Mixing and Compaction Temperatures of Binders,their Activation Energy for Flow and the Boltzmann Distribution

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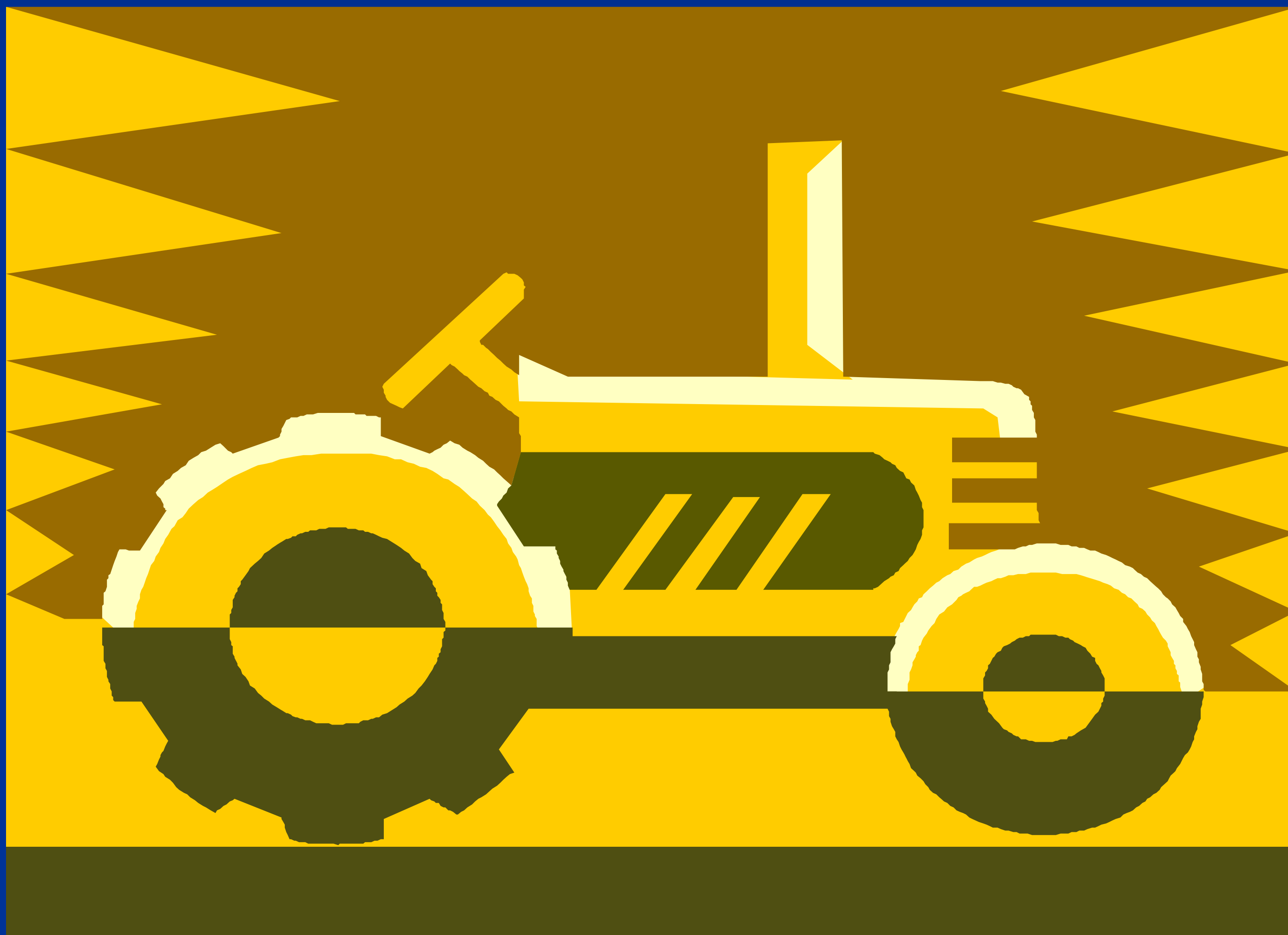
Outline

- Background to Energy Model
- Boltzmann Energy Distribution
- Arrhenius equation for energy
- Viscosity and fluidity of binders
- Activation energy for flow
- Relation to compaction effort
- Conclusions

Kinetic model and the Boltzmann Distribution

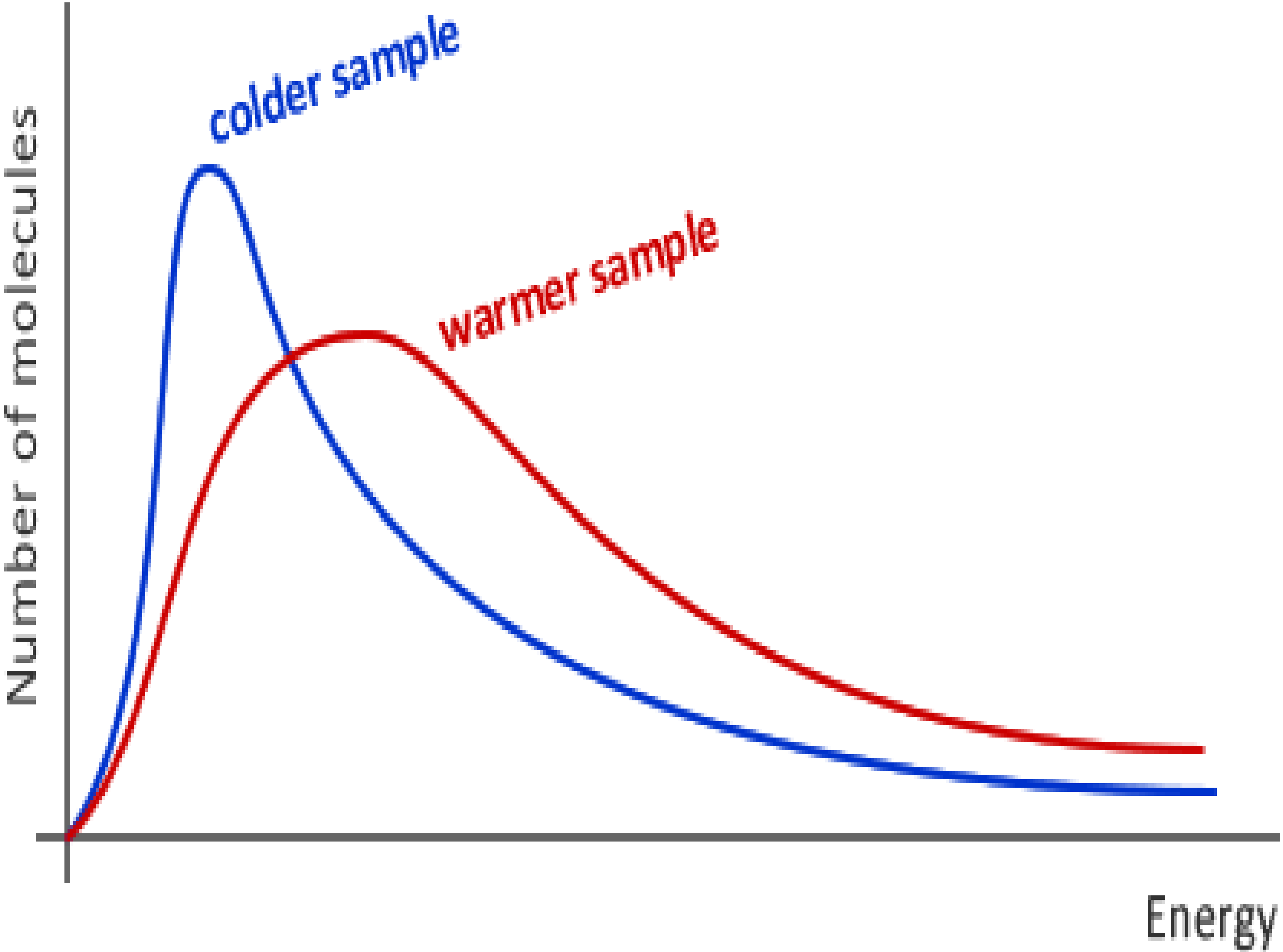
- Statistical concepts are used to determine most probable distribution of energy
- Determines the most probable distribution of a system at equilibrium
- The Boltzmann distribution is the most dominant energy configuration for a thermally activated systems at equilibrium

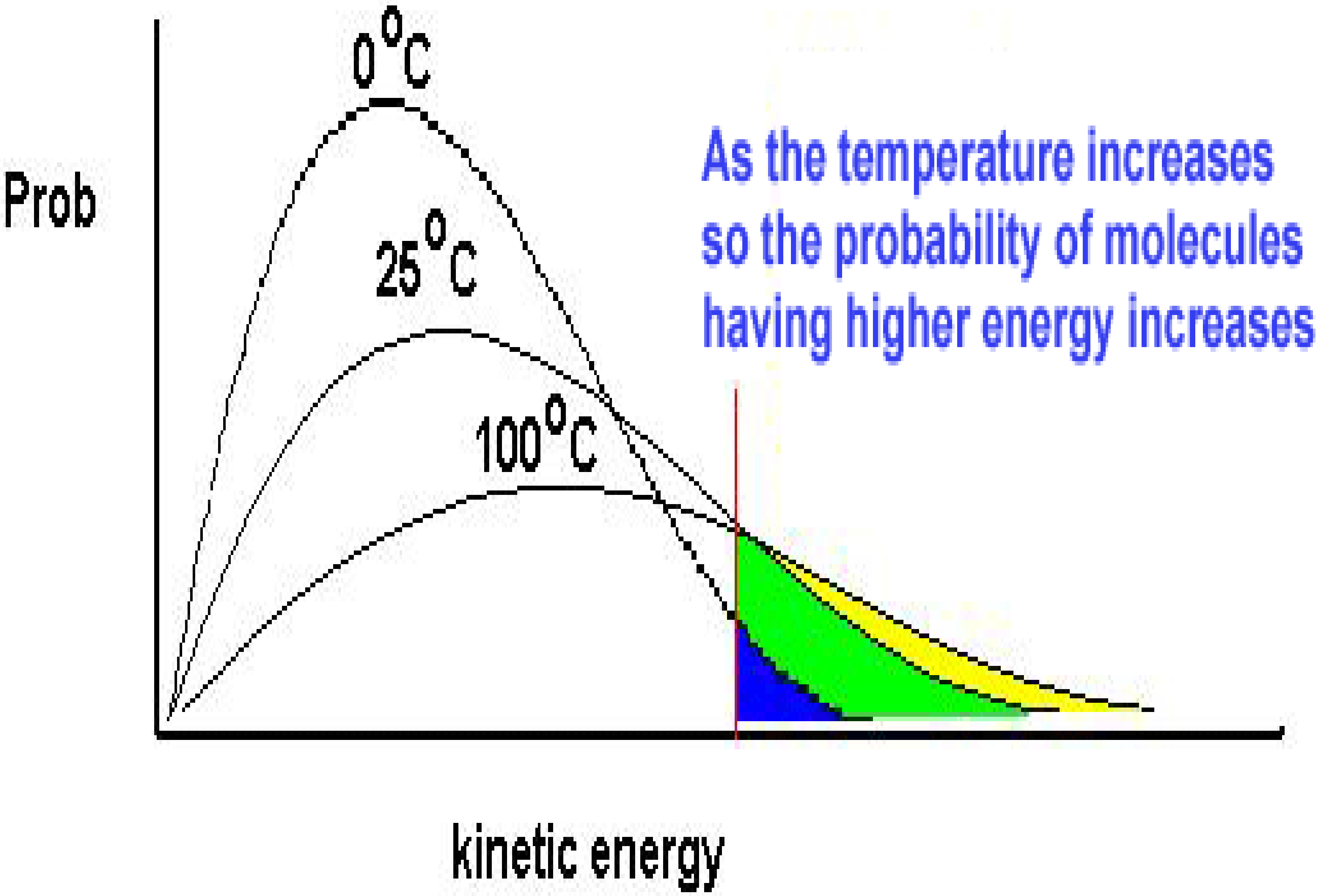
Another view on Compaction Effort



Kinetic model (Boltzmann distribution) and viscosity

- Viscosity is resistance to flow
- Intermolecular forces in liquid asphalt are responsible for resistance to flow
- Energy is needed to overcome resistance to flow
- Temperature is the property that tells us the direction of flow of energy or a measure of the average kinetic energy of molecules


colder sample
warmer sample
Number of molecules
Energy


Prob
0°C
25°C
100°C
As the temperature increases
so the probability of molecules
having higher energy increases
kinetic energy

Boltzmann Distribution

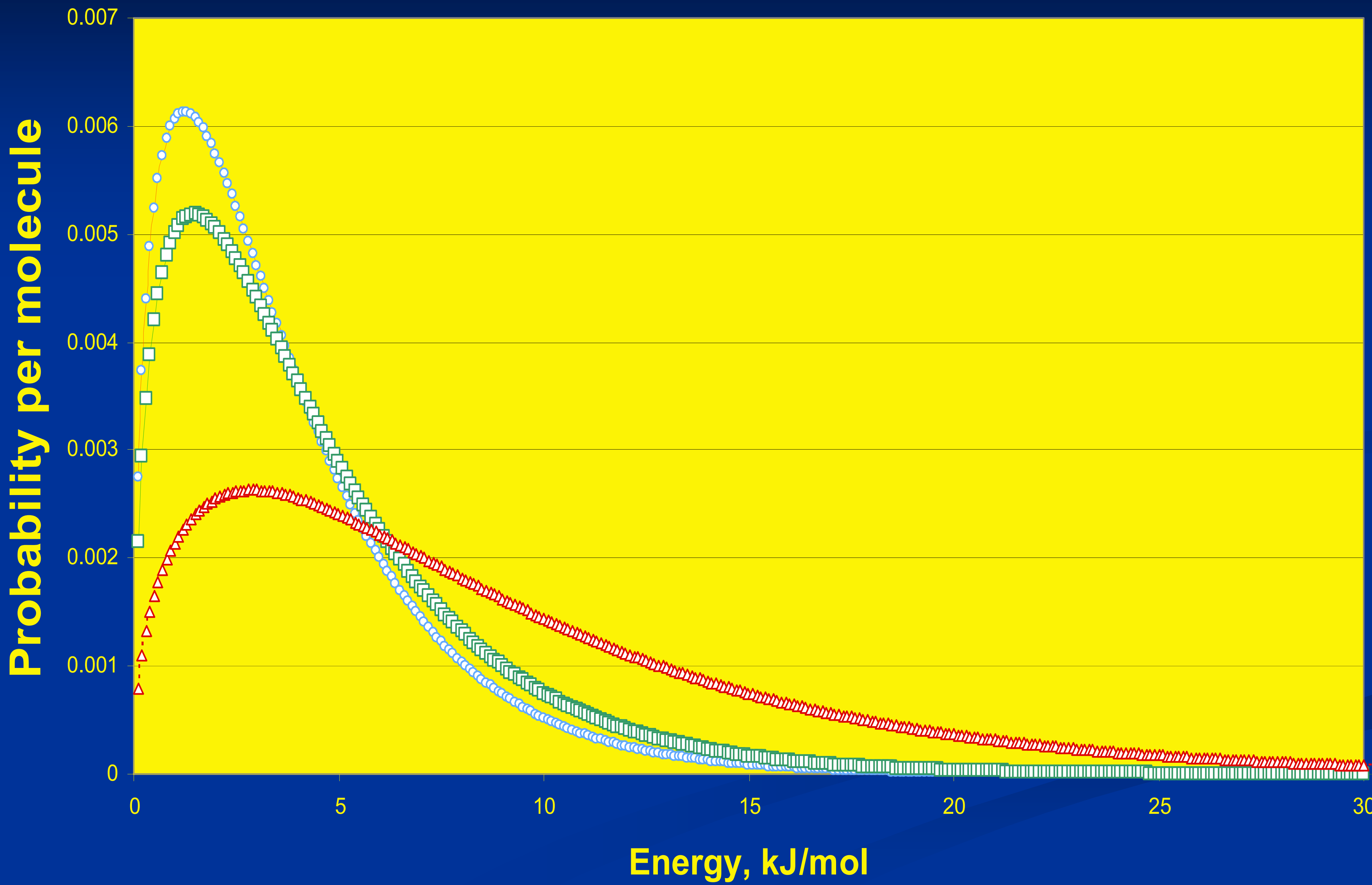
$$P(E)dE = 2/\pi^{1/2} ((RT)^{-3/2} E^{1/2} e^{-E/RT} dE$$

↓

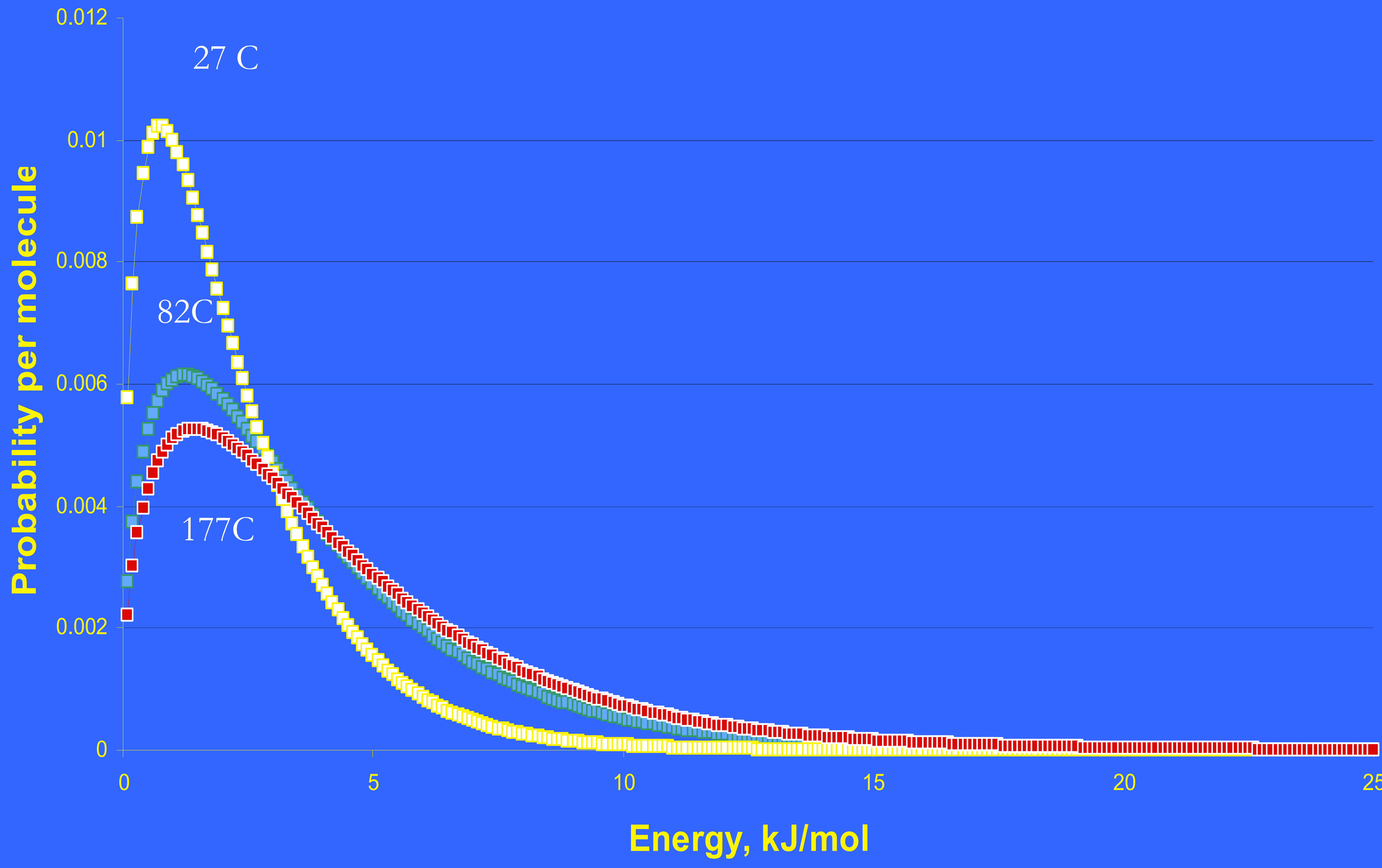
↓

$$\int_{E_f}^{\infty} P(E)dE = 2/\pi^{1/2} ((RT)^{-3/2} \int_{E_f}^{\infty} E^{1/2} e^{-E/RT} dE$$

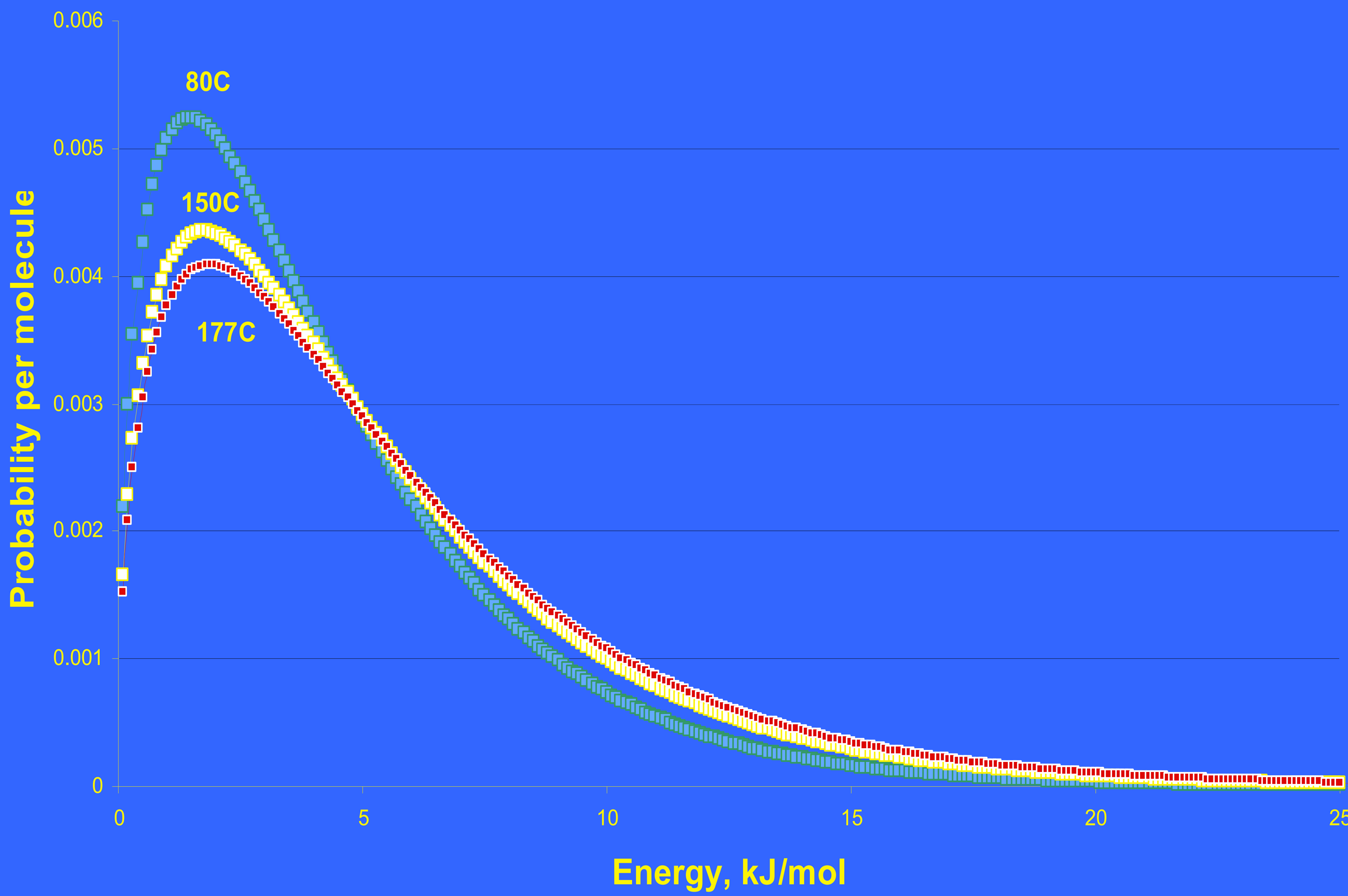
Boltzmann Plot for 3 Temperatures



Boltzmann Plot for lowest compaction temperature(82C),and mix temperature (177C) compared to ambient Temperature(25C)



Boltzmann Plot for 80C, 150 C, and 177C



Arrhenius Law

$$\eta = Ae^{\Delta E_\eta / RT}$$

ΔE_η : Activation Energy

R: Universal Gas Constant, 8.314 J/mol K

A: a constant

$$\ln \eta = \ln A + \frac{\Delta E_\eta}{RT}$$

Fluidity: measures the ease of flow

$$\Phi = 1/\eta$$

$$\Phi = A \exp(-E_f/RT)$$

$$\ln \Phi = \ln A - (E_f/R)\, 1/T$$

Boltzmann factor in the Arrhenius Expression: Comparison

- Viscosity =A exp(E/RT)
- Viscosity for liquids decreases with increase with temperature
- Define fluidity as

$\Phi = 1/\eta$

$\Phi = A \exp(-E_f/RT)$

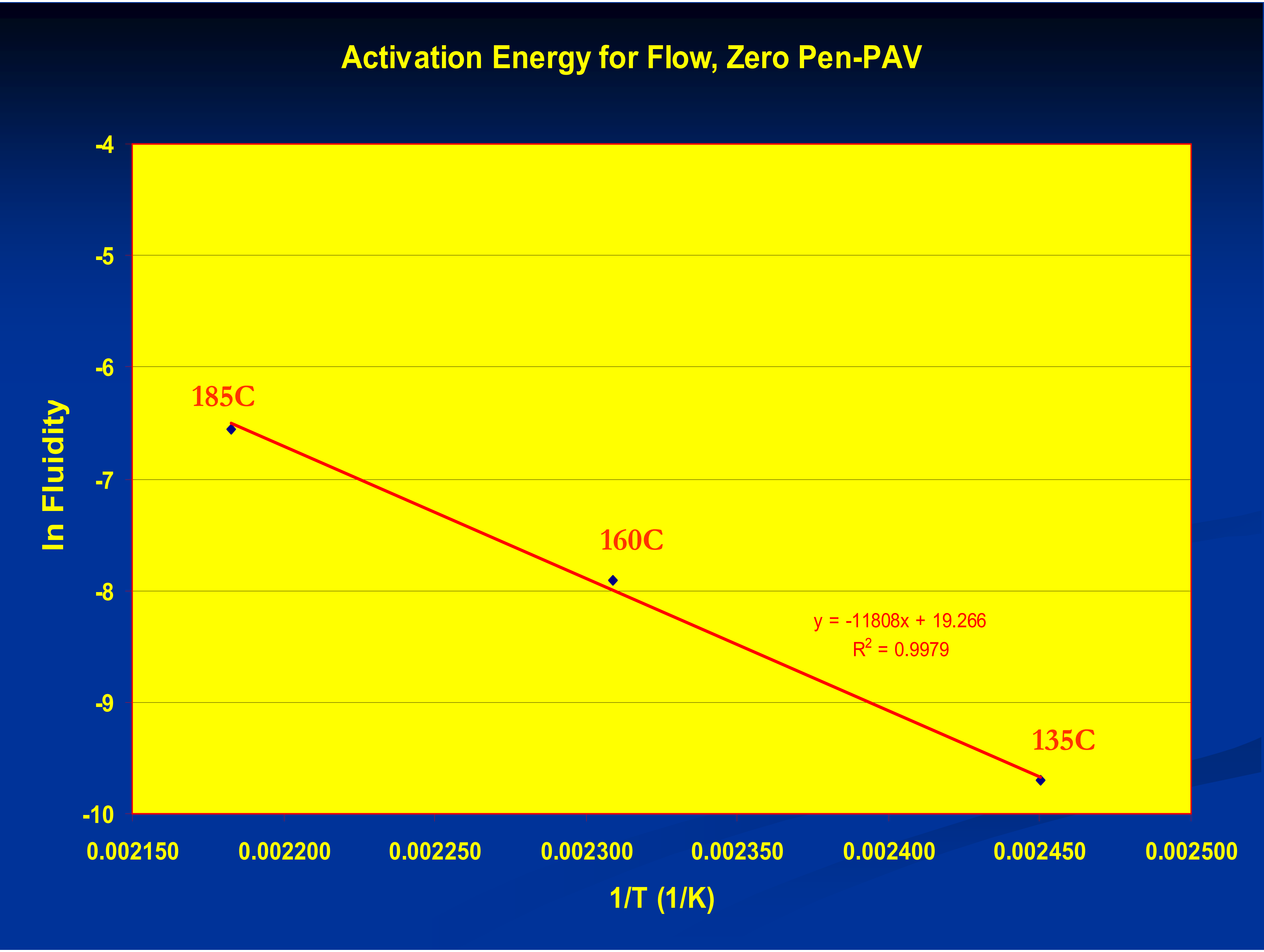
$\ln \Phi = \ln A - (E_f/R)\, 1/T$

Boltzmann factor:

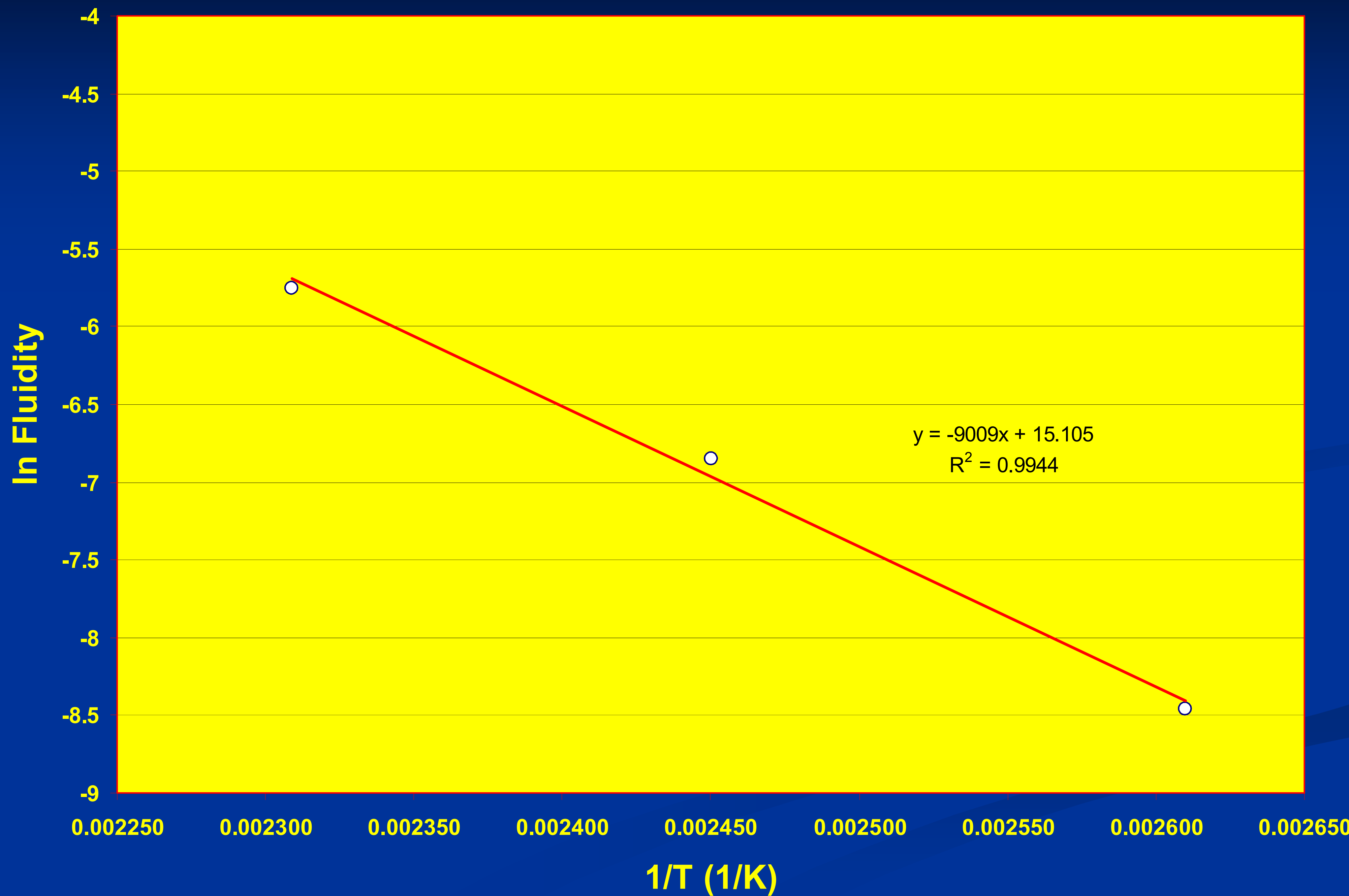
$\exp(-E_f/RT)$

- Rate (k) =Aexp(-E/RT)
- $\ln k = \ln A - (E/R)\, 1/T$
- Reaction rate increases with temperature
- Exponential dependence
- $\ln k = \ln A - (E/R)\, 1/T$
- Boltzmann factor:

$\text{Exp}(-E/RT)$


Activation Energy for Flow, Zero Pen-PAV
ln Fluidity
-4
-5
-6
-7
-8
-9
-10
185C
160C
135C
y = -11808x + 19.266
R2 = 0.9979
0.002150
0.002200
0.002250
0.002300
0.002350
0.002400
0.002450
0.002500
1/T (1/K)

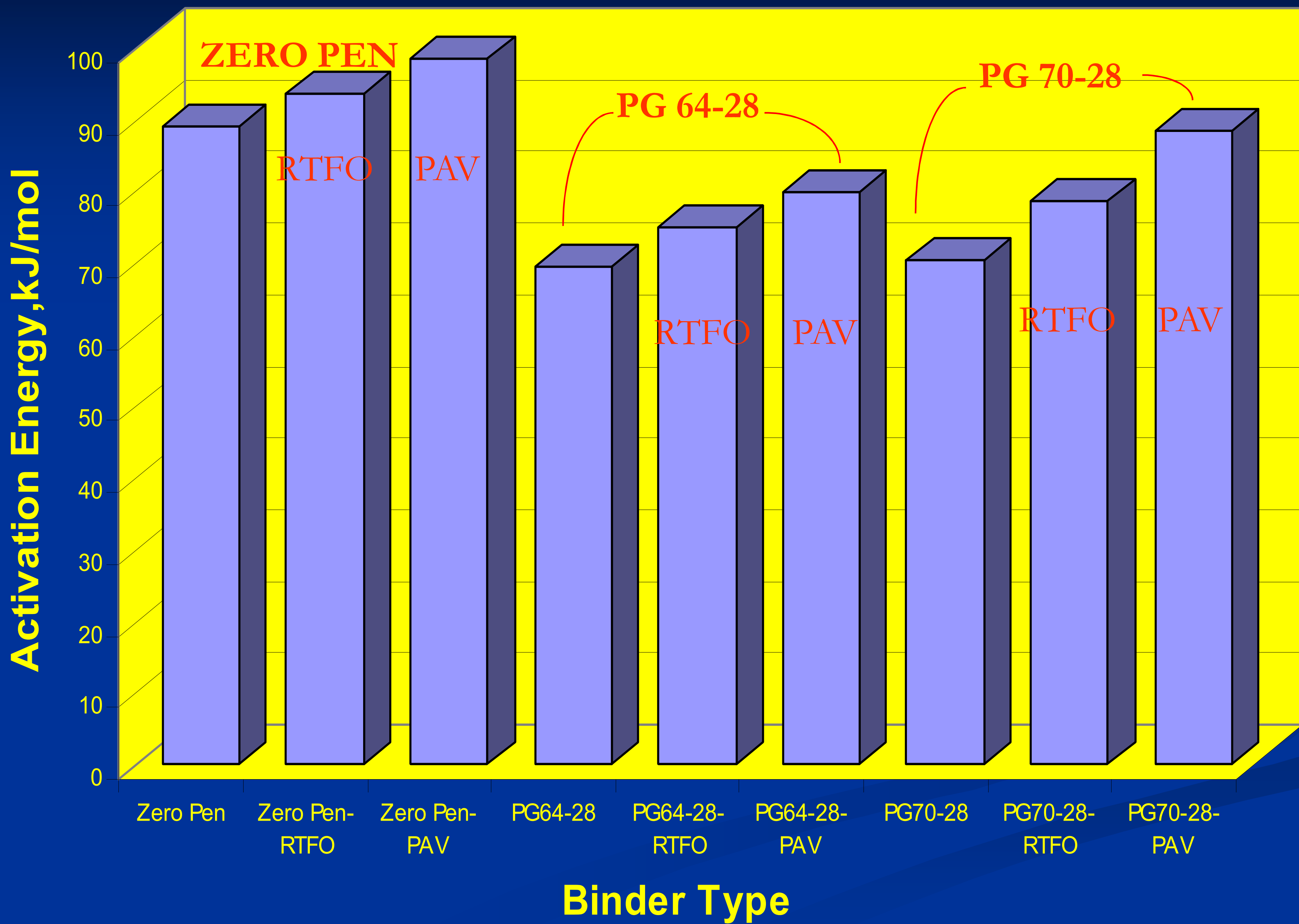
Activation Energy for Flow, PG64-34

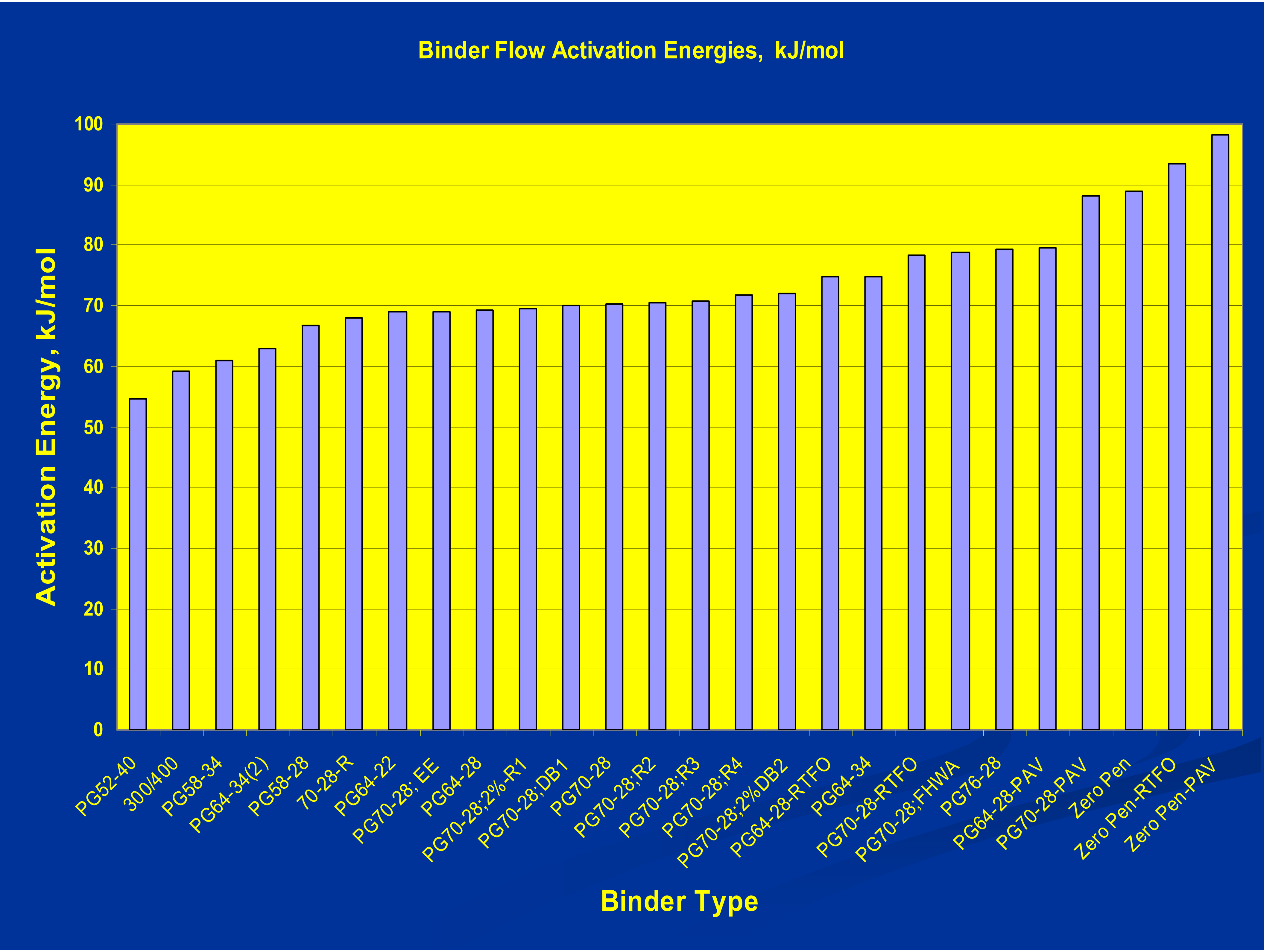


Boltzmann factor

Binder	A	E_f, kJ/mol	110C	135C	177C
PG64-28	1.67E+06	69.163	2.2659E-10	8.83526E-10	2.94412E-09
PG64-28-RTFO	5.70E+06	74.761	3.75493E-11	1.63461E-10	6.00425E-10
PG64-28-PAV	1.51E+07	79.676	7.74831E-12	3.71548E-11	1.48665E-10
PG70-28	1.08E+06	70.253	1.59677E-10	6.36111E-10	2.16026E-09
PG70-28-RTFO	6.09E+06	78.298	1.20606E-11	5.62862E-11	2.19877E-10
PG70-28-PAV	5.64E+07	88.108	5.16853E-13	2.92566E-12	1.35565E-11
300/400	2.09E+05	59.209	5.53762E-09	1.7752E-08	4.97451E-08
PG52-40	2.91E+04	54.684	2.36774E-08	6.94372E-08	1.79844E-07

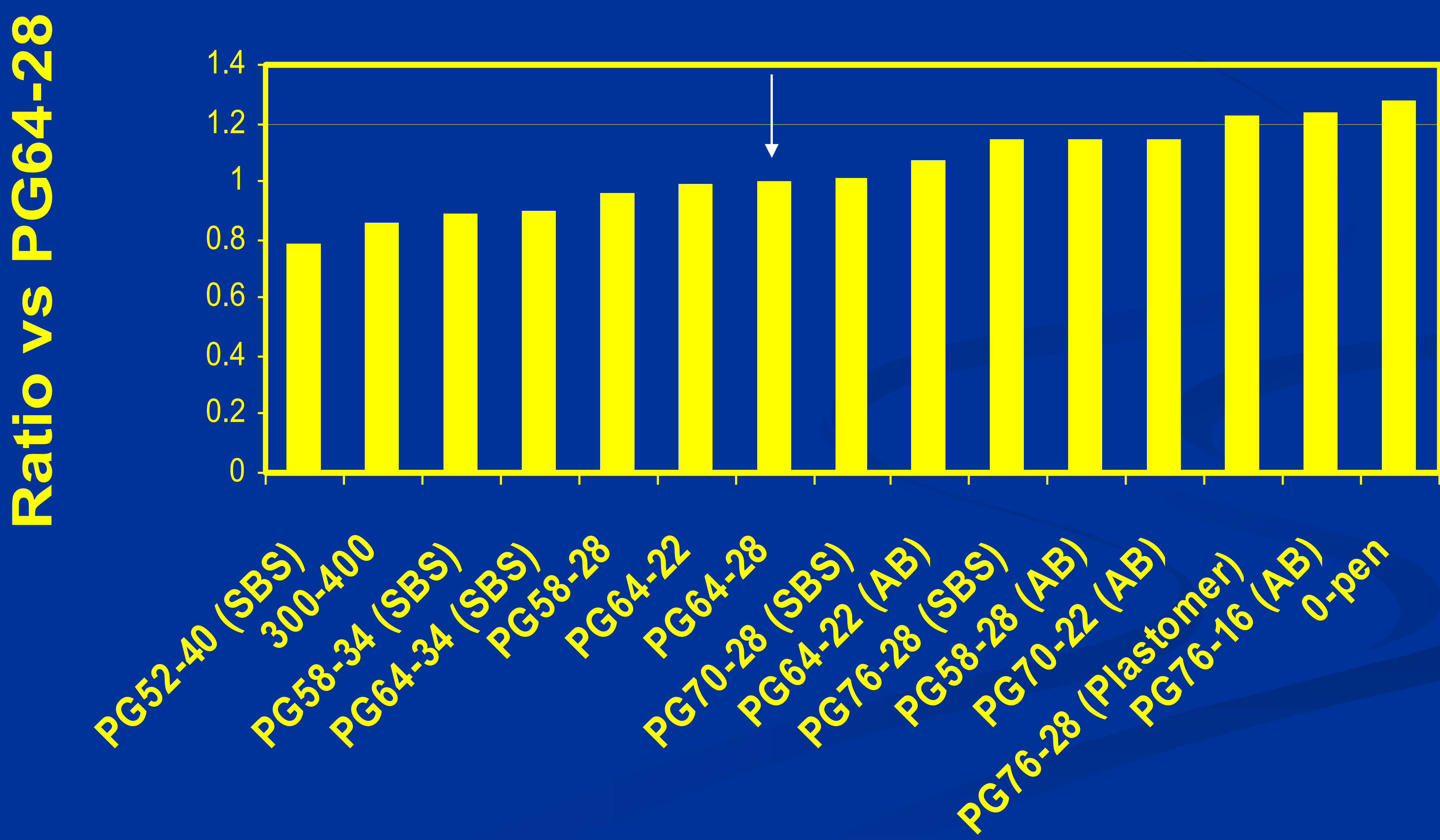
Effect of Binder Aging on Activation Energy





Binder Flow Activation Energies, kJ/mol
Activation Energy, kJ/mol
100
90
80
70
60
50
40
30
20
10
0
PG52-40
300/400
PG58-34
PG64-34(2)
PG58-28
70-28-R
PG64-22
PG70-28; EE
PG64-28
PG70-28;2%-R1
PG70-28;DB1
PG70-28
PG70-28;R2
PG70-28;R3
PG70-28;R4
PG70-28;2%DB2
PG64-28-RTFO
PG64-34
PG70-28-RTFO
PG70-28;FHWA
PG76-28
PG64-28-PAV
PG70-28-PAV
Zero Pen
Zero Pen-RTFO
Zero Pen-PAV
Binder Type

Flow activation energy, E_f , for different binders relative to PG64-28



Conclusions and future research

- The kinetic model (Boltzmann distribution) is proposed as a model for understanding compaction effort of binders, where the Boltzmann factor, exp ($-E_f/RT$) represents the probability that a particle any system will have sufficient energy to flow.
- The Arrehnius law, $\ln \Phi = \ln A - E_f/RT$ is used to obtain E_f
- The use of flow activation energy provides a procedure for ranking compaction effort of a mix; however E_f, should be obtained at high pressures similar to load applied in the field during compaction;
- Shear resistance of the mix obtained from SGC would offer a more complete description of compaction effort.

References

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- Eyring, H. (1936), "Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates", *Journal of Chemical Physics*, Vol. 4, April 1936, pp.283-291.

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Thank You!!

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