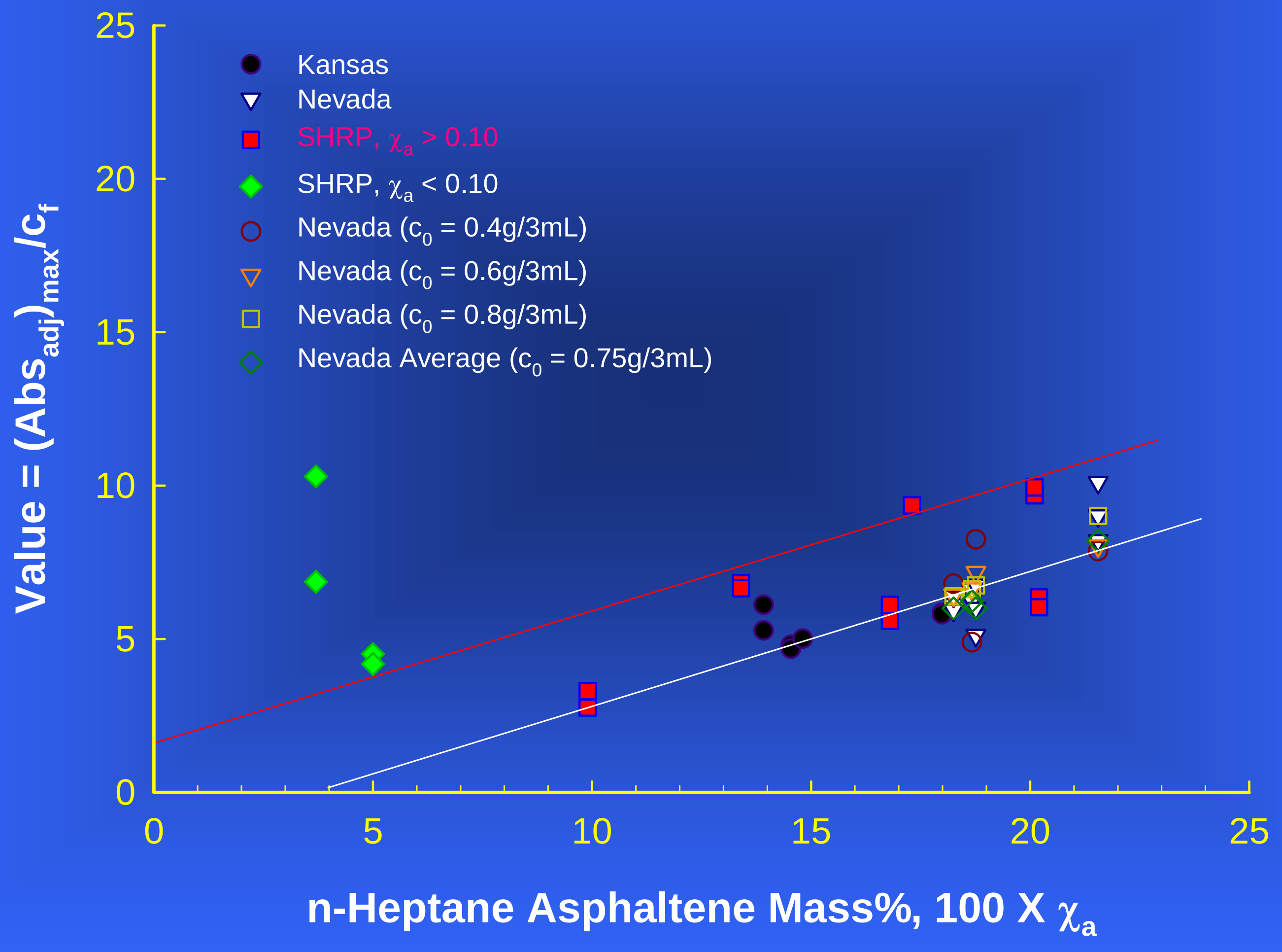
Flocculation Process Plot Measured for SHRP Asphalt AAD-1



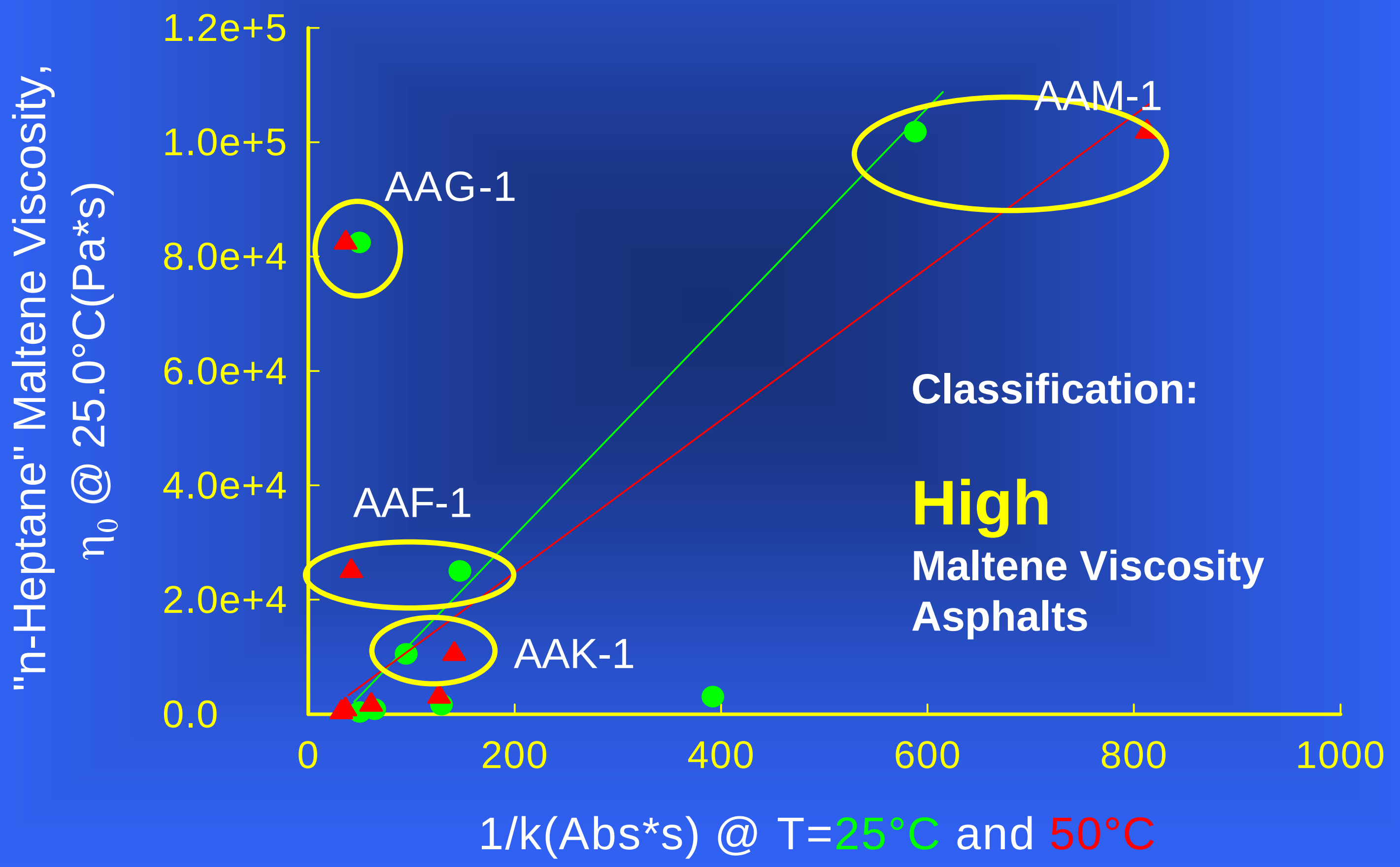
Determination of Asphaltene Content from "Set-One" Kinetic Titration Data (0.02 mm cell)



Determination of Asphaltene Content from “Second-Set” of Kinetic Titration Data (0.1 mm cell)



SHRP Asphalt "n-Heptane Soluble" Maltene Viscosity, η_0 as a Function of 1/k



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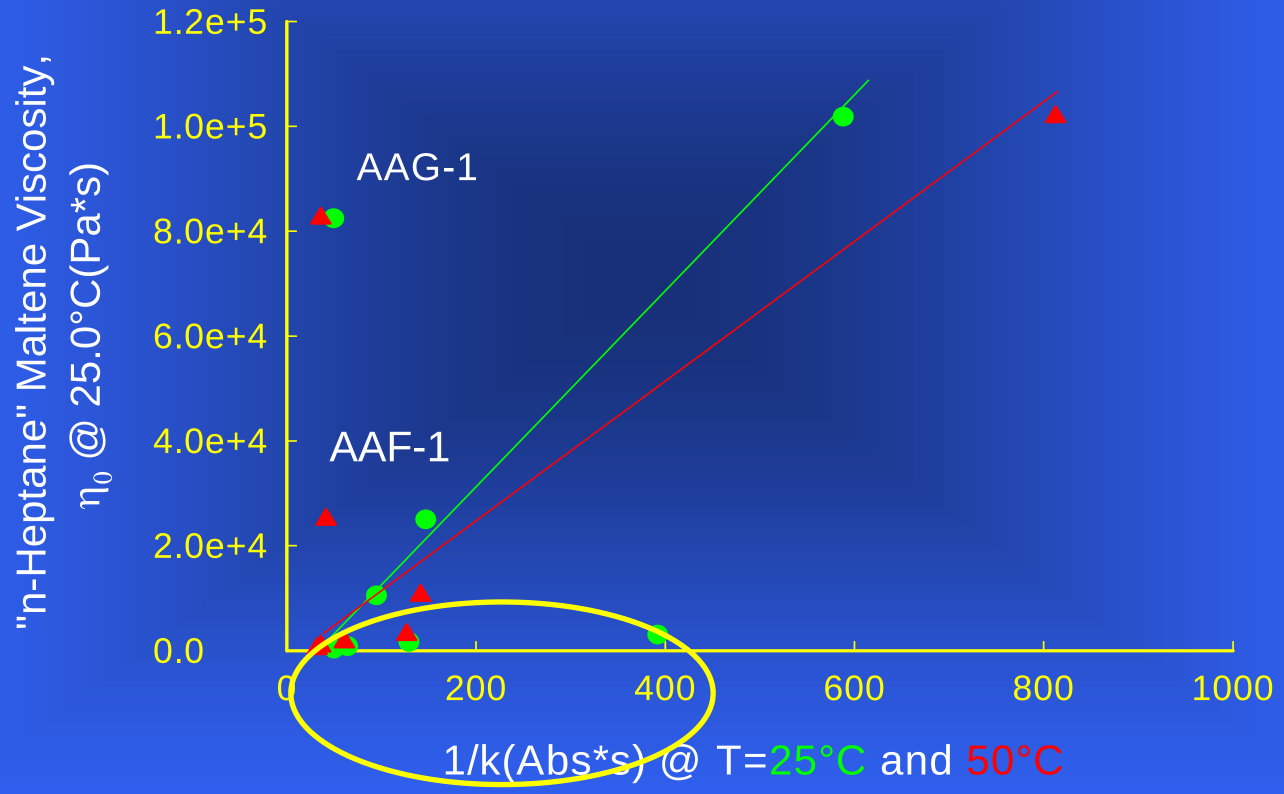
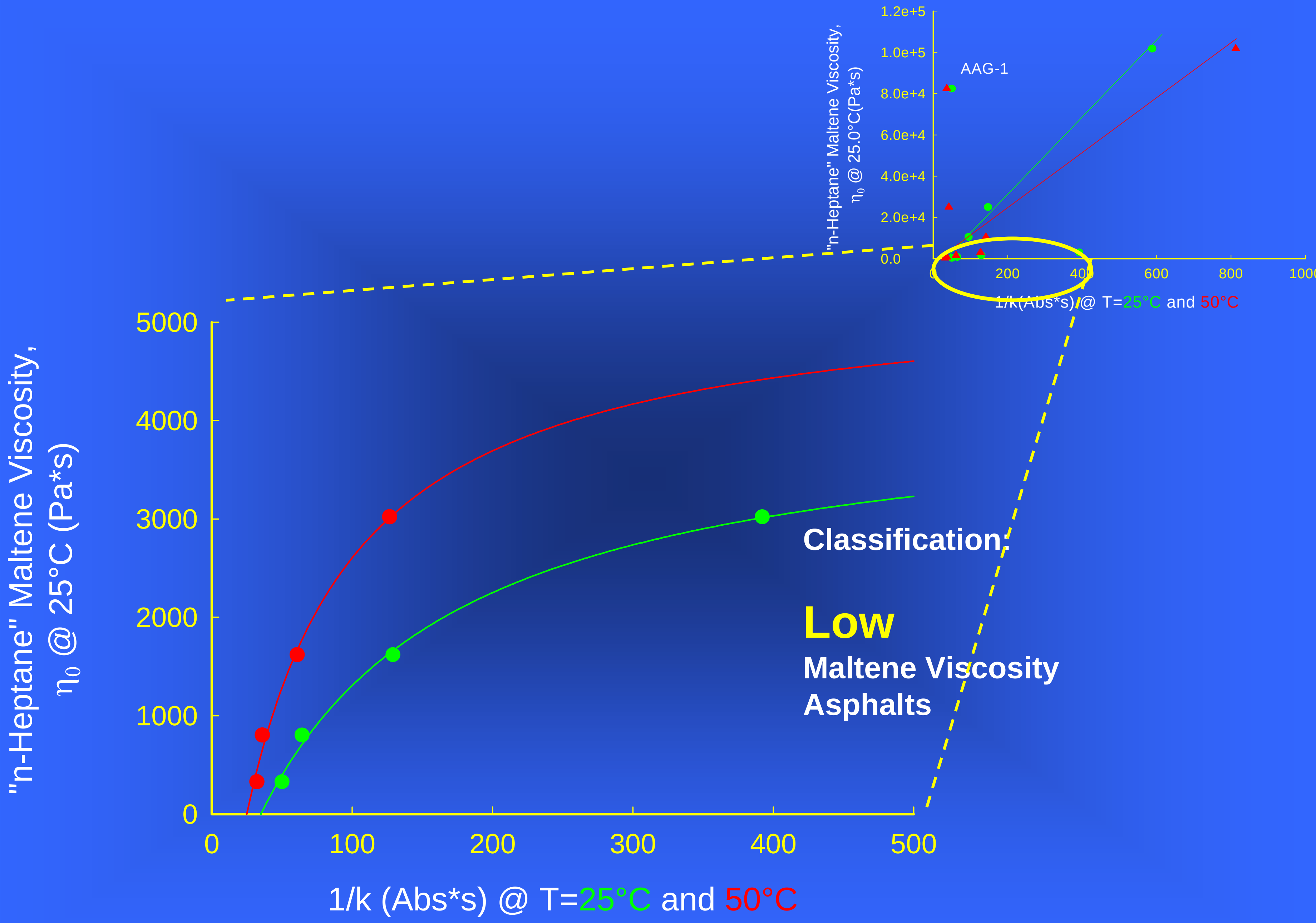
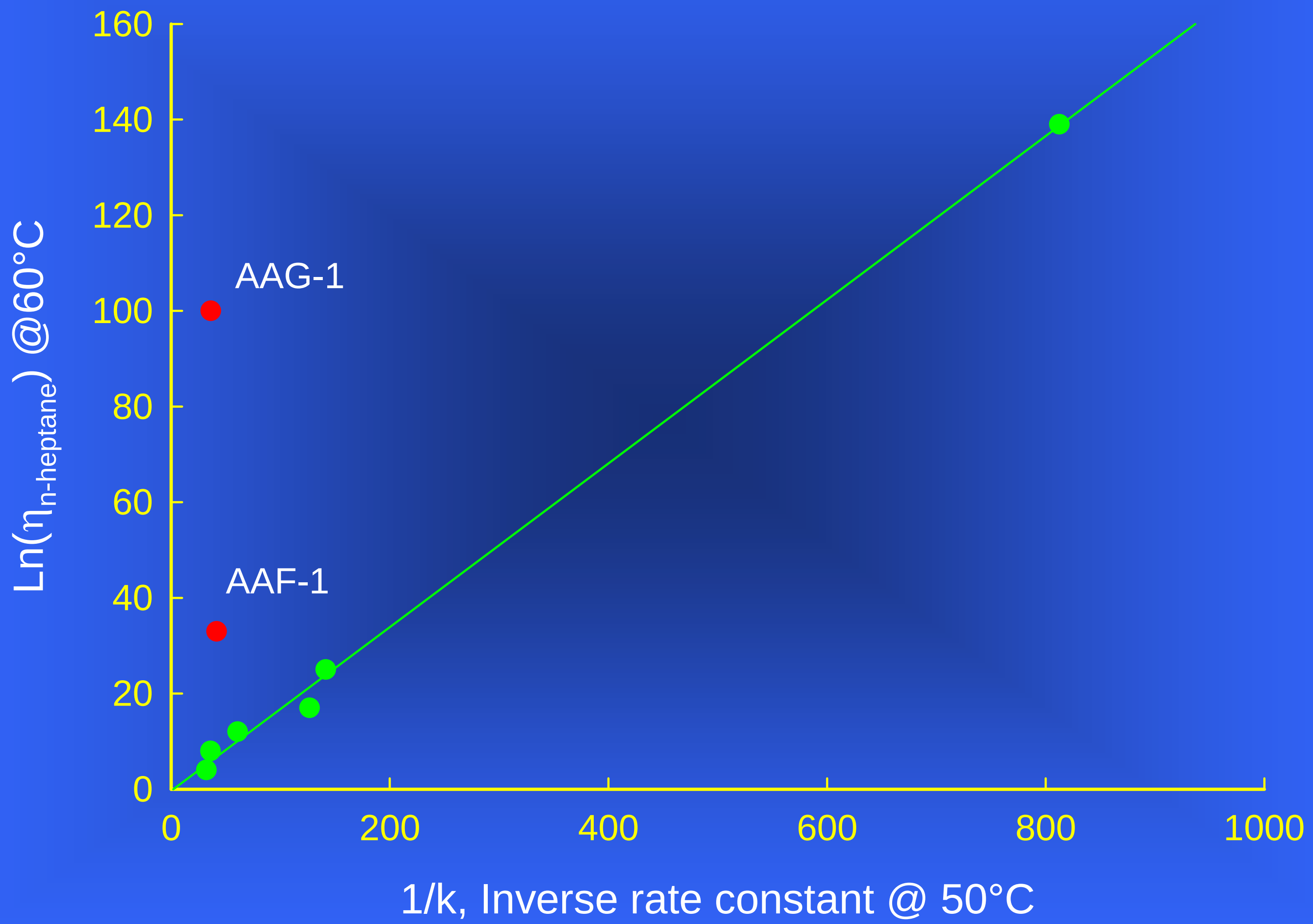




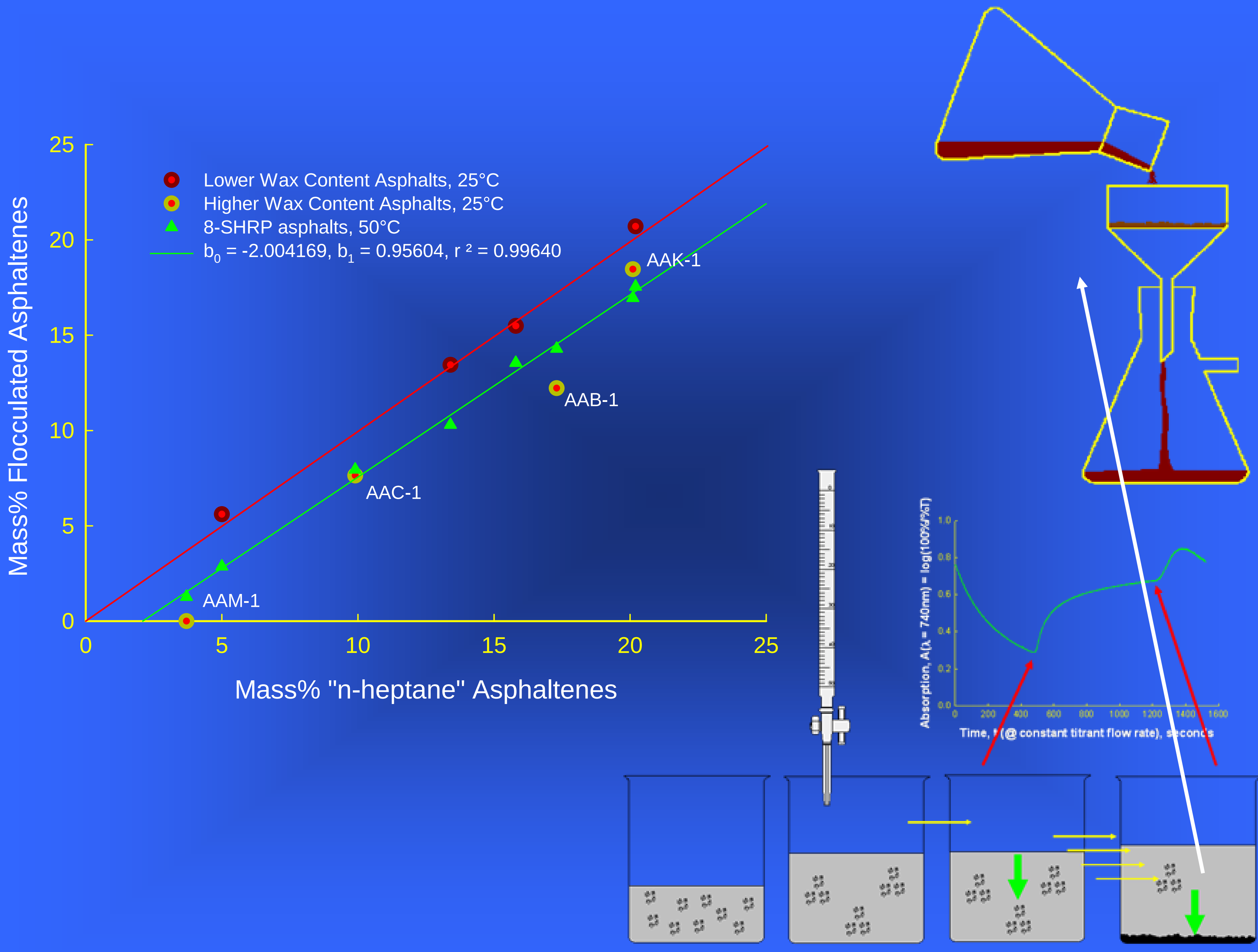
Classification:

Low

Maltene Viscosity Asphalts



160
140
120
100
80
60
40
20
0
0
200
400
600
800
1000
AAG-1
AAF-1
Ln(η n-heptane) @60°C
1/k, Inverse rate constant @ 50°C


Lower Wax Content Asphalts, 25°C
Higher Wax Content Asphalts, 25°C
8-SHRP asphalts, 50°C
b_0 = -2.004169, b_1 = 0.95604, r^2 = 0.99640
AAK-1
AAB-1
AAC-1
AAM-1
Mass% Flocculated Asphaltenes
Mass% "n-heptane" Asphaltenes
0
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Absorption, A(λ = 740nm) = log(100%/%T)
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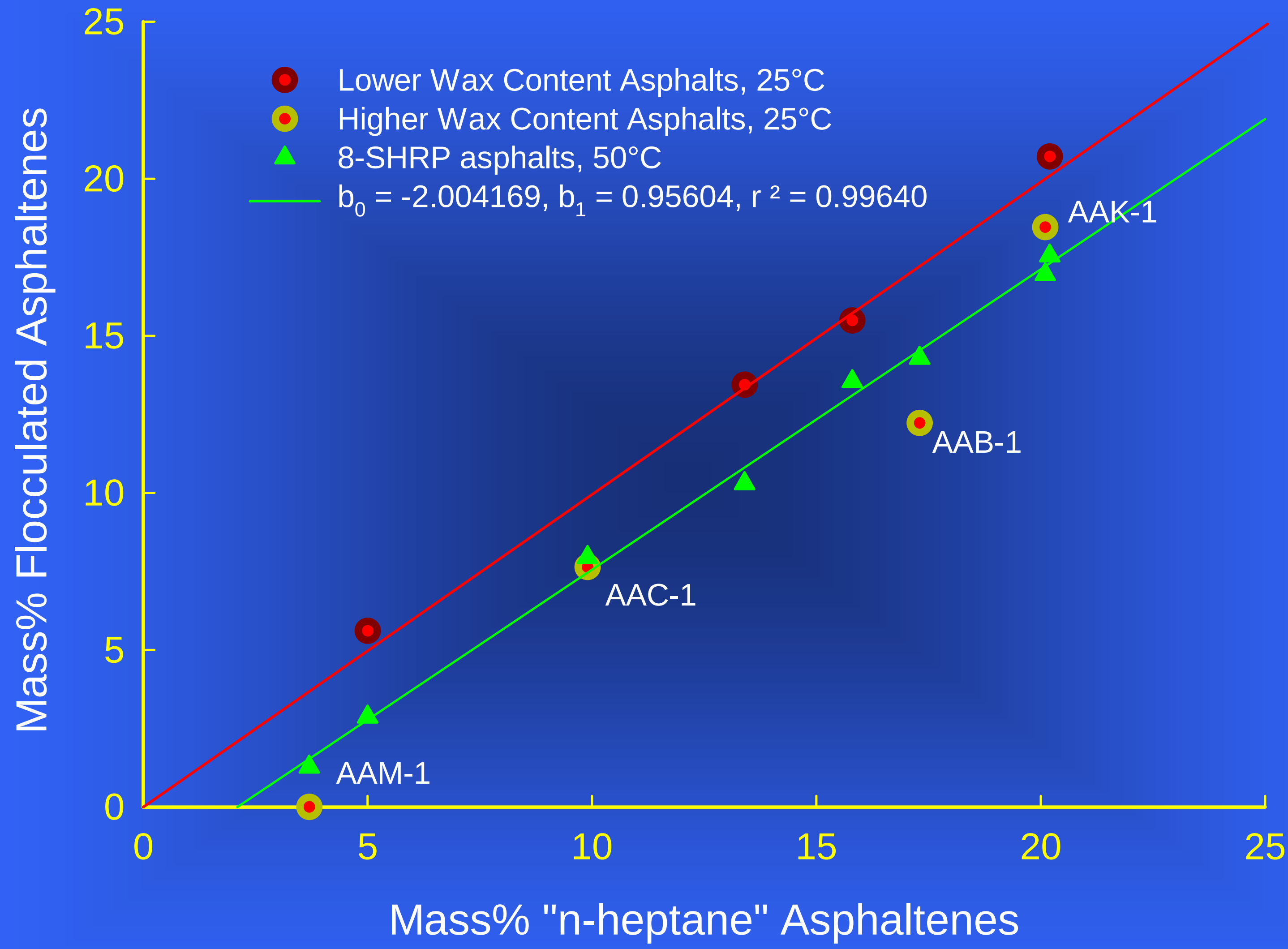
Time, t (@ constant titrant flow rate), seconds


Lower Wax Content Asphalts, 25°C
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AAK-1
AAB-1
AAC-1
AAM-1
0
5
10
15
20
25
Mass% Flocculated Asphaltenes
Mass% "n-heptane" Asphaltenes

$$K_0 = 1 - (\phi)_{max} - m = \alpha - m$$

$$= 1 - (\phi)_{max} + \frac{c_{min}}{(\phi)_{max}}$$

$$= \alpha + \frac{c_{min}}{1-\alpha}$$

$$= \alpha + c_{min} K_\alpha$$

$$K = K_0 K_\alpha$$

$$= \frac{K_0}{1-\alpha}$$

$$= \frac{\alpha}{1-\alpha} + \frac{c_{min} K_\alpha}{1-\alpha}$$

$$= \alpha K_\alpha + c_{min} K_\alpha{}^2$$

$$= K_\alpha (\alpha + c_{min} K_\alpha)$$

$$= K_\alpha K_0$$

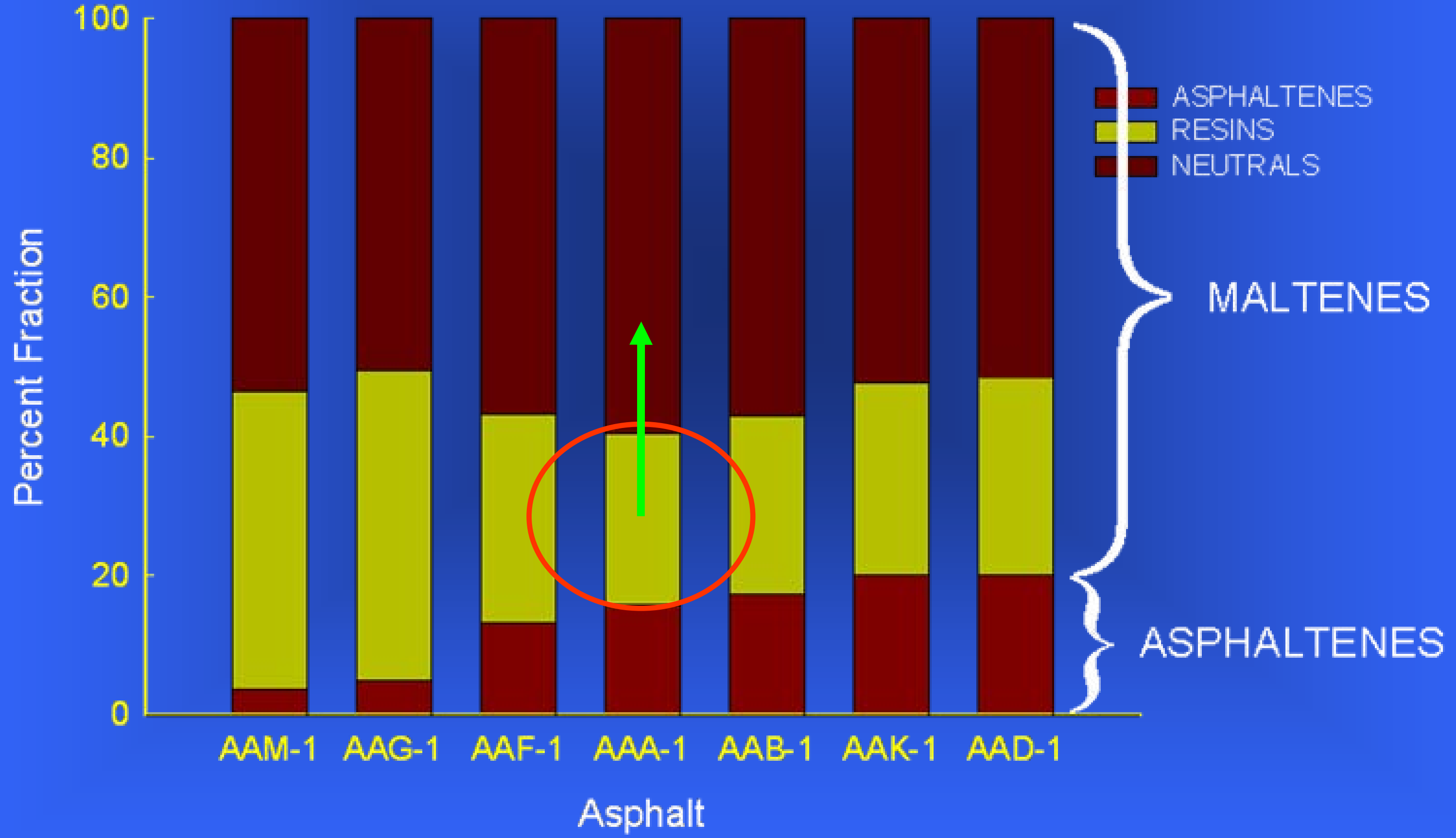
$$p_a{}^{rev} = 1 - (FR^{rev})_{max}$$

$$p_o{}^{rev} = (FR^{rev})_{\max} - m = (FR^{rev})_{\max} \left[\frac{1}{(C^{rev})_{\min}} + 1 \right]$$

$$P_{rev} = \frac{p_o{}^{rev}}{1 - p_a{}^{rev}}$$

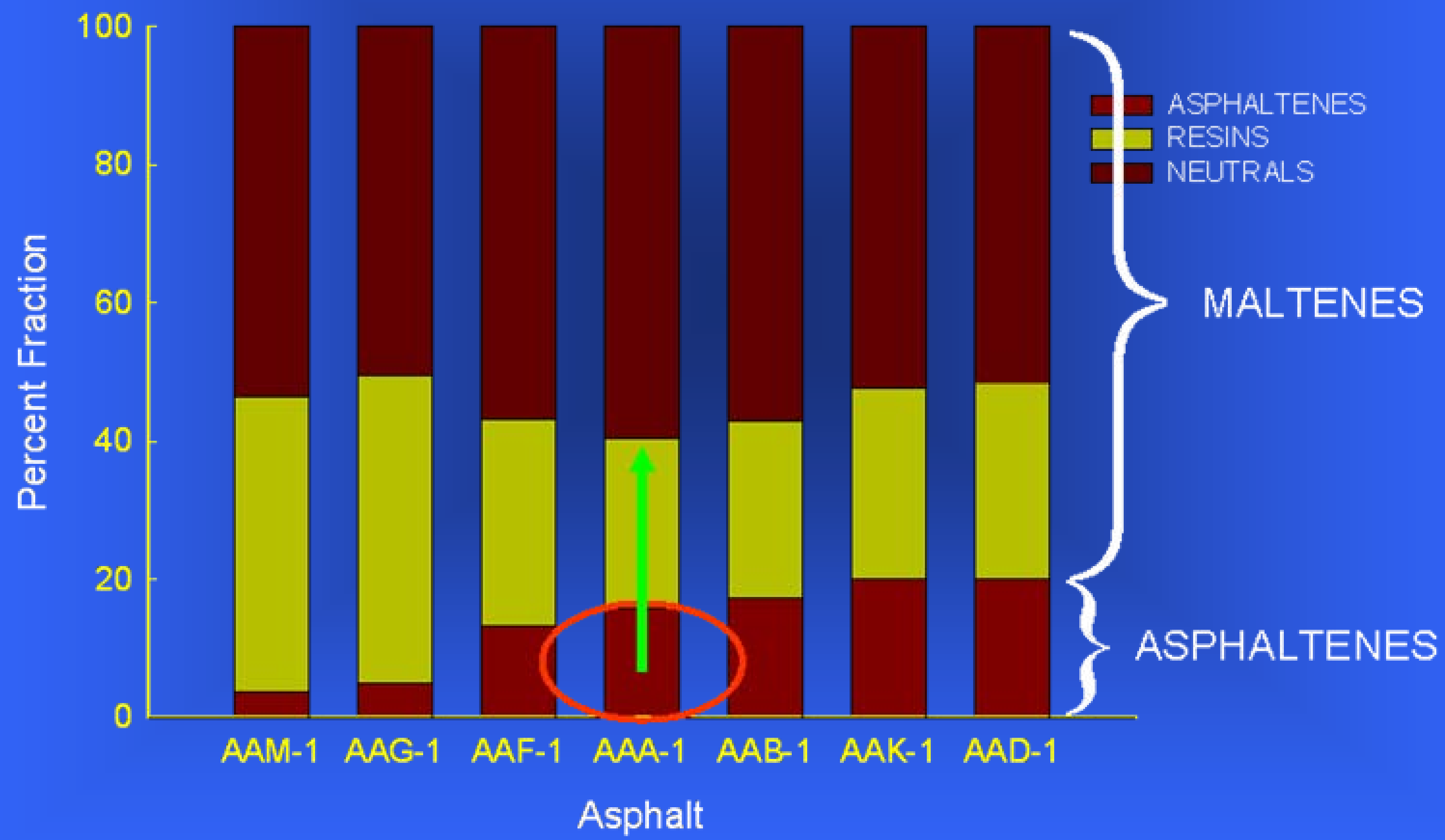
Effect of adding resins to neutrals

$$\Delta T = \frac{x_r RT^{*2}}{\Delta H_f}$$



Effect of adding asphaltenes to maltenes

$$\Delta T = \frac{x_a R T^{*2}}{\Delta H_f}$$



Conclusions

The Present Modeling Approach;

Provides a unique fingerprint of a heavy crude oil

Defines an ideal heavy crude oil based on compositional properties and fundamental thermodynamic principles

Accurately predicts rheological properties of heavy crude oils

Potentially will predict compatibility of blends using measurements of starting materials alone

Potentially ranks crude oils best suited for a particular paving application based on the crude source

Potentially will make initial select of crude oils best suited for a particular paving application fast, simple, and reliable

Questions ?