

Metalworking Fluids & VOC, Today and Tomorrow
A Joint Symposium by SCAQMD & ILMA
South Coast Air Quality Management District
Diamond Bar, CA, USA
March 8, 2012

Understanding & Determining the Normal
Boiling Point of a High Boiling Liquid



INNOVATION

BY TAMINCO

Presentation Outline

- **Relationship of Vapor Pressure to Temperature**
- **Examples of VP/T Curves**
- **Calculation of Airborne Vapor Concentration**
- **Binary Systems**
- **Relative Volatility as a function of Temperature**
- **GC Data and Volatility**
- **Everything Needs a Correlation**
- **Conclusions**



Vapor Pressure Models

(pure vapor over pure liquid)

Correlative:

- Clapeyron: $\text{Log}(P) = A/T + B$
- Antoine: $\text{Log}(P) = A/(T-C) + B$
- Riedel: $\text{Log}P = A/T + B + C\text{log}(T) + DT^E$

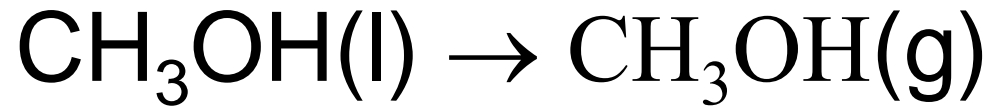
Predictive:

- ACD Group Additive Methods
- Riedel: $\text{Log}P = A/T + B + C\text{log}(T) + DT^E$
Coefficients defined, Reduced $T = T/T_c$
- Variations: Frost-Kalkwarf-Thodos, *etc.*



Two Parameters: $\text{Log}(P) = A/T + B$

Vaporization as an
activated process



$$K = [\text{CH}_3\text{OH}(\text{g})]/[\text{CH}_3\text{OH}(\text{l})]$$

$$[\text{CH}_3\text{OH}(\text{g})] = \text{partial } P$$

$$[\text{CH}_3\text{OH}(\text{l})] = 1 \text{ (pure liquid)}$$

$$K = P$$

$$\ln(P) = \ln(K)$$

$$\Delta G = -RT \ln(K) = -RT \ln(P)$$

$$\Delta G = \Delta H - T\Delta S$$

$$\ln(P) = -\Delta G/RT$$

$$\ln(P) = -\Delta H/RT + \Delta S/R$$

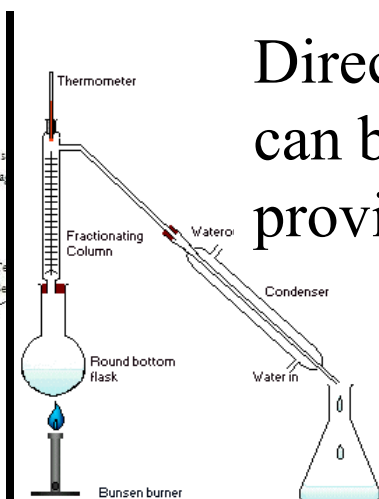
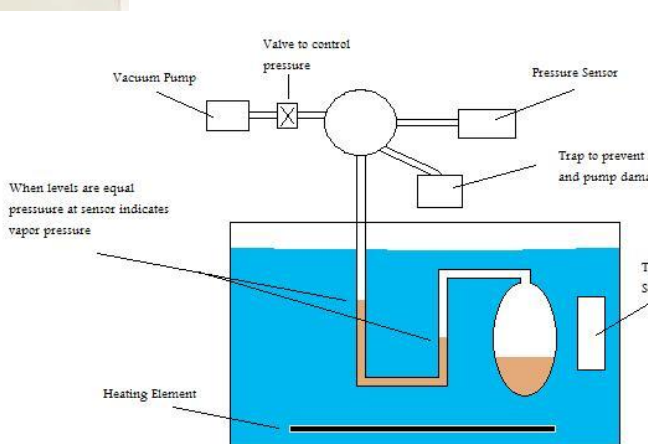
$$\Delta S/R = B$$

$$\Delta H/R = -A$$



Vapor pressure Measurement: Direct versus Distillation

- Direct vapor pressure measurement (e.g., isoteniscope) requires pure material while distillation based determination can employ a middle cut with a relatively high purity. Distillation allows for extrapolation and/or interpolation of data to approximate VP.
- Direct vapor pressure measurement requires multiple freeze-thaw cycles to remove atmospheric gases while distillation (especially atmospheric distillation) purges atmospheric gases as part of the process.
- Direct measurement OK for “volatile materials” (normal BP < 100 °C) but involved for “high boilers” (normal BP > 100 °C).



Direct vapor pressure measurement can be more accurate, but distillation provides a reasonable approximation

Ebulliometry
“accurate distillation”

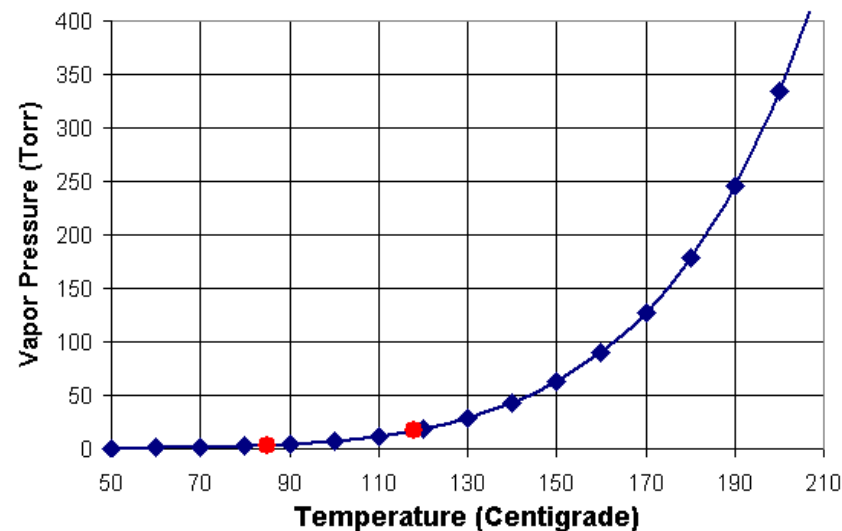
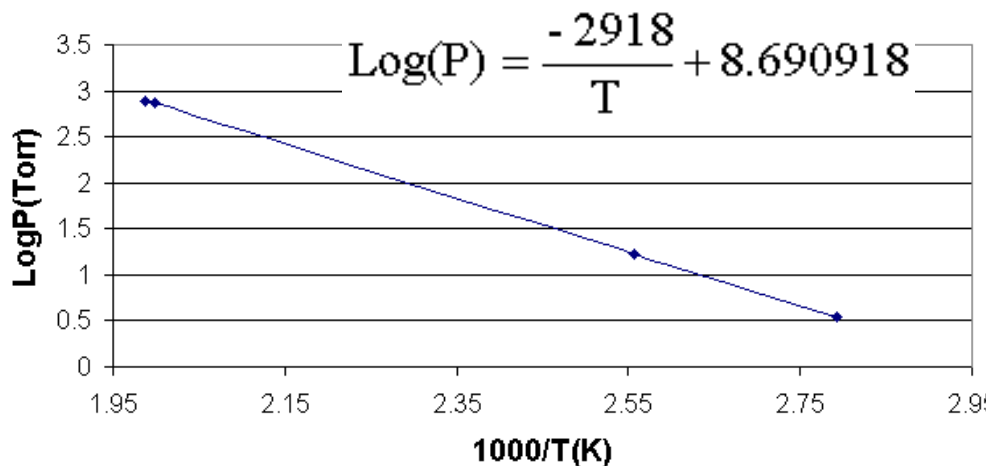


Two Parameters: $\text{Log}(P) = A/T + B$

DBAE (GMW = 173.30, CAS RN 102-81-8):

Below is a table of the literature data that we could find for the boiling point of DBAE versus pressure.

BP (°C)	BP (°K)	P (torr)	P (KPa)	Reference
230	503.15	760	101.3232	Bouilloux; Bull.Soc.Chim.Fr.; 1958; 1446.
227	500.15	738	98.3902	Burnett et al.; J.Amer.Chem.Soc.; 59; 1937; 2249.
118	391.15	17	2.2664	Leonard; Simet; J.Amer.Chem.Soc.; 77; 1955; 2855, 2857.
400	373.15	0.8	0.1067	Perrine; J.Org.Chem.; 18; 1953; 1356,1361.
85	358.15	3.5	0.46662	Hannig; Haendler; Arch.Pharm.(Weinheim Ger.); 290; 1957; 131,133.



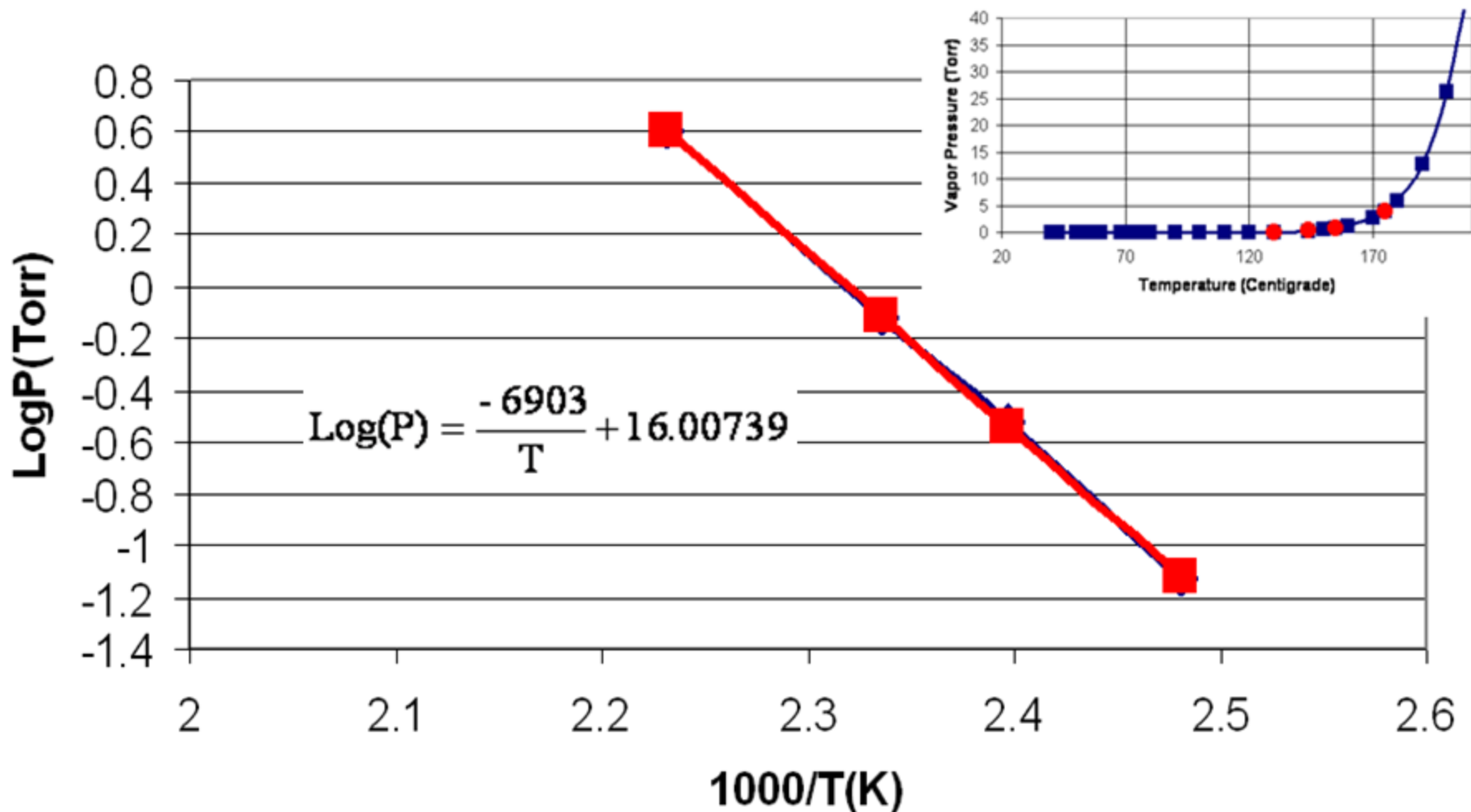
$$r^2 = 0.999942$$

Apparent $\Delta H_{\text{vaporization}} = 55.86 \text{ KJ/mole}$ & $\Delta S_{\text{vaporization}} (1 \text{ Torr}) = 166.39 \text{ J/(mole-K)}$



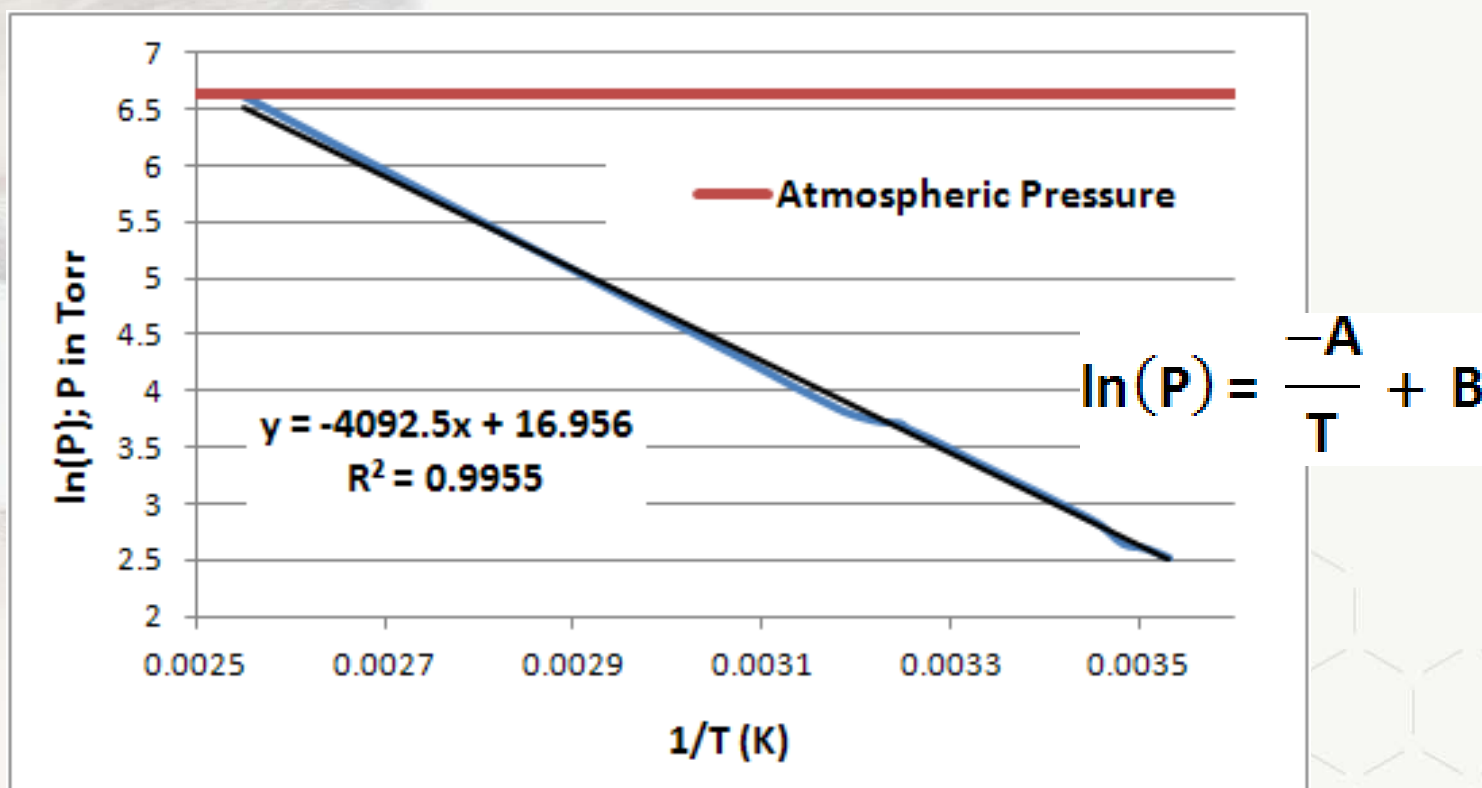
ODEA (GMW = 217.35, CAS RN 15520-05-5):

BP (°C)	BP (°K)	P (torr)	P (KPa)	Reference
175	448.15	4	0.5333	Bush; <i>US Patent 2541088, 1946.</i>
155	428.15	0.75	0.1000	King of Prussia data
144	417.15	0.3	0.0400	Zuniga, H.; Bartulin, J.; Ramirez, A.; Muller, H.; Taylor, T. R.; <i>Mol. Cryst. Liq. Cryst.</i> , 1990, 185, 131-140.
130	403.15	0.075	0.0100	King of Prussia data

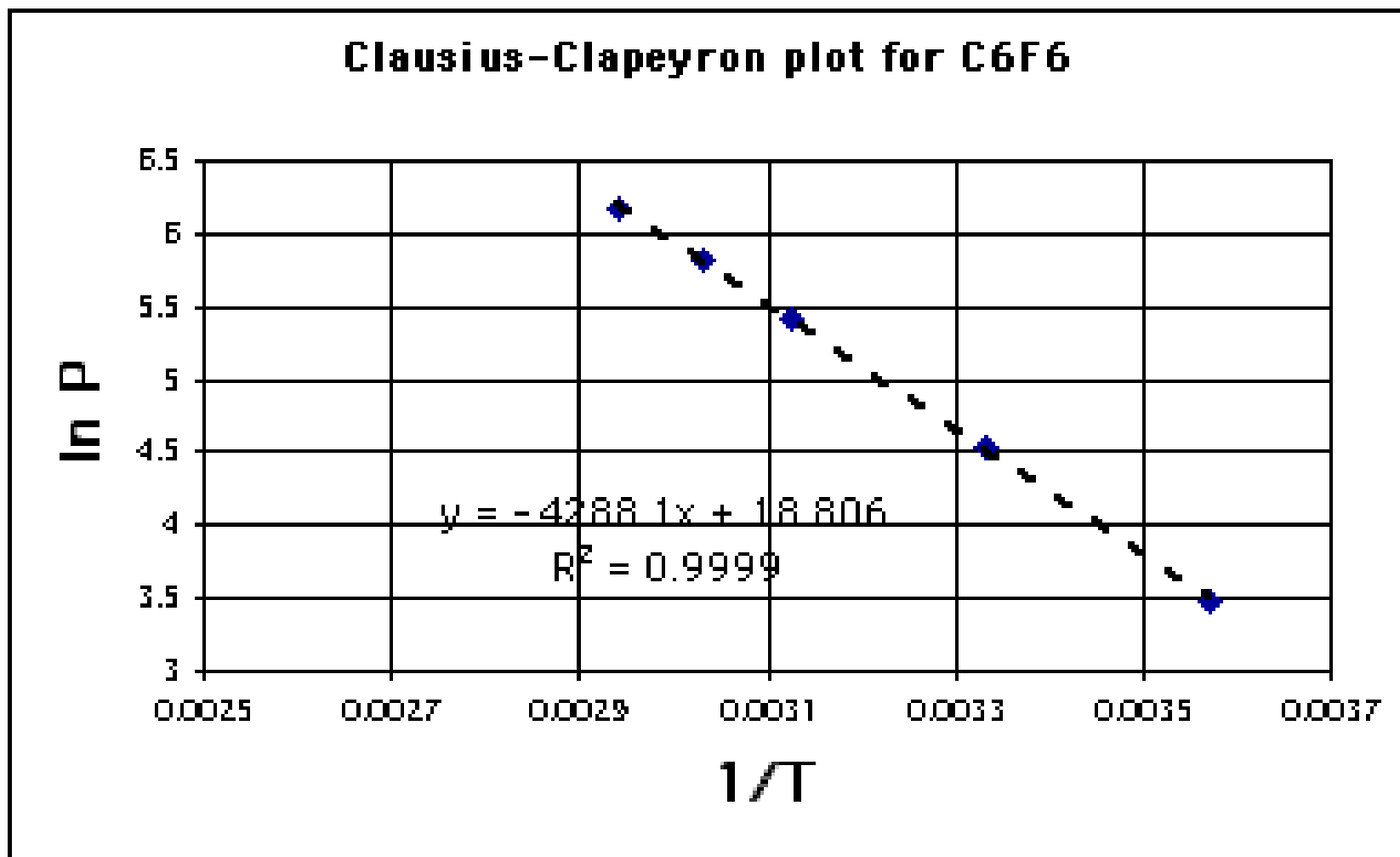


Vapor Pressure of Methyl Isothiocyanate (MITC; CAS RN = 556-61-6) as a function of T:

- Haenssgen; Pohl; *Chem. Ber.* 1979, 112, 2798.
- Yanchuk, N. I.; *Russ. J. Gen. Chem.* 1996, 66(9), 1436-1441.
- Bauer, H.; Burschkes, K.; *"Thermophysical data", Ber. Dtsch. Chem. Ges.,* 1935 68, 1243.



P in torr; Standard State = 1 torr; T in K (absolute); A = 4092; B = 16.956; R = 8.3144621
 ΔH (vaporization) = 34 kJ/mole (assumed to be constant over range of T from 10 °C – 120 °C)
 ΔS (vaporization) = 141 J/(K-mole) @ 1 Torr (determined from value of B)
 ΔS (vaporization) = 87 J/(K-mole) @ 760 Torr (determined as $\Delta H/T$ at the boiling point)



Hexafluorobenzene: Normal BP = 82 °C



Compound	Enthalpy (kJ/mol)	Entropy (1 Torr; J/mol-K)	T Range (°C)	r ² value	Predicted Normal BP (°C)
Hexadecane I	≈ 61	≈ 164 (109 adjust to 1 atm) (109 by ΔH/BP)	200 – 287	0.9968	285
Hexadecane II	≈ 64	≈ 170	100 – 287	0.9987	282
Hexadecane III	≈ 61	≈ 164	150 – 287	0.9984	285
Hexadecane is thermally stable up to the normal BP					
BDEA	≈ 61	≈ 166 (111 adjust to 1 atm) (109 by ΔH/BP)	80 – 170	0.9981	284
BDEA	≈ 70	≈ 185	100 – 280	0.9828	276
BDEA is thermally stable up to ≈ 180 °C					

I) Camin D.L.; Forziati A.F.; Rossini F.D.; *J. Phys. Chem.* **1954** 58, 440-442.

II) Myers H.S.; Fenske M.R.; *Ind. Eng. Chem.* **1955**, 47(8), 1652-1658.

III) Krafft F., *Ber.Dtsch.Chem.Ges.*, 15, 1687-1711, 1882

IV) Laboratory Data

V) Literature Data

Entropy of vaporization @ 1 atmosphere ≈ 85 J/mol-K with a range from 70 J/K-mol to 120 J/K-mol for “average size” rigid molecules ; entropy of vaporization is higher for long “floppy” molecules. Predicted entropy of vaporization given by different formulas; $85 + 0.67(n-5) \approx 95$ J/mol-K for hexadecane at normal BP;

T range of correlation from T_{low} to T_{high} ; $\Delta T = T_{high} - T_{low}$
 T_{low} = T at which VP is equal to low set point (liquid); VP = 0.01 Torr is convenient
 T_{high} = T at which VP is equal to high set point (liquid); normal BP is convenient
 $\Delta\Delta H$ = decrease in Enthalpy from T_{low} to T_{high}
 Enthalpy change fairly linear over range of T where liquid has VP < 0.1 Torr to the normal BP

$$\ln(P) = \frac{\left\{ \Delta H_{T_{low}} - \Delta\Delta H \frac{(T - T_{low})}{(\Delta T)} \right\}}{RT} + \frac{\Delta S}{R}$$

$$\ln(P) = \frac{\Delta H_{T_{low}} + \Delta\Delta H \frac{(T_{low})}{(\Delta T)}}{RT} - \frac{\Delta\Delta H}{R(\Delta T)} + \frac{\Delta S}{R}$$

$$\ln(P) = \frac{\Delta H_{effective}}{RT} + \frac{\Delta S_{effective}}{R}$$

$$\Delta H_{effective} = \Delta H_{T_{low}} + \Delta\Delta H \frac{(T_{low})}{(\Delta T)}$$

$$\Delta S_{effective} = \Delta S_{theoretical} - \frac{\Delta\Delta H}{(\Delta T)}$$

$\Delta\Delta H \approx 4$ kJ from 0 °C - 100 °C

$\Delta H_{effective} = 43.3$ kJ/mol

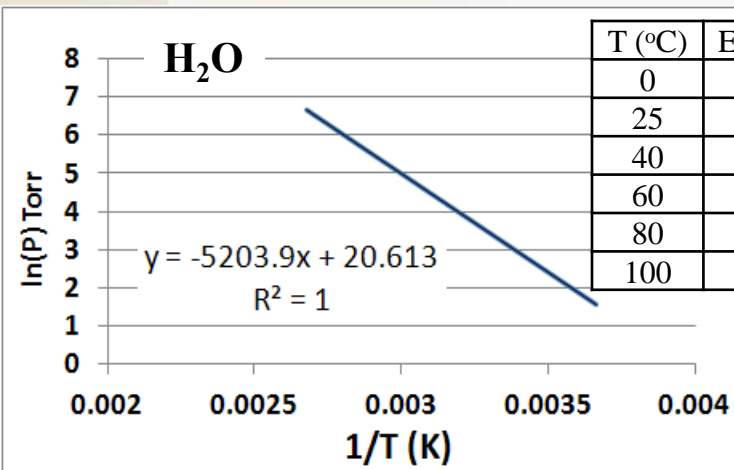
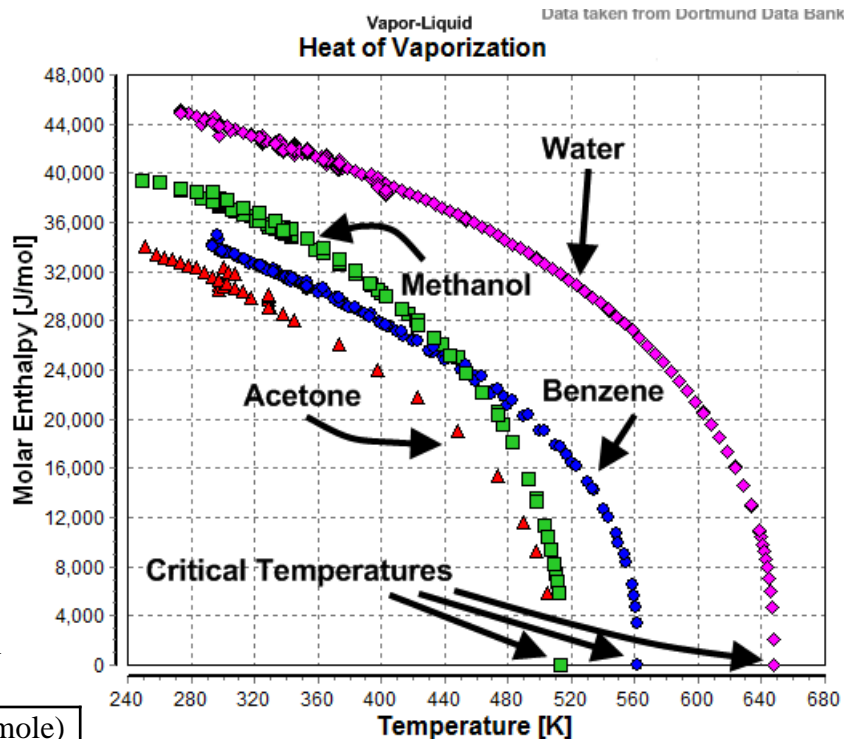
$\Delta H_{T_{low}} = 54.2$ kJ/mol

$\Delta S_{effective} = 171.4$ J/mol-K

$\Delta S_{effective @ 1 atm} = 116.2$ J/mol-K

$\Delta S_{theoretical} = 131.4$ J/mol-K

$\Delta S_{theoretical @ 1 atm} = 76.23$ J/mol-K

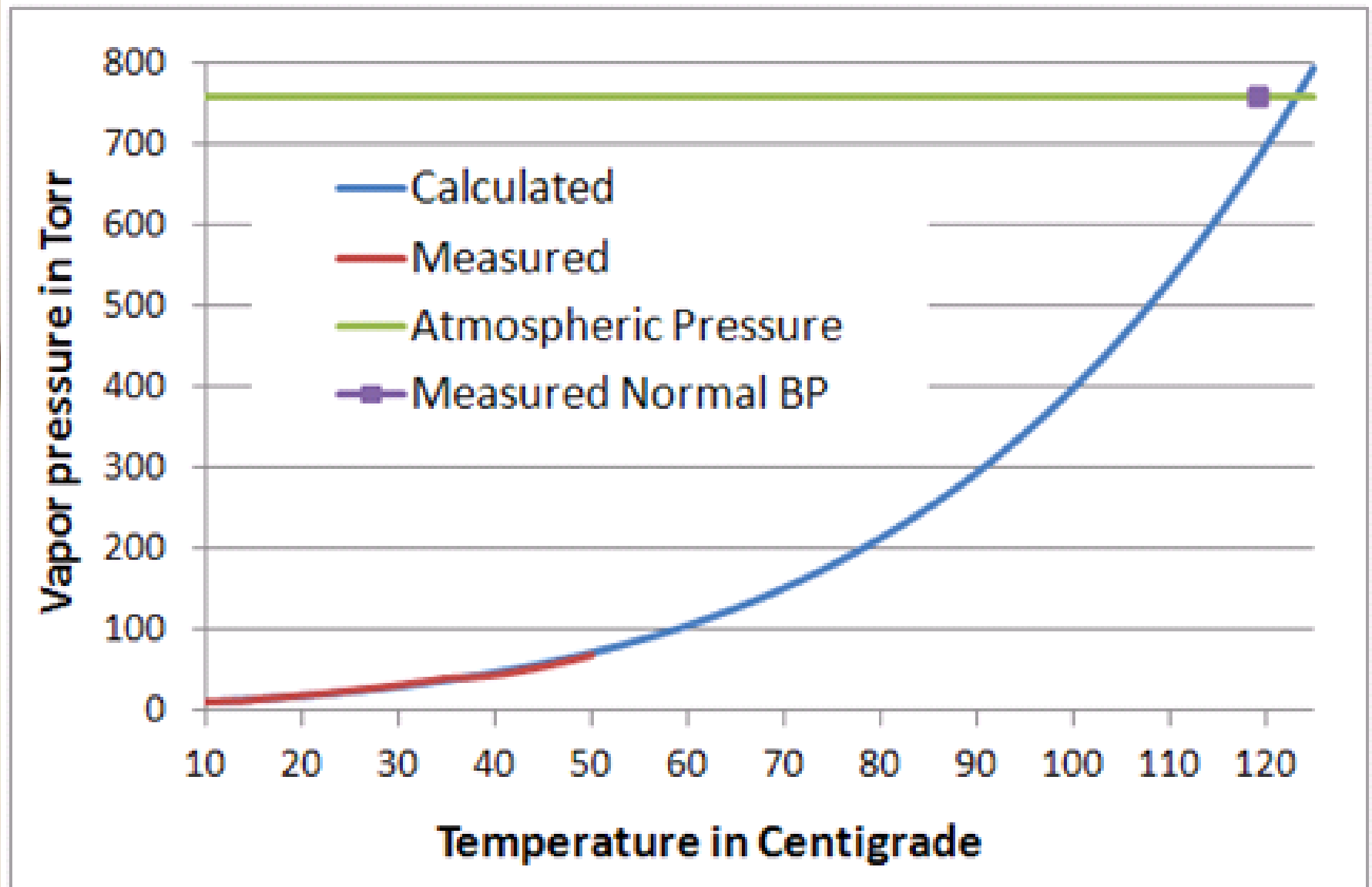


T (°C)	Enthalpy Vaporization (kJ/mole)
0	45.054
25	43.990
40	43.350
60	42.482
80	41.585
100	40.657

T	VP (Torr)	1/T	ln(P)
273.15	4.768	0.003661	1.561927
283.15	9.345	0.003532	2.234841
293.15	17.492	0.003411	2.861744
313.15	54.351	0.003193	3.995463
333.15	147.39	0.003002	4.993082
353.15	356.988	0.002832	5.877702
373.15	786.42	0.00268	6.667491

Marsh, K. N., Ed., *Recommended Reference Materials for the Realization of Physicochemical Properties*, Blackwell, Oxford, 1987.

Calculated & Measured Vapor Pressure of MITC



Accounting for liquid composition

Raoult's Law

$$P_T = x_A P_A + x_B P_B$$



Raoult's Law Graph Constructed with Excel

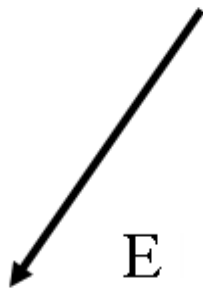
$$=10^{((-2928/(H2+273.15))+9.4834)*E2/G2}$$

$$=10^{((-4299/A2)+10.05438)}$$

$$=10^{((-2928/A2) + 9.4834)}$$

Found with goal seek function;
look for T at which:
VP (mixture) = 1 atmosphere

A

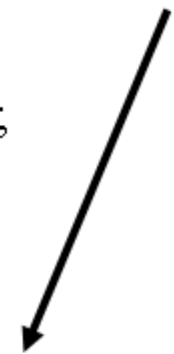


E

F

G

H



Temperature (K)	Temperature (oC)	VP (MEA - Torr)	VP (TEA - Torr)	MF (MEA)	MF (TEA)	VP (mixture)	BP(mixture)	Vapor Fraction (MEA)	Vapor fraction (TEA)
373.15	100	43.32011111	0.034162046	1	0	759.9999999	170.3125795	1	0
374.15	101	45.46337365	0.03667211	0.99	0.01	760.0001986	170.6050493	0.999969395	3.06048E-05
375.15	102	47.70039235	0.039351724	0.98	0.02	760.0000032	170.9008472	0.999937874	6.21259E-05
376.15	103	50.0347032	0.042211305	0.97	0.03	759.9999734	171.2000678	0.999905402	9.45983E-05
377.15	104	52.46995263	0.045261844	0.96	0.04	759.9995709	171.5027654	0.999871942	0.000128058
378.15	105	55.00990017	0.048514933	0.95	0.05	760.0000002	171.8090644	0.999837455	0.000162545
379.15	106	57.6584211	0.051982795	0.94	0.06	760.0000011	172.1189962	0.999801902	0.000198098
380.15	107	60.41950922	0.055678312	0.93	0.07	760.0000037	172.4326605	0.999765241	0.000234759
381.15	108	63.2972796	0.059615061	0.92	0.08	760.0000103	172.7501431	0.999727426	0.000272574

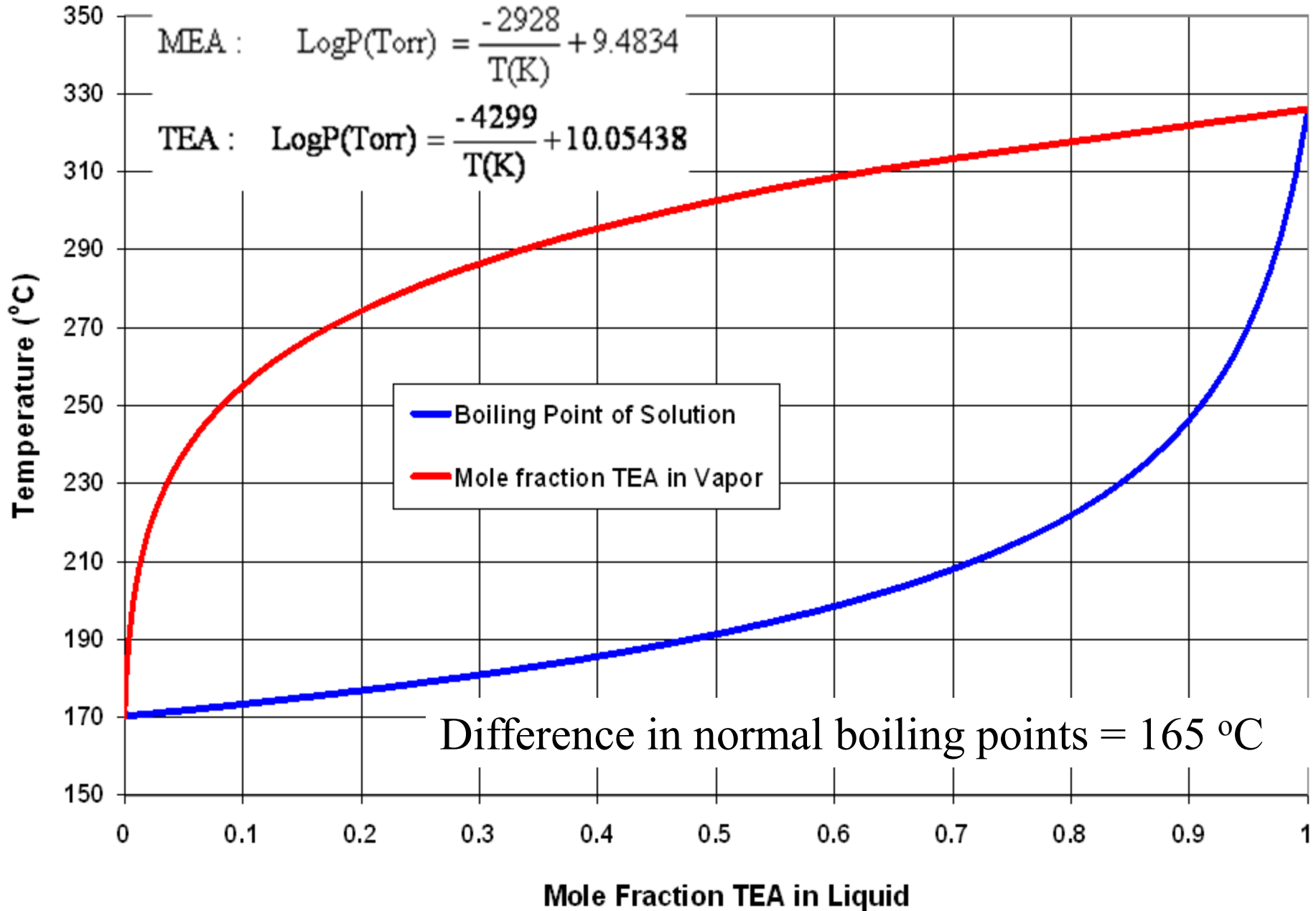


$$=10^{((-2928/(H2+273.15))+9.4834)*E2}+10^{((-4299/(H2+273.15))+10.05438)*F2}$$

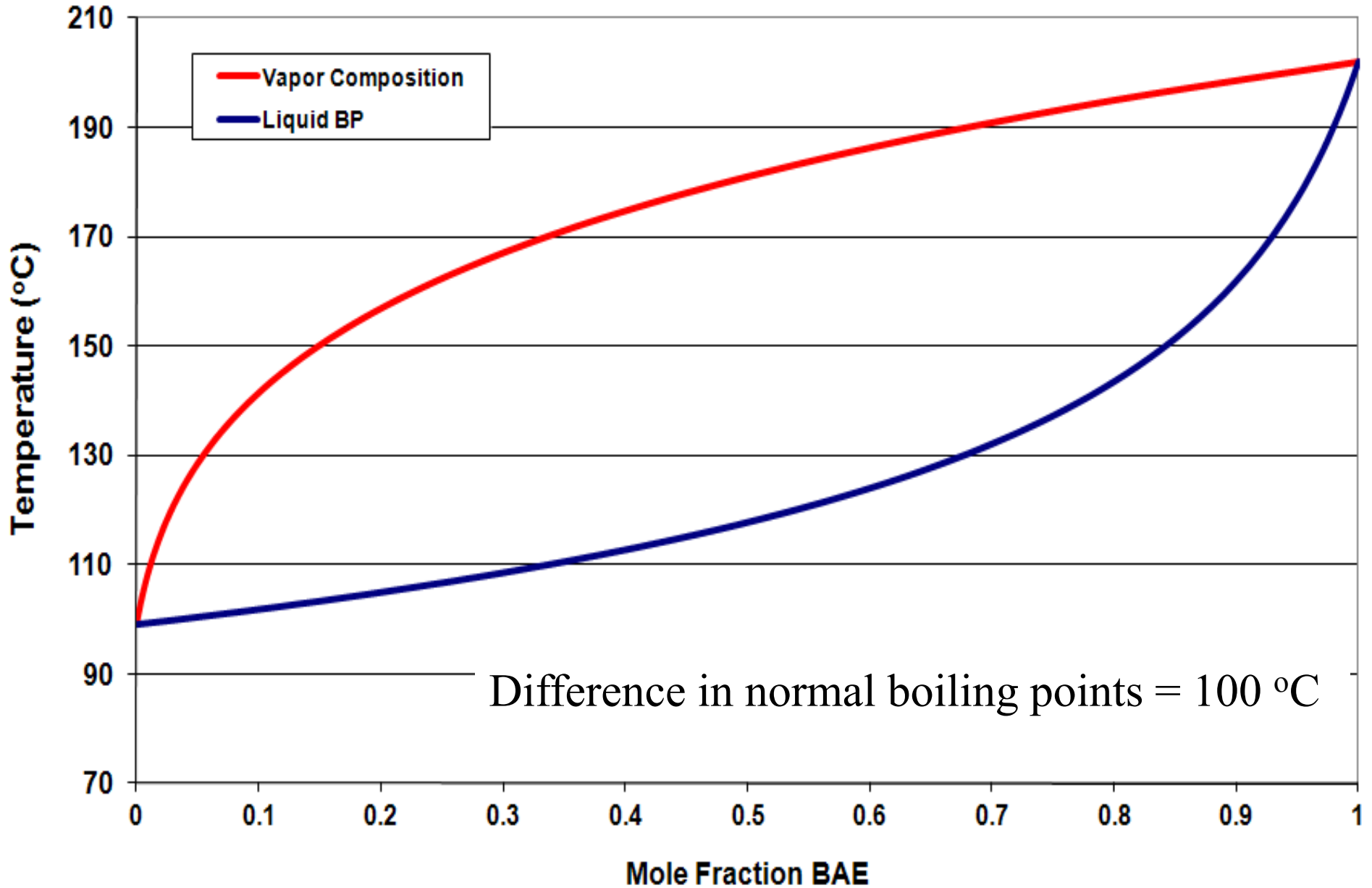
$$10^{((-4299/(H2+273.15))+10.05438)*F2/G2}$$



Raoult's Law (TEA/MEA)

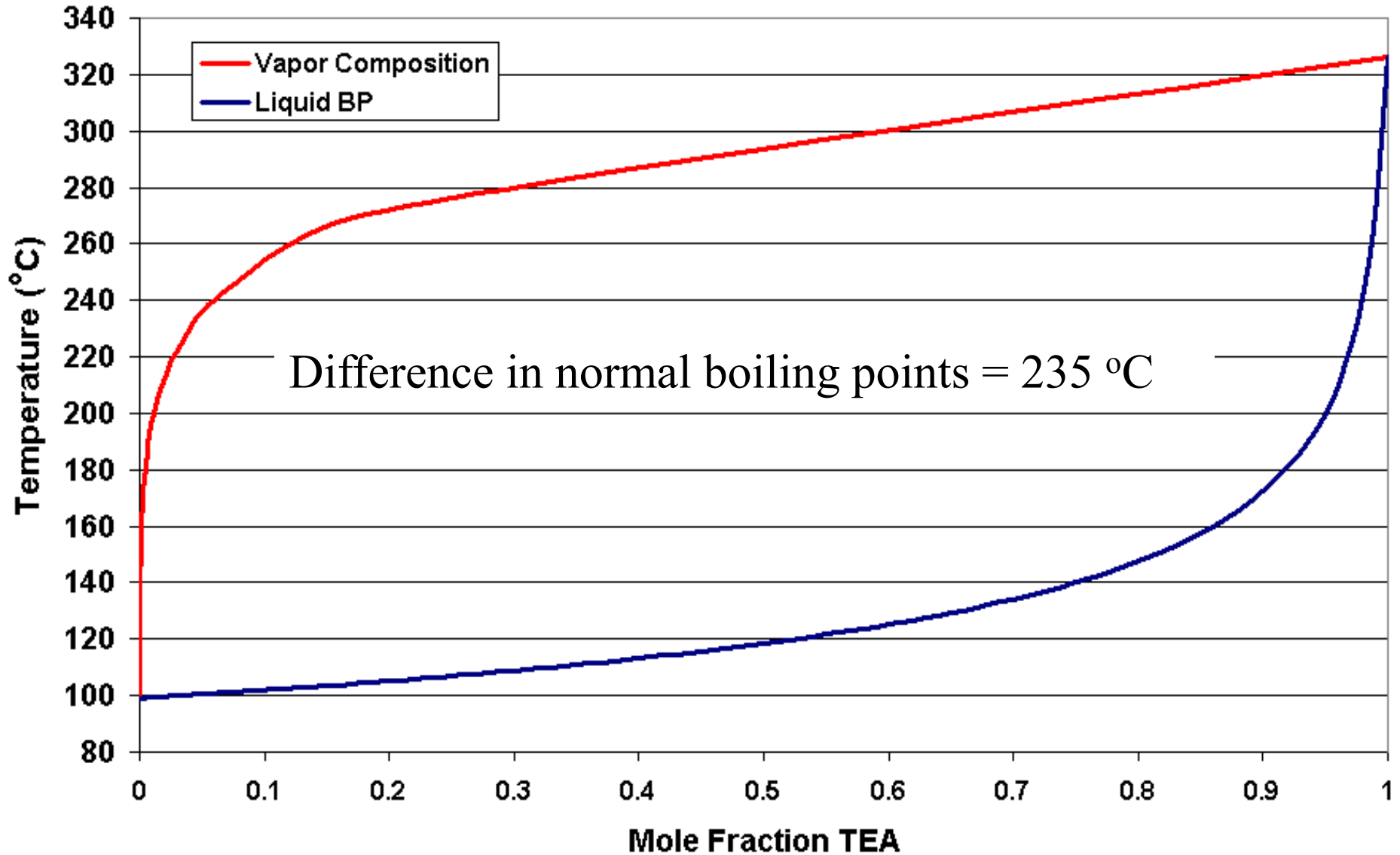


Phase Diagram Ideal BAE/Water System



The Impact of Water?

Phase Diagram Ideal TEA/Water System

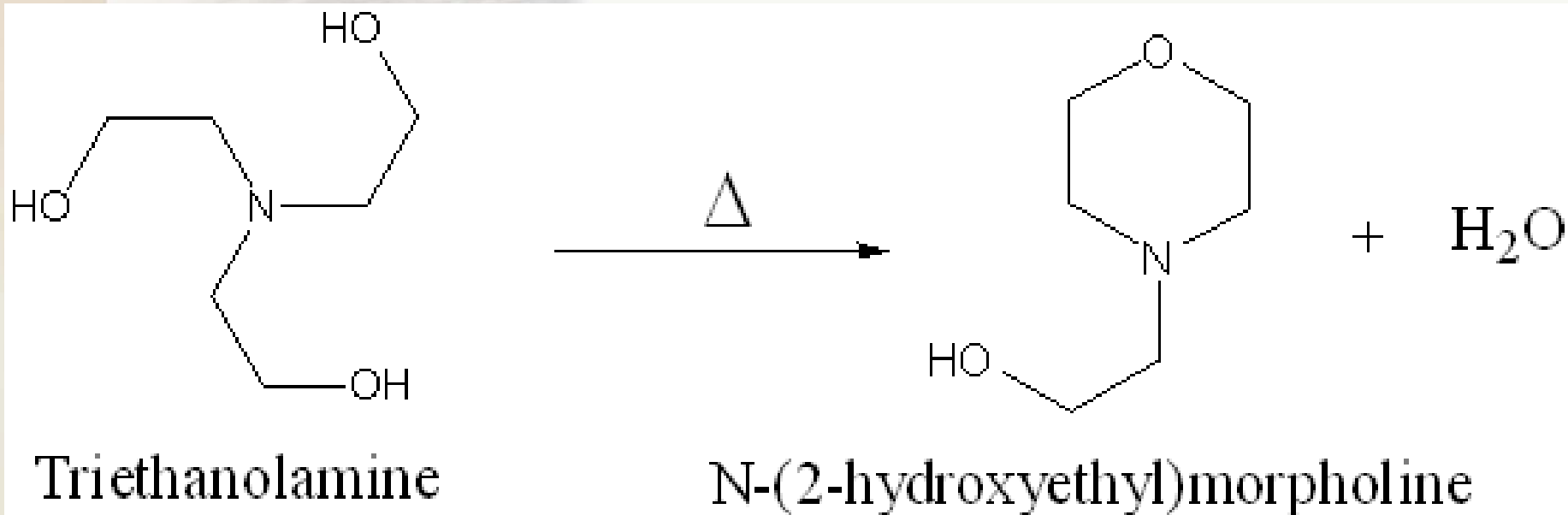


Why don't we just distill it at Atmospheric Pressure?

Continuous decomposition is the problem!



Distilling Triethanolamine (TEA) at 1 bar?

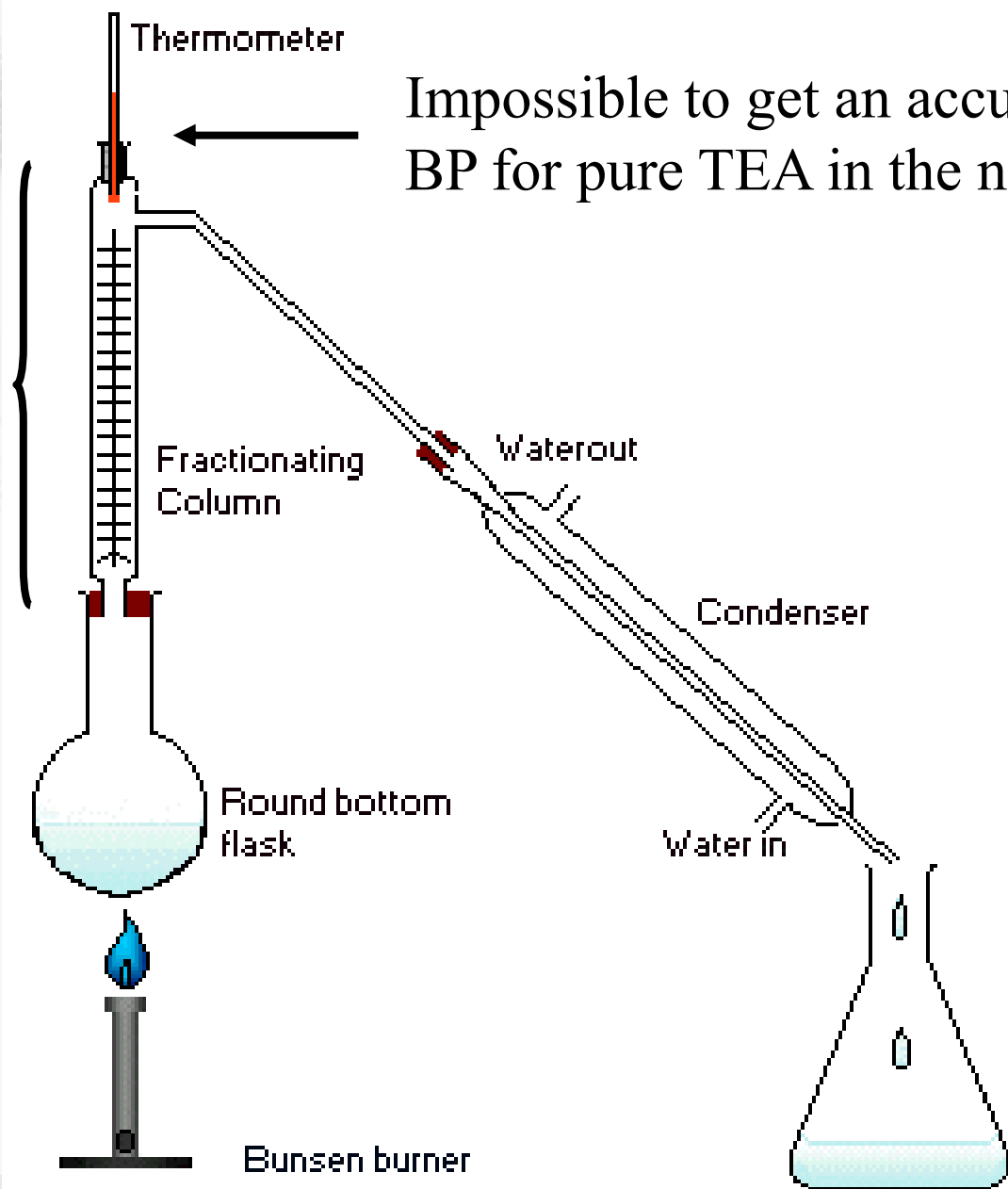


TEA: normal BP = 335 °C

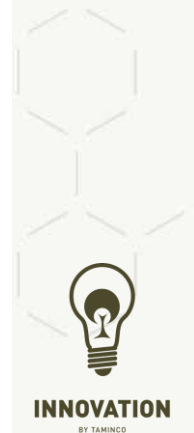
NHEM: normal BP = 224 °C



A temperature gradient sets up in the neck of the distillation!

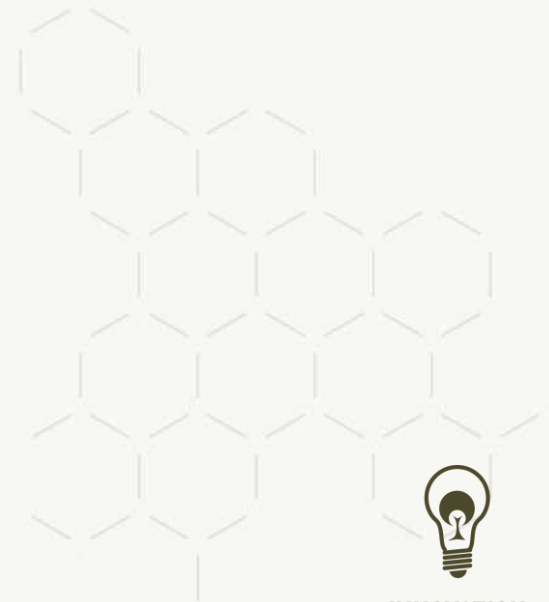


Impossible to get an accurate BP for pure TEA in the neck



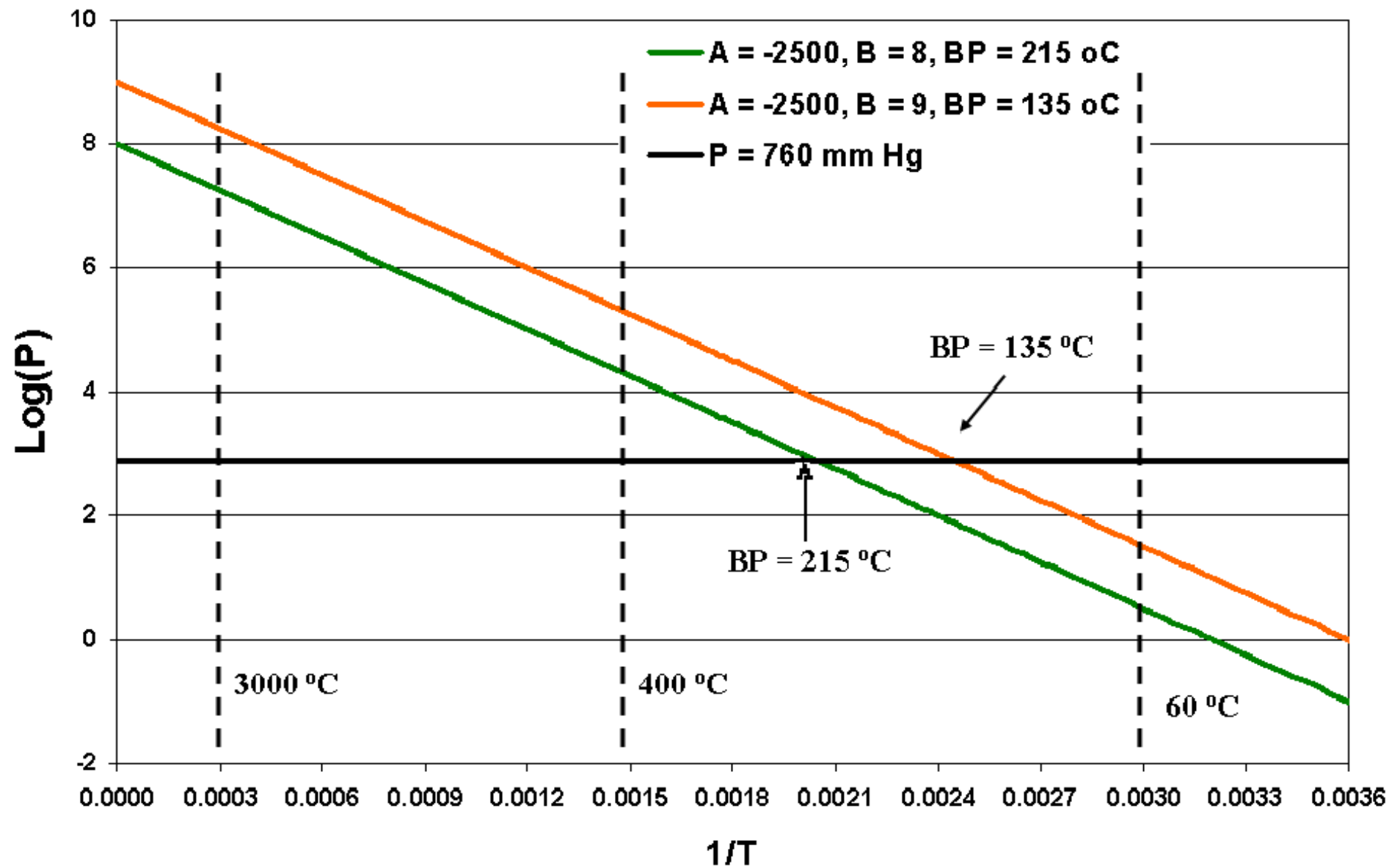


Relative Volatility Changes with Temperature



Theoretical VP Functions

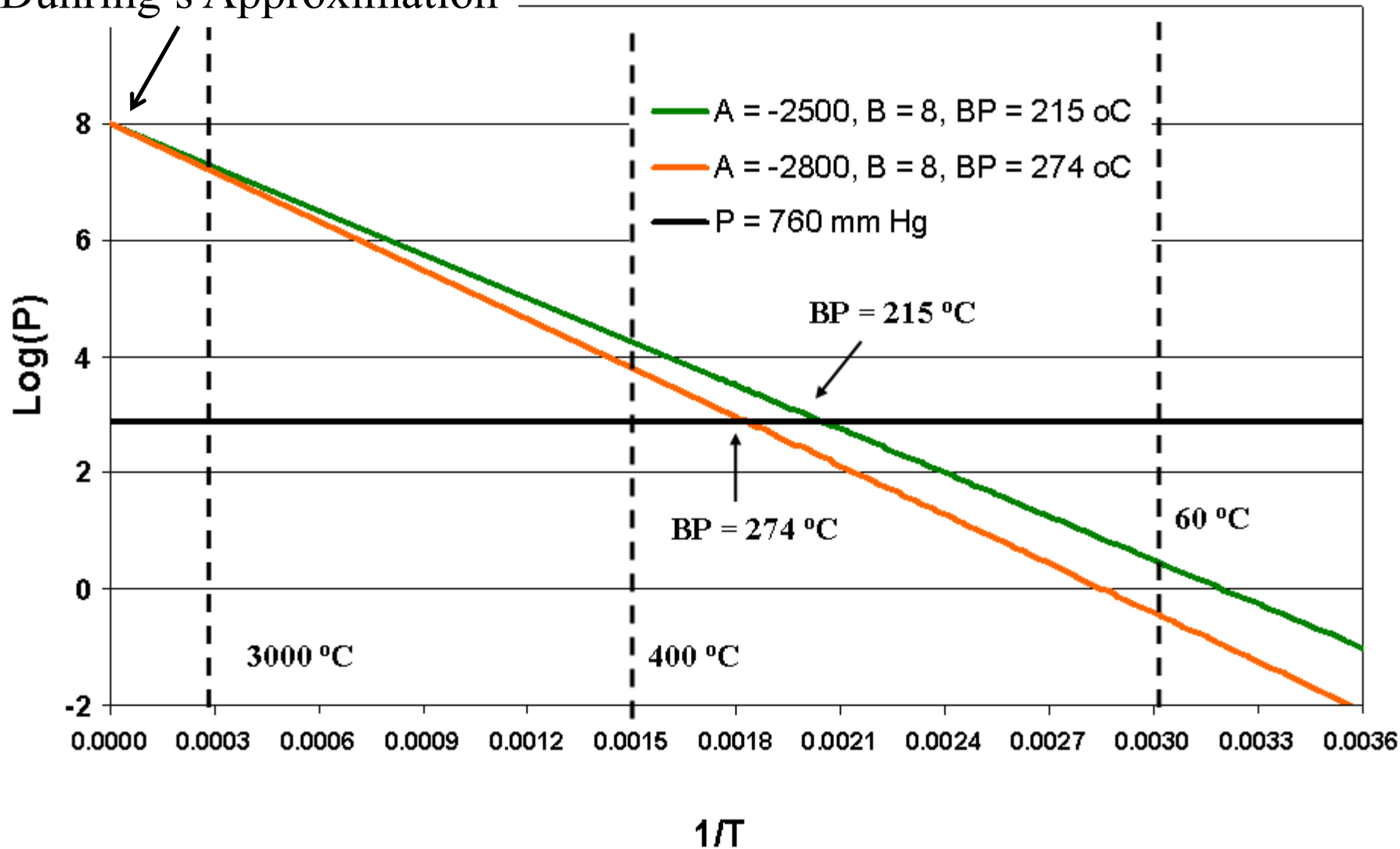
$$\text{Log}(P) = A/T + B$$



Theoretical VP Functions

$$\text{Log}(P) = A/T + B$$

Duhring's Approximation



VOC – or Not?
 Determination of an Important Environmental
 Parameter

Theoretical VP Functions

$$\text{Log}(P) = A/T + B$$

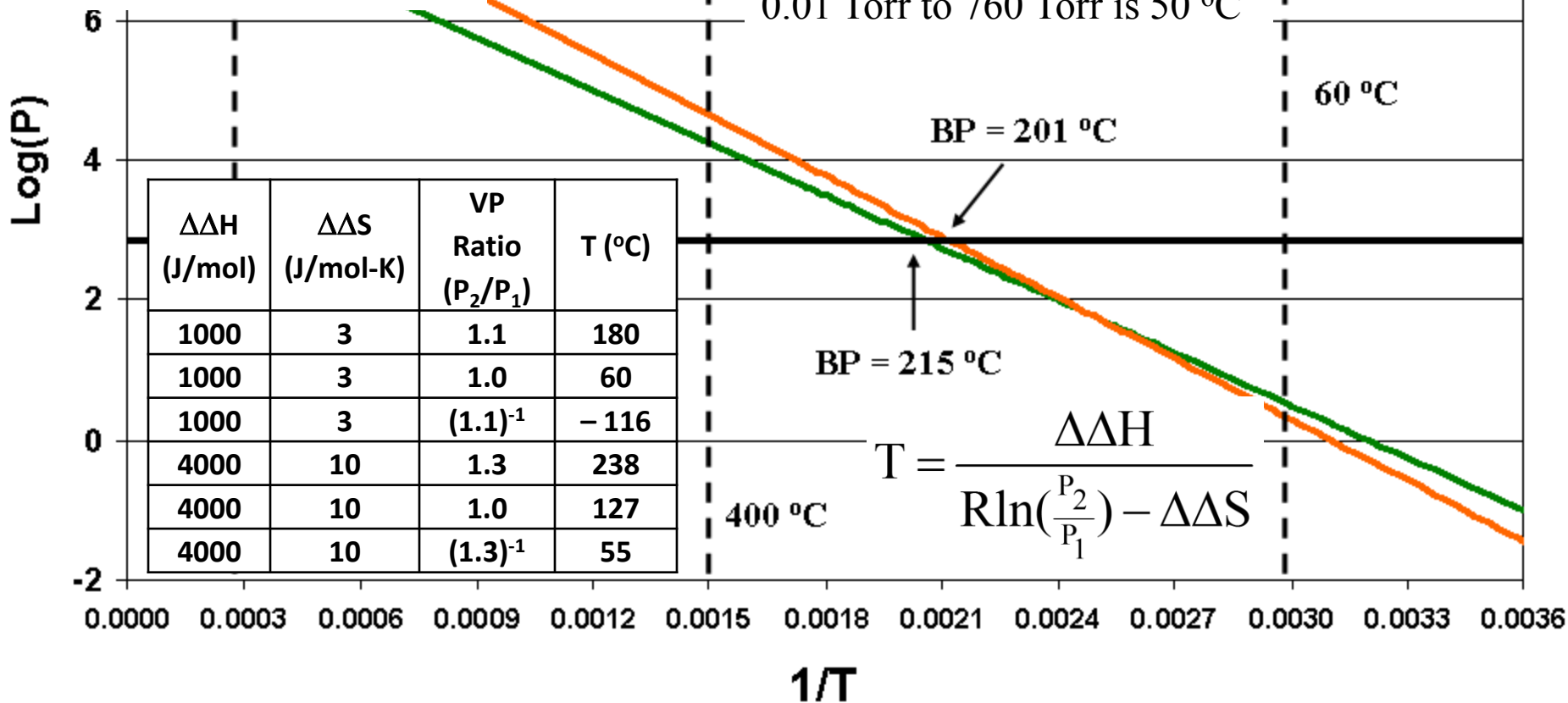
VOC or not: boiling point limits

A screening of the literature¹¹ for experimental values of the boiling point temperatures and vapour pressures at 23°C gave the following:

- no organic solvents boiling below 170°C have a vapour pressure below 10 Pa at 23°C
- all solvents boiling above 260°C have a vapour pressure which is below 10 Pa at 23°C
- only three solvents, two ethers and a chlorinated compound, were found to have a vapour pressure above 10 Pa in the boiling point range 235-260°C
- for common organic solvents such as linear hydrocarbons, alcohols and polyols the boiling point is below 220°C before the solvents become a VOC according to their vapour pressure at room temperature.

- A = -2500, B = 8, BP = 215 °C
- A = -2900, B = 9, BP = 201 °C
- P = 760 mm Hg

Average ΔT inversion from
 0.01 Torr to 760 Torr is 50 °C

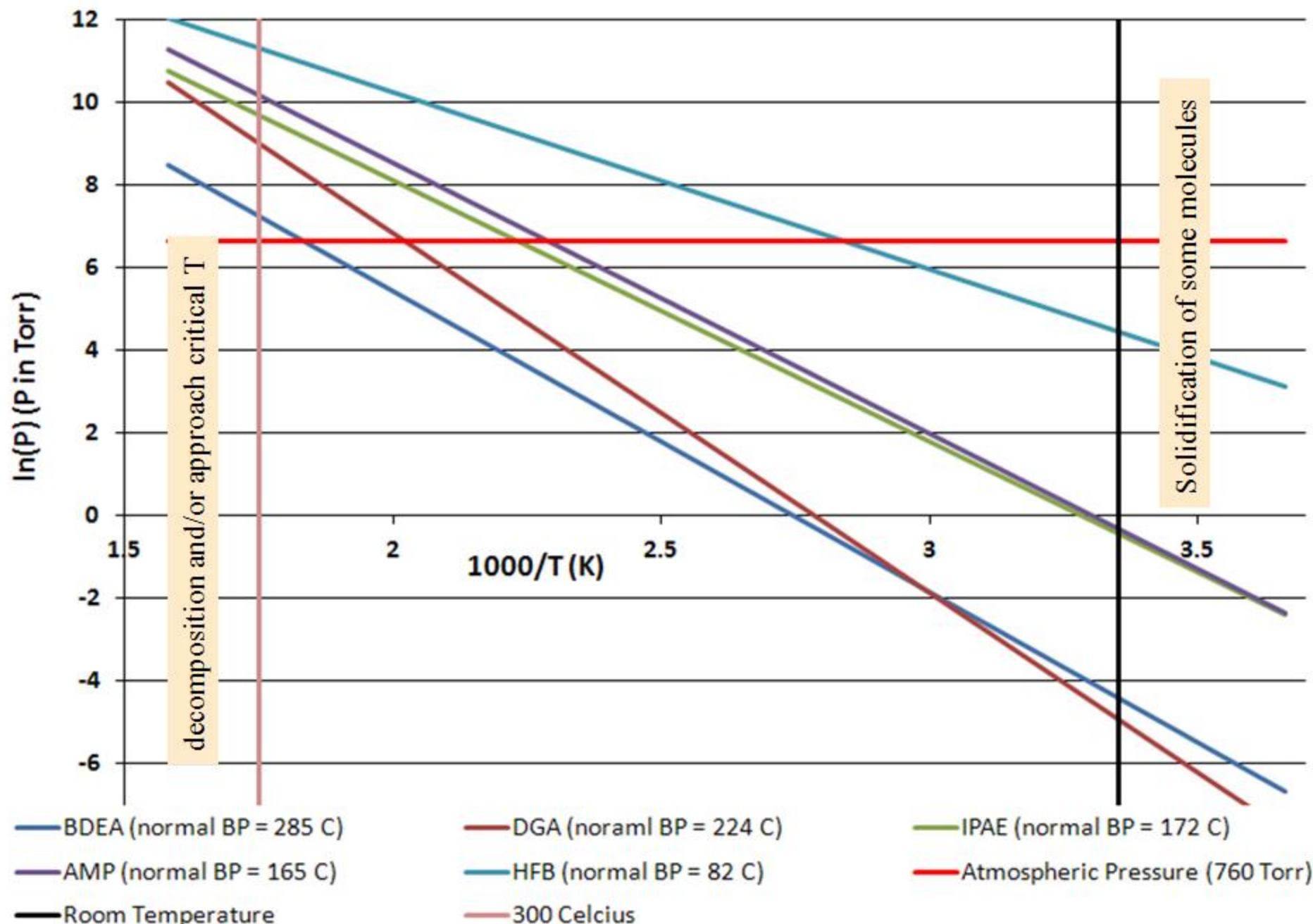


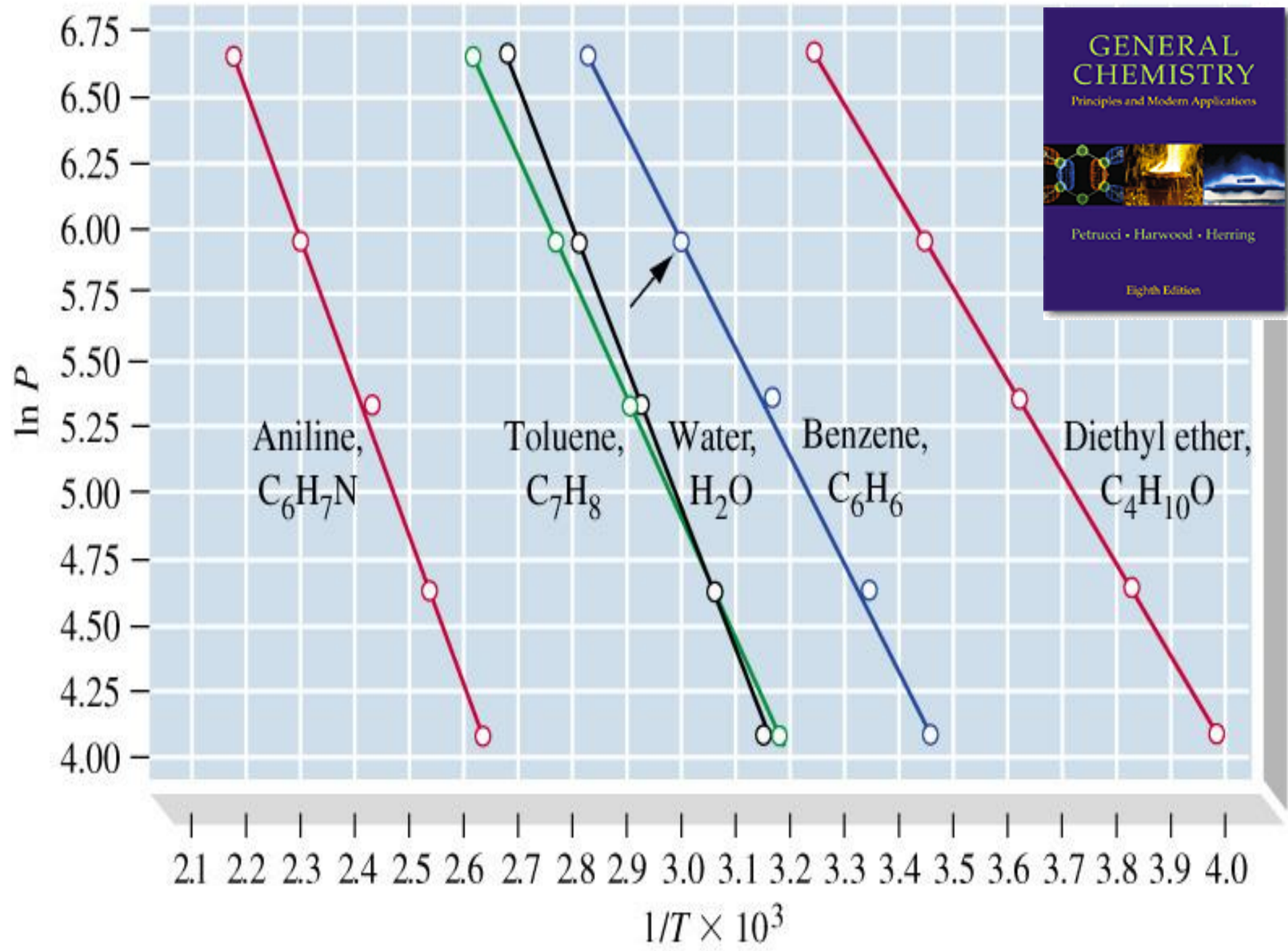
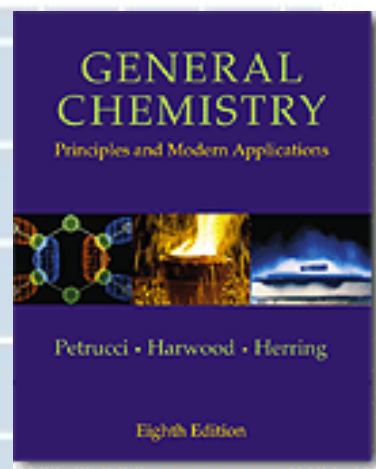
Real Relative Volatility

Measure as close to the use temperature as is possible

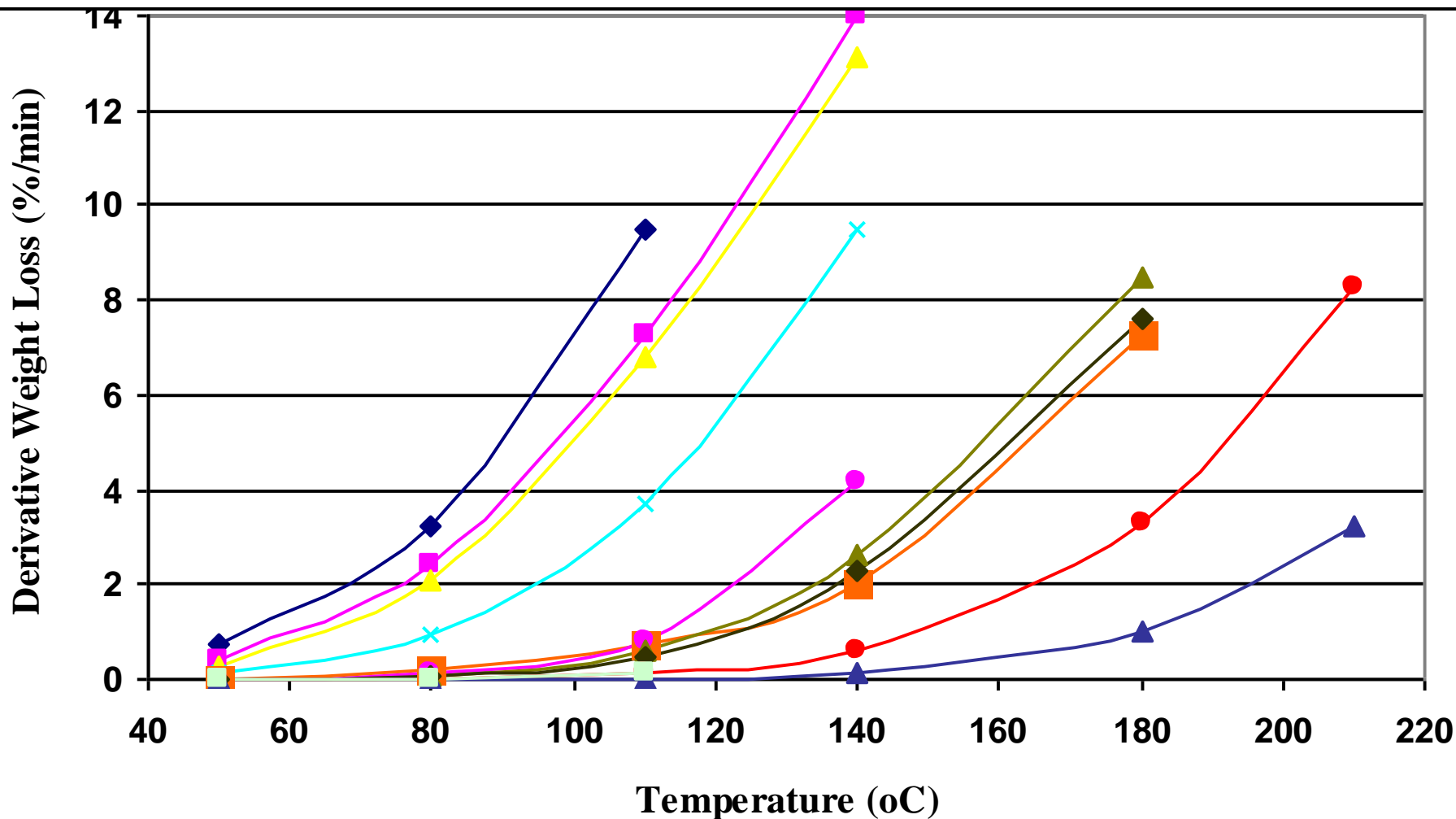


Log P versus 1000/T Correlations (real data for 5 different molecules)

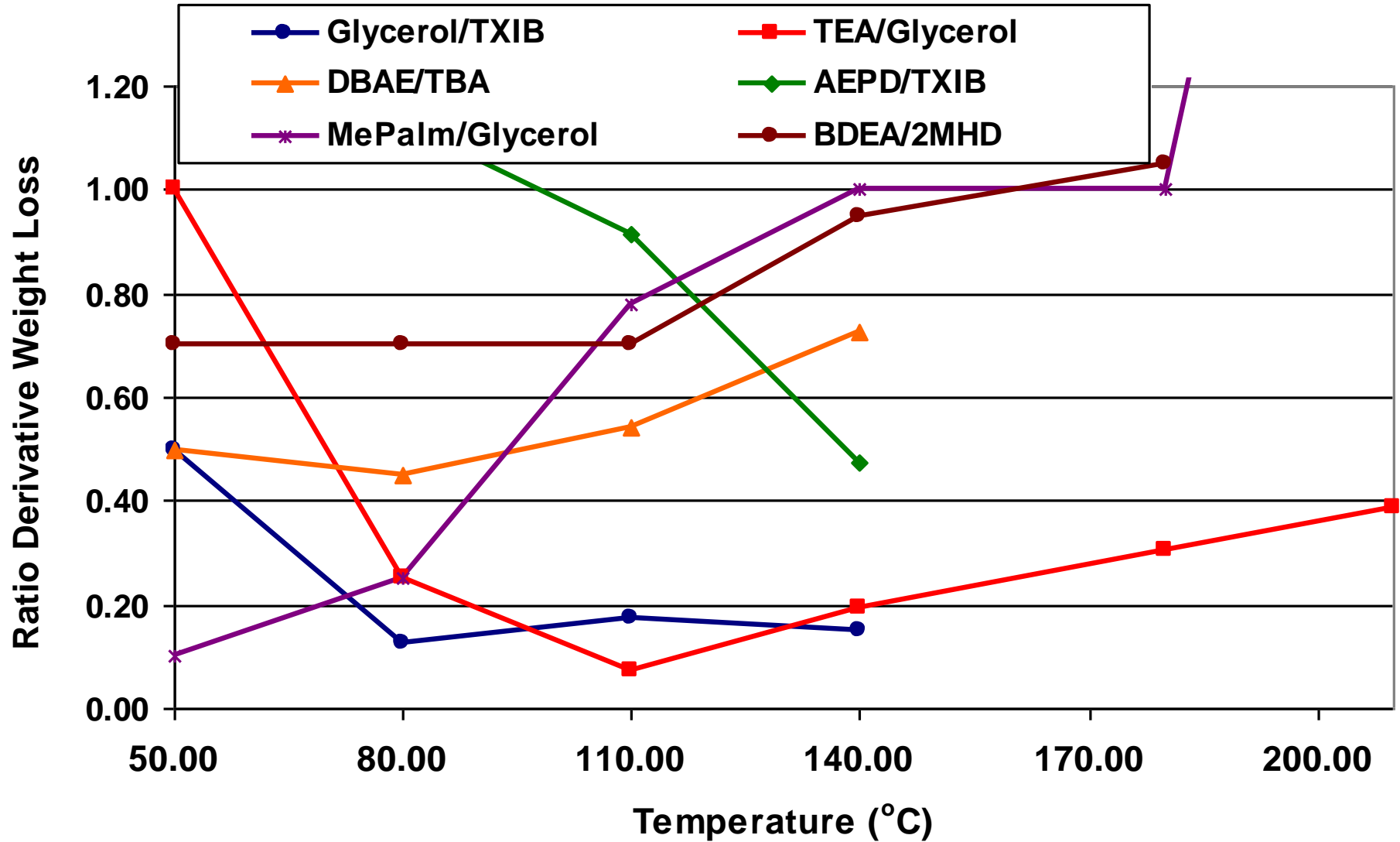




Derivative Weight Loss as a function of Temperature



Exemplary Derivative Weight Loss Ratios



What about GC Rt as an assessment of volatility?

Correlations of GC Rt with volatility are sometimes OK for homologous series of molecules.

Relationship not good across different types of molecules

Isothermal GC experiments used like BP versus absolute P, but the method needs an anchor



The GC Conundrum: 1/Rt does not really match volatility

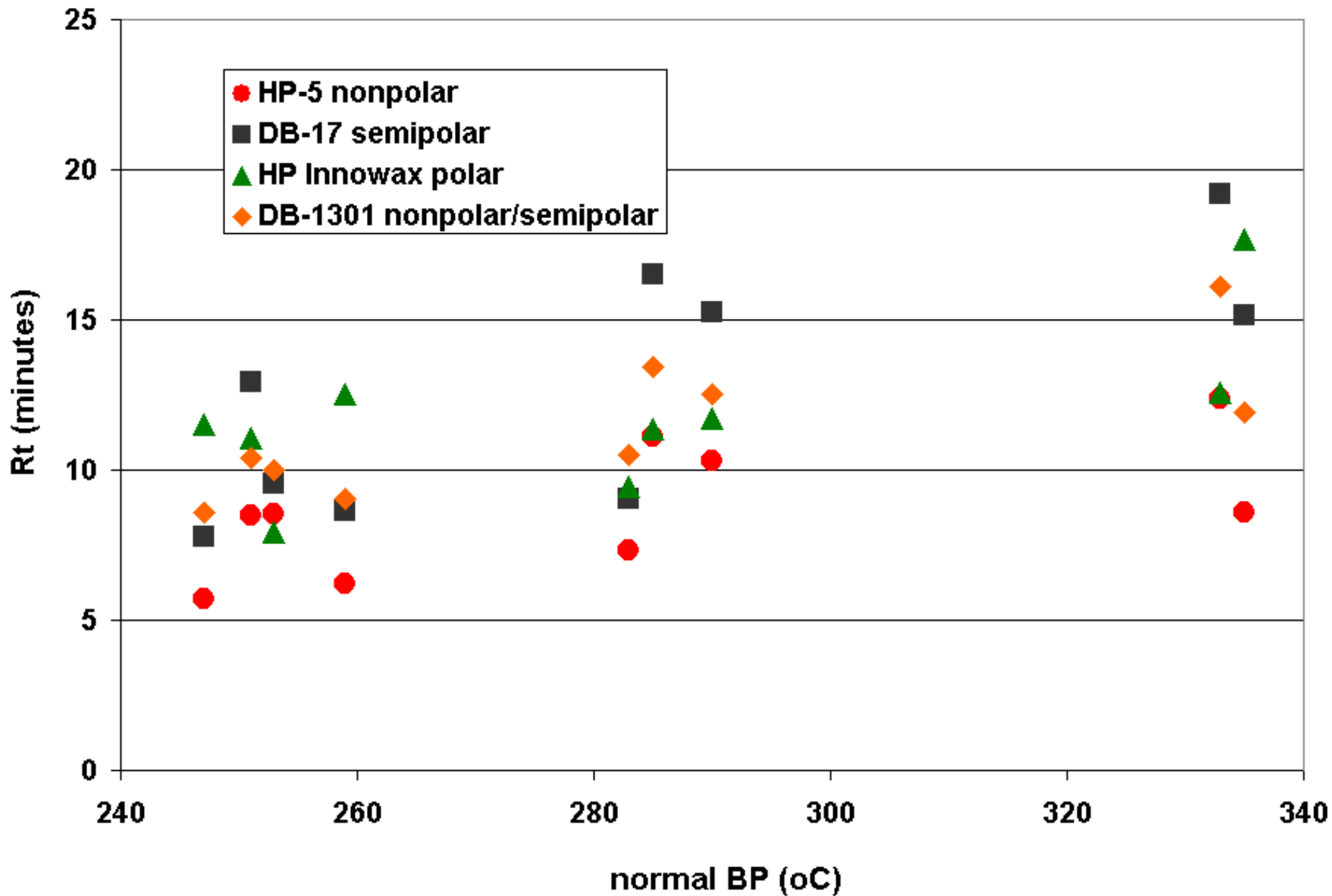
HP-5 (apolar)		
Compound	boiling point °C	RT min
Methyldiethanolamine	247	5.70
2-amino 2-ethyl 1,3 propaandiol	259	6.20
Butyldiethanolamine	283	7.30
Diethyladipate	251	8.50
Tetradecane	253	8.53
Triethanolamine	335	8.60
BisDMAPA-PO	290	10.30
Tris-DMAPA	285	11.10

DB-1301 (apolar)		
Compound	boiling point °C	RT min
Methyldiethanolamine	247	8.58
2-amino 2-ethyl 1,3 propaandiol	259	9.04
Tetradecane	253	10.00
Diethyladipate	251	10.40
Butyldiethanolamine	283	10.52
Triethanolamine	335	11.91
BisDMAPA-PO	290	12.55
Tris-DMAPA	285	13.42
Methyl palmitate	333	16.10

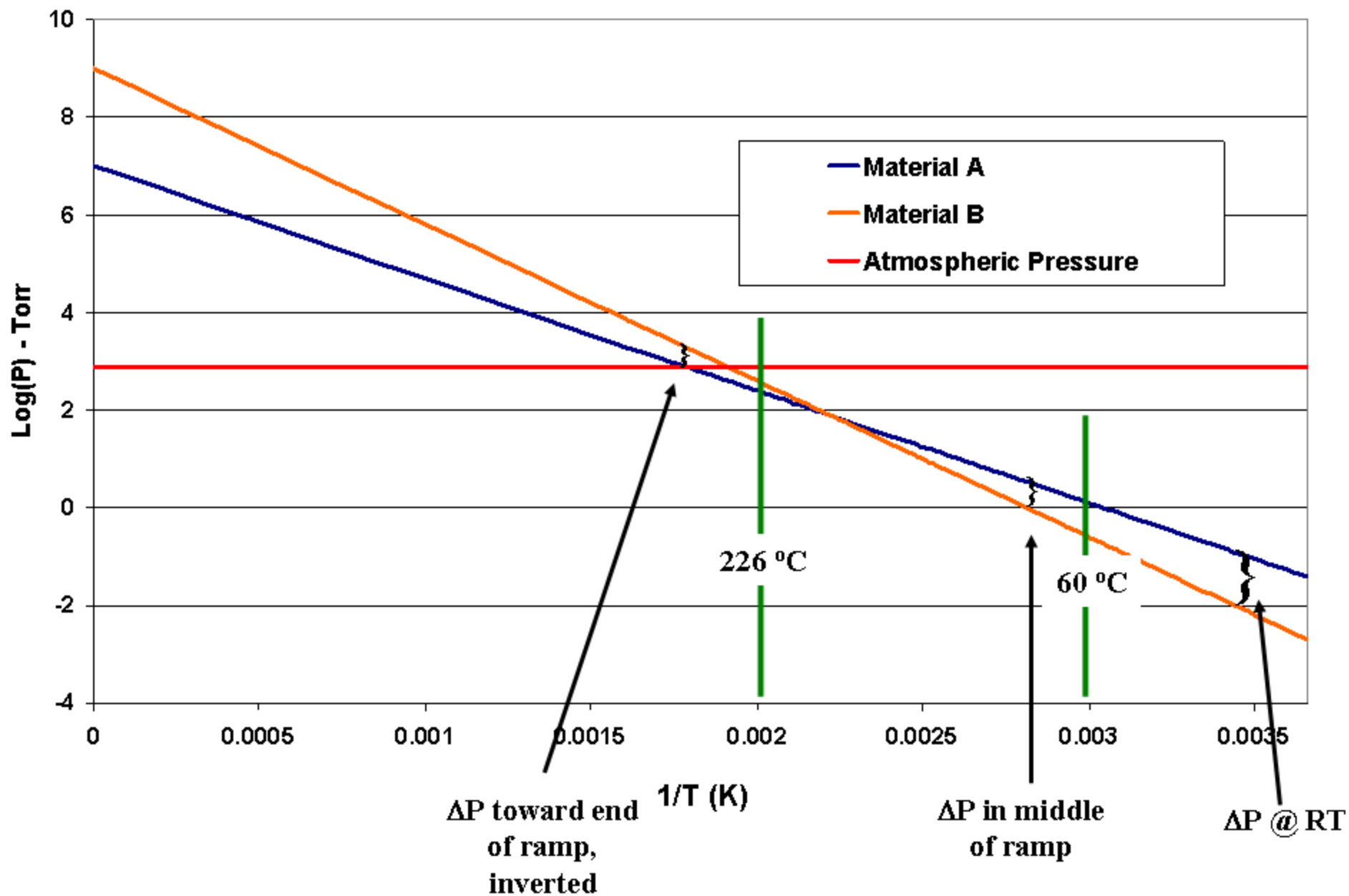
HP-Innowax (polar)		
Compound	boiling point °C	RT min
Tetradecane	253	7.94
Butyldiethanolamine	283	9.45
Diethyladipate	251	11.05
Tris-DMAPA	285	11.35
Methyldiethanolamine	247	11.50
BisDMAPA-PO	290	11.70
2-amino 2-ethyl 1,3 propaandiol	259	12.53
Triethanolamine	335	17.70

DB-17 (semi-polar)		
Compound	boiling point °C	RT min
Methyldiethanolamine	247	7.80
2-amino 2-ethyl 1,3 propaandiol	259	8.65
Butyldiethanolamine	283	9.05
Tetradecane	253	9.55
Diethyladipate	251	12.95
Triethanolamine	335	15.15
BisDMAPA-PO	290	15.25
Tris-DMAPA	285	16.50

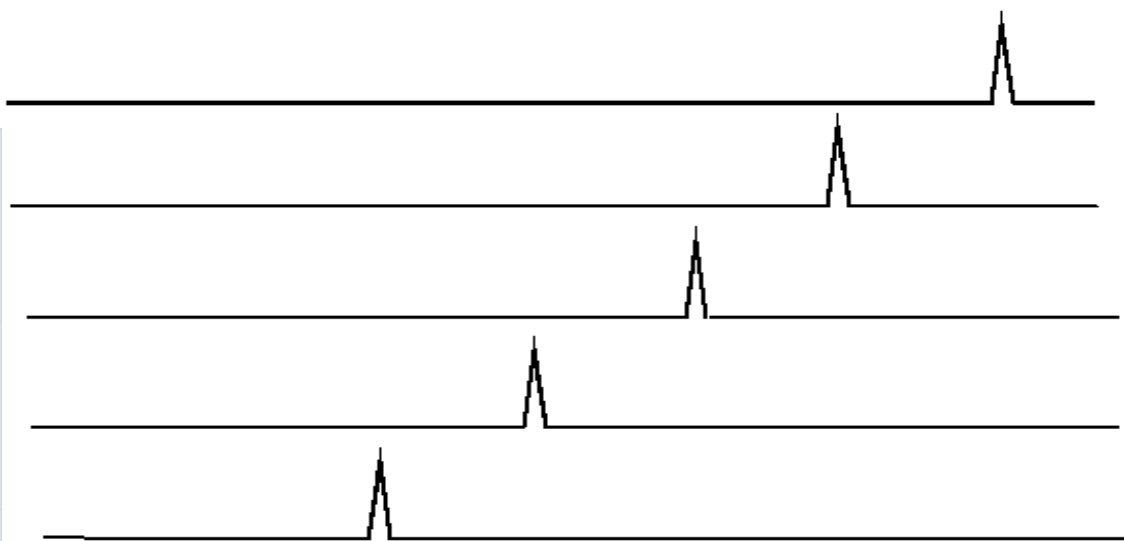




GC ramp integrates differential ΔVP over large T range



GC Rt data must be isothermal and must be anchored



T = 50 °C, Rt = 20 minutes

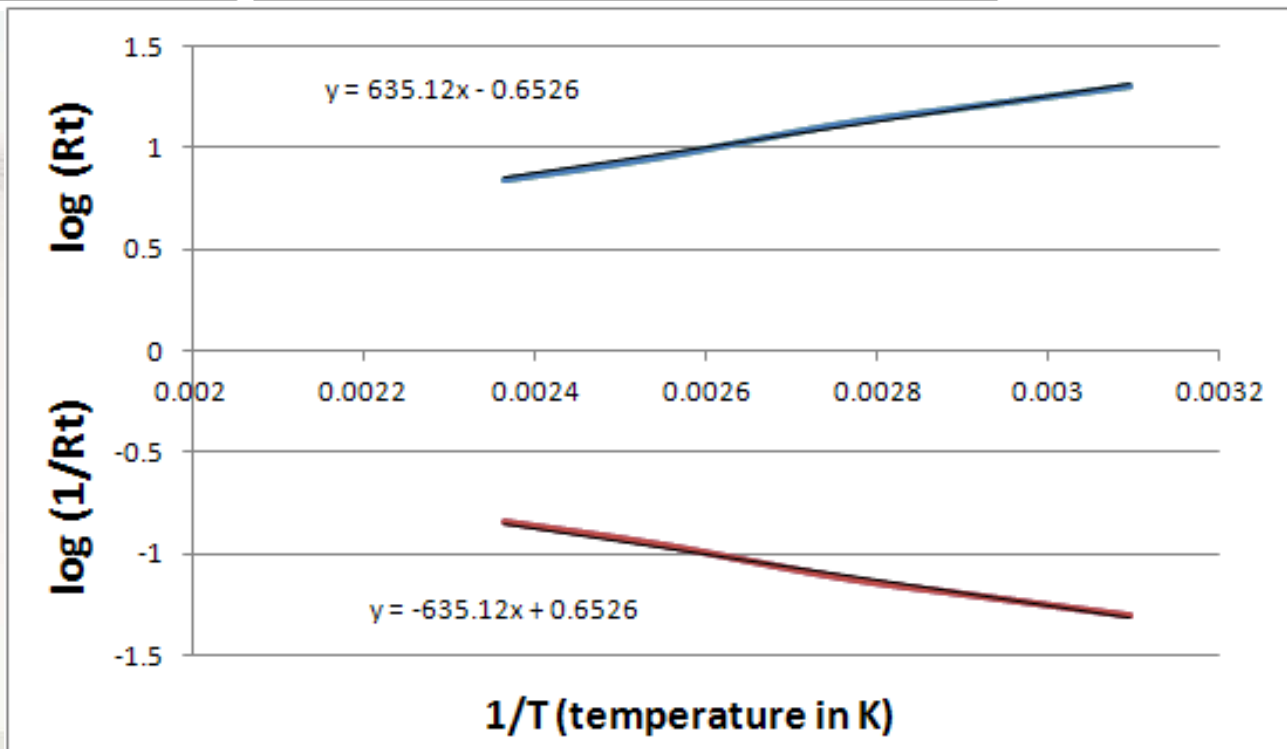
T = 70 °C, Rt = 16 minutes

T = 90 °C, Rt = 13 minutes

T = 120 °C, Rt = 9 minutes

T = 150 °C, Rt = 7 minutes

Rt (minutes)	T (°C)	T (K)	1/T (K)	log(Rt)	1/Rt	log(1/Rt)
20	50	323.15	0.003094538	1.301029996	0.05	-1.301029996
16	70	343.15	0.002914177	1.204119983	0.0625	-1.204119983
13	90	363.15	0.002753683	1.113943352	0.076923077	-1.113943352
9	120	393.15	0.002543558	0.954242509	0.111111111	-0.954242509
7	150	423.15	0.002363228	0.84509804	0.142857143	-0.84509804



Thermal Analysis Methods

TGA

DTA/TGA

DSC

Hybrid Methods



Derivative Weight Loss versus Temperature

Compound	dW/dt @ 50 °C	dW/dt @ 80 °C	dW/dt @ 110 °C
Methyl Palmitate	ND	0.005 >180 min	0.11 (12 min)
TEA	0.005 180 min	0.005 150 min	0.01 60 min
Glycerol	0.005 180 min	0.02 37 min	0.14 6 min
BDEA	0.005 180 min	0.08 14 min	0.46 2 min
2-methylhexadecane	0.007 130 minutes	0.10 11.5 min	0.64 2 min
Hexadecane	0.01 120 min	0.10 14 min	0.62 2 min
TXIB	0.01 80 min	0.16 6 min	0.80 1 min
AEPD	0.03 40 min	0.18 6 min	0.73 1.7 min
DBAE	0.15 8 min	0.94 1.3 min	3.7 0.33 min
TBA	0.3 3 min	2.1 0.6 min	6.8 0.2 min
MEA	0.40 3 min	2.4 0.5 min	7.4 0.2 min
AMP	0.76 1.6 min	3.2 0.4 min	9.5 0.1 min

The derivative weight loss (% weight loss per minute) of 12 compounds at different temperatures after 1.25% (\approx 40 mg total weight, 0.5 mg weight loss) of material evaporated with nitrogen purge. The time in minutes at which the derivative weight loss was taken is given below the weight loss value.

Glycerol

T (°C)	T (K)	1/T(K)	dW/dT	log(dW/dT)
50	323.15	0.003095	0.005	-2.301029996
80	353.15	0.002832	0.02	-1.698970004
110	383.15	0.00261	0.14	-0.853871964

BDEA

T (°C)	T (K)	1/T(K)	dW/dT	log(dW/dT)
50	323.15	0.003095	0.005	-2.301029996
80	353.15	0.002832	0.08	-1.096910013
110	383.15	0.00261	0.46	-0.337242168

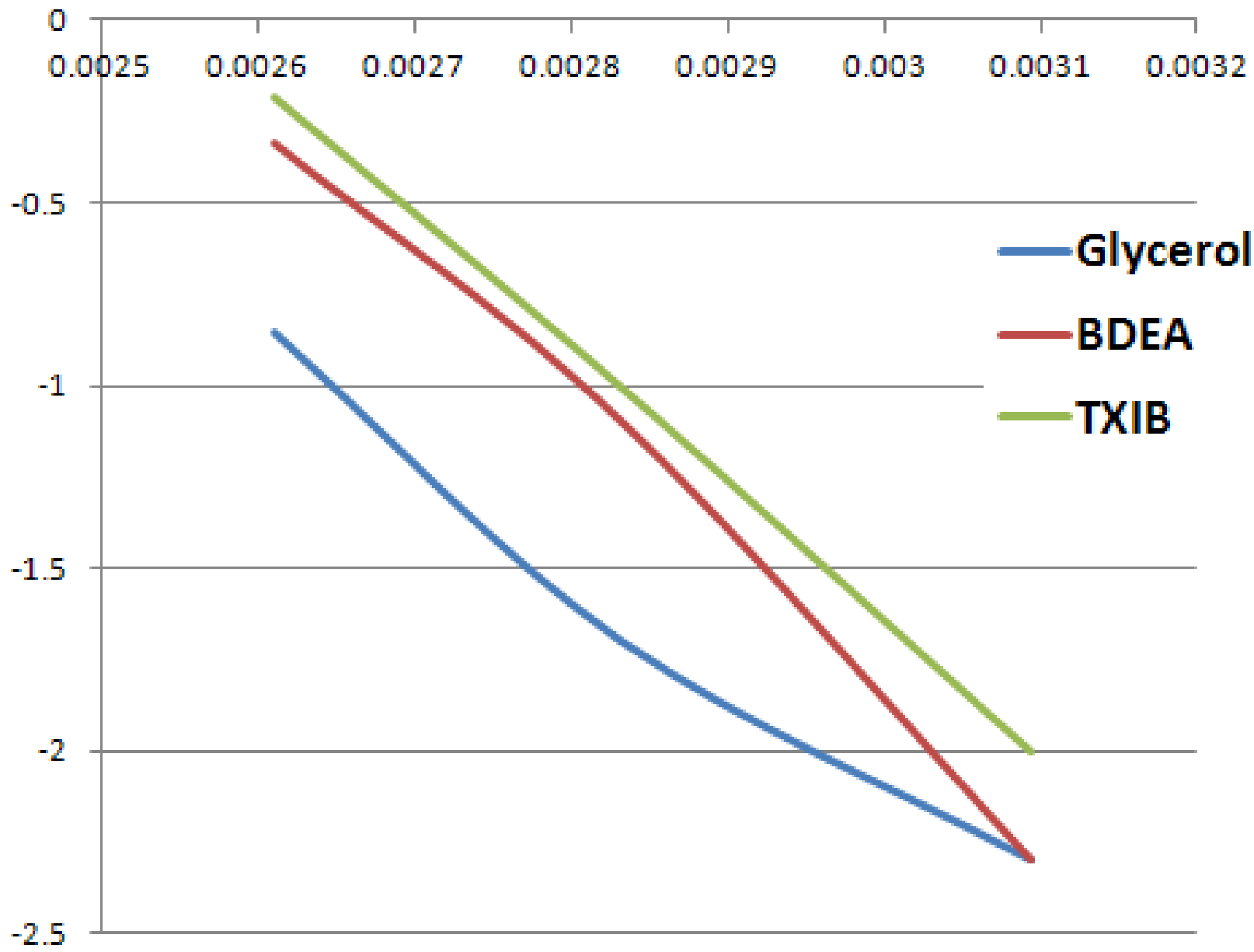
TXIB

T (°C)	T (K)	1/T(K)	dW/dT	log(dW/dT)
50	323.15	0.003095	0.01	-2
80	353.15	0.002832	0.1	-1
110	383.15	0.00261	0.62	-0.207608311



$1/T(K)$

$\log(dw/dT)$ in weight % per minute



Conclusions

- The normal boiling point of a “high boiling” material can be determined several ways. Various methods should track and be approximately equivalent, but they do not all yield exactly the same value.
- Real **relative** volatility changes with temperature.
- Continuous decomposition can impact the accuracy of normal boiling point determination.
- GC retention time comparisons are more prone to deviation from “real volatility” than are normal boiling points.

