

CBE 34487

7/7/20

# PHASE EQUILIBRIUM CALCULATIONS USING A CUBIC EQUATION OF STATE

--- REVIEW

BASE OUR CALCULATIONS ON

FUGACITY

$$f_i^I = f_i^II$$

# FOR CONVIENCE IN CALCULATIONS

— BASED IN PART ON INTUITIVENESS AND SUCCESS OF RAOULT'S LAW

WE DEFINE A FUNCTION WITH DIMENSIONS OF PRESSURE THAT DEMONSTRATES CLEARLY THE DEGREE OF DEVIATION FROM IDEALITY

$$f \equiv P \exp \left\{ \frac{G(T,P) - G^{\text{IDEAL GAS}}(T,P)}{RT} \right\}$$

$$f = P \exp \left\{ \frac{1}{RT} \int_0^P \left( \underset{\substack{\text{REAL} \\ \text{GAS OR} \\ \text{LIQUID}}}{V} - \frac{RT}{P} \right) dP \right\}$$

UNITS OF PRESSURE                      REAL GAS OR LIQUID                      IDEAL GAS

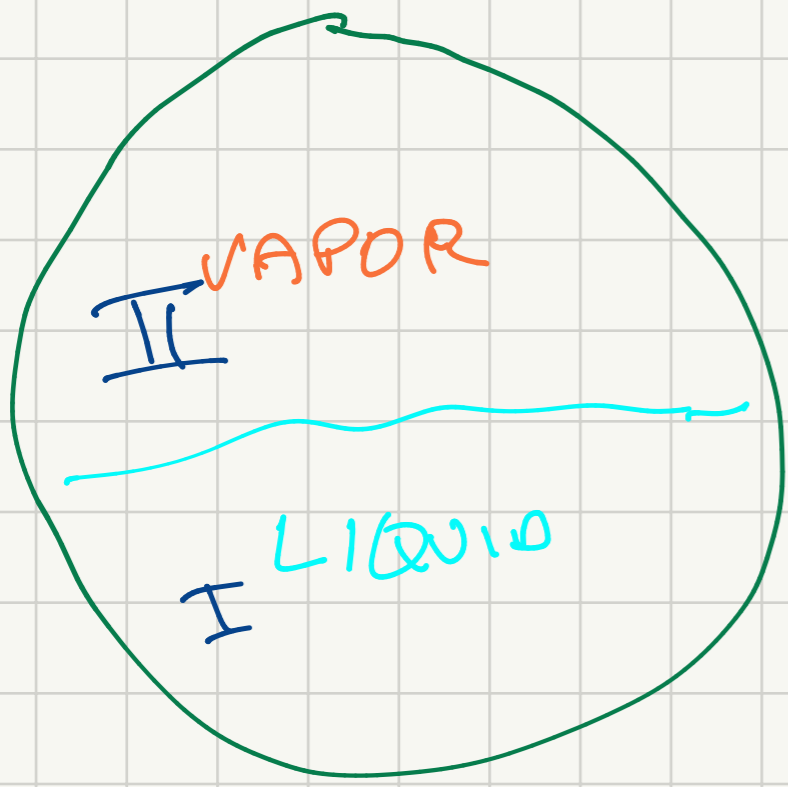
\* CAN BE CALCULATED FROM VOLUMETRIC

ASTOUNDINGLY \* INFORMATION ABOUT A SUBSTANCE

USEFUL \*

\* CAN GET THIS FROM AN EQUATION OF STATE

SO THE CONDITIONS OF  
 VAPOR-LIQUID COEXISTENCE  
 FOR A PURE SUBSTANCE  
 CAN BE OBTAINED USING:



$$f^I = f^{II}$$

$$p_{exp} \left\{ \frac{1}{RT} \int_0^p \left( \frac{V^L - \frac{RT}{p}}{p} \right) dp \right\} = p_{exp} \left\{ \frac{1}{RT} \int_0^p \left( \frac{V^G - \frac{RT}{p}}{p} \right) dp \right\}$$

↓ LIQUID
↓ VAPOR

ALSO  
 DEFINE

$$\phi \equiv \frac{f}{p} = \exp \left\{ \frac{1}{RT} \int_0^p \left( \frac{V - \frac{RT}{p}}{p} \right) dp \right\}$$

IF SUBSTANCE IS AN  
 IDEAL GAS

$$f = p, \quad \phi \equiv 1$$

THIS GIVES POSSIBILITY

$$f^L = f^V$$

$$\phi^L p = \phi^V p$$

$$\phi^L = \phi^V$$

$$\phi \equiv \frac{f}{f^0} = \exp \left\{ \frac{1}{RT} \int_0^P \left( V - \frac{RT}{P} \right) dP \right\}$$

THIS AMAZINGNESS IS AUGMENTED  
BECAUSE FOR MANY SUBSTANCES  
IT IS POSSIBLE TO USE A  
CUBIC EQUATION OF STATE TO  
GET  $V$  "LOS ENDOUGH" EVEN  
FOR THE LIQUID.

LET'S SEE HOW: !!

HOW CAN AN EQUATION OF STATE  
GET A GOOD VALUE FOR LIQUID FUGACITY?

$$f = p \exp \left\{ \frac{1}{RT} \int_0^p \left( \underline{V}^L - \frac{RT}{p} \right) dp \right\}$$

BREAK INTO  
2 PIECES.

LIQUID HAS NOT YET  
CONDENSED SAT

$\underline{V} \approx \frac{RT}{p}$   
"LIQUID" IS  
IDEAL  
GAS

$$= p \exp \left\{ \frac{1}{RT} \int_0^p \left( \underline{V} - \frac{RT}{p} \right) dp \right\} +$$

AFTER CONDENSATION  
LIQUID VOLUME  
IS NOT A  
FUNCTION OF  
PRESSURE

$$\int_{p^{SAT}}^p \left( \underline{V}_L - \frac{RT}{p} \right) dp$$

$$= p \exp \left( \frac{1}{RT} \left( p \underline{V}_L - RT \ln \frac{p}{p^{SAT}} \right) \right)$$

$$= p^{SAT} \exp \left( \frac{p \underline{V}_L}{RT} \right)$$

THIS IS "z"  
FOR A LIQUID  
WHICH IS  
MUCH LESS  
THAN 1.

$\therefore$  SINCE  $\underline{V}_L \ll \frac{RT}{p}$

THE F.O.S DOESN'T HAVE

TO BE PARTICULARLY ACCURATE

TO GET CORRECT LIQUID FUGACITY

$$f^L = p^{VAP}$$

# "CUBIC" EQUATIONS OF STATE

VAN der Waals :

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

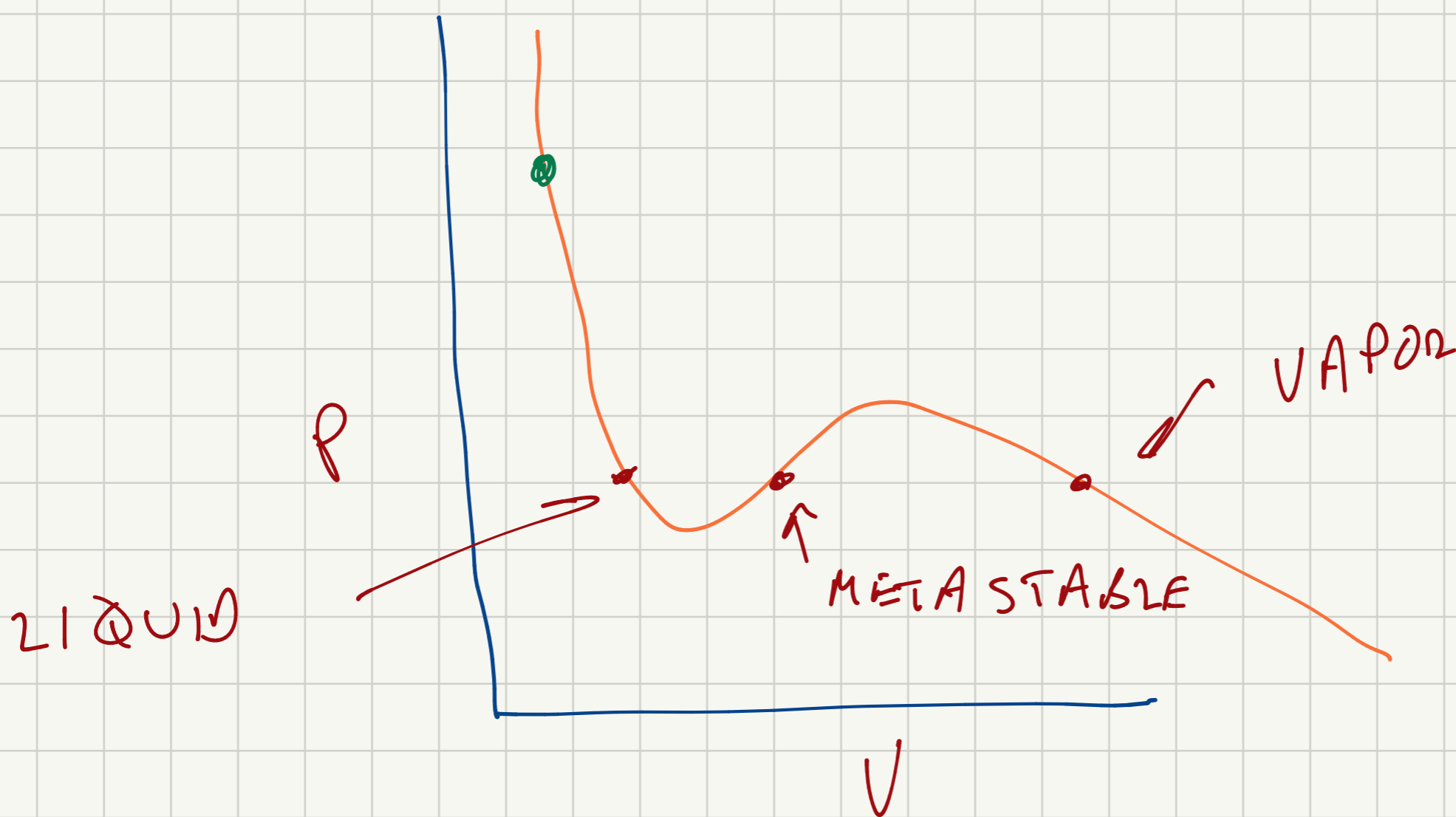
↙ ATTRACTION

↗ EXCLUDED VOLUME

IF YOU PICK  $T, P$   
3 ROOTS FOR  $V$

1 REAL — 2 COMPLEX CONJUGATE

3 — REAL



VAN DER WAALS DOES NOT  
WORK VERY WELL BUT  
PENG-ROBINSON (1976)

$$P = \frac{RT}{\underline{V}-b} - \frac{a(T)}{\underline{V}(\underline{V}+b)+b(\underline{V}-b)}$$

ENTHALPIES & ENTROPIES  
ARE ALSO COMPUTED USING  
E.O.S. WITH THE  
"IDEAL GAS HEAT CAPACITY"

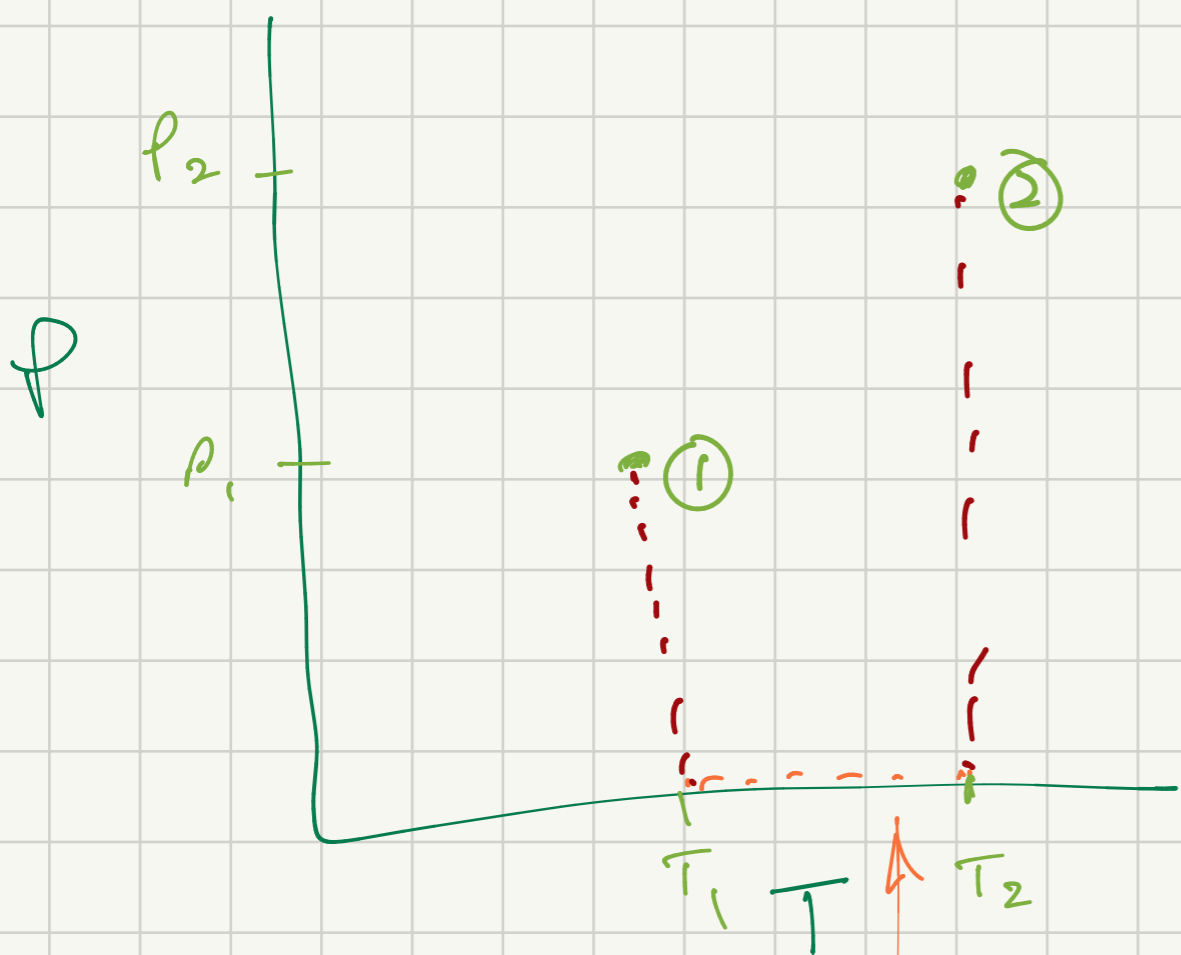
THIS "TRICK" IS TO USE A  
PATH THAT IS CONST T FROM  
 $P \rightarrow P=0$ , THEN CHANGE FOR  
AN IDEAL GAS  $\rightarrow$  THEN INCREASE  
 $P$  TO FINAL VALUE.



# CUBIC EQUATION OF STATE

GIVES  $P, V, T$  (VOLUMETRIC) BEHAVIOR.

HOW DO WE COMPLETE THE PICTURE FOR A SUBSTANCE AND GET "THERMAL" PROPERTIES, AND THUS CALCULATE,  $\Delta H, \Delta U, \Delta S,$   $Q$  AND MAYBE EVEN  $W$ , (WORK)?



$$H_2(T_2, P_2) - H_1(T_1, P_1) =$$

$$\int_{P_1, T_1}^{P=0, T_1} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP +$$

$$\int_{P=0, T_1}^{P=0, T_2} C_p^* dT + \int_{P=0, T_2}^{P_2, T_2} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

$$\Delta H^{IG} \parallel$$

$$\left( H - H^{IG} \right)$$

"DEPARTURE FUNCTION"



$$S^{ig}(T_2, P_2) - S^{ig}(T_1, P_1) = \int_{T_1}^{T_2} \frac{C_p^*}{T} dT - R \ln \frac{P_2}{P_1}$$

$$(S - S^{ig})_{T,P} = - \int_{T,P=0}^{T,P} \left( \frac{\partial U}{\partial T} \bigg|_P - \frac{R}{P} \right) dP$$

DEPARTURE FUNCTION

FOR PENG-ROBINSON EQUATION:

$$\underline{H}(T, P) - \underline{H}^{lb.}(T, P) = RT(z-1) + \frac{T \left( \frac{da}{dT} \right) - a}{2\sqrt{2}b}$$

$$\times \ln \left[ \frac{z + (1 + \sqrt{2})B}{z + (1 - \sqrt{2})B} \right]$$

$$z \equiv \frac{PV}{RT} \quad B \equiv \frac{Pb}{RT}$$

$$S(T, P) - S^{IG}(T, P) = R \ln(z-B) +$$

$$\frac{da}{dT} \ln \left[ \frac{z + (1 + \sqrt{2})B}{z + (1 - \sqrt{2})B} \right]$$

- WITH THIS ANALYTIC EXPRESSION, YOU CAN DETERMINE HOW  $a$  OR  $B$  AFFECTS, SAY C.O.P. FOR A REFRIGERATION CYCLE.
- CAN ALSO DO MIXTURES

# DIMENSIONAL ANALYSIS

QUICK EXAMPLE: WINDMILL POWER

$$\text{POWER} = \rho_{\text{AIR}} V_{\text{WIND}}^3 d_{\text{BLADE}}^2$$

SHOWS DIFFICULTY OF USING  
WIND FOR ELECTRICITY  
GENERATION

ANOTHER: PIPE FLOW  
(DATA MINING)

DATA  $Q, \Delta P$

I THINK  
THIS IS  
GENERAL

FROM DIMENSIONAL ANALYSIS, SEE  
NEED  $\rho$  OR  $\mu, D$  TO  
RELATE VARIABLES.

WHEN THIS DOESN'T WORK  
ALSO NEED  $\mu$

HW

# HEAT TRANSFER

$h$

$h$

$M$

$C_p$

$d$

$v$

$S$

$\Theta$

$L$

$M$

$^{\circ}K$

ENERGY

$$m \frac{L^2}{\Theta^2}$$

$$7 - 4 = 3$$

$$Nu \equiv \frac{hd}{k}, \quad Pr \equiv \frac{C_p M}{k}, \quad Re \equiv \frac{d v \rho}{\mu}$$

BUT IF YOU PICK THERMAL ENERGY AS DIFFERENT FROM  $m v^2$

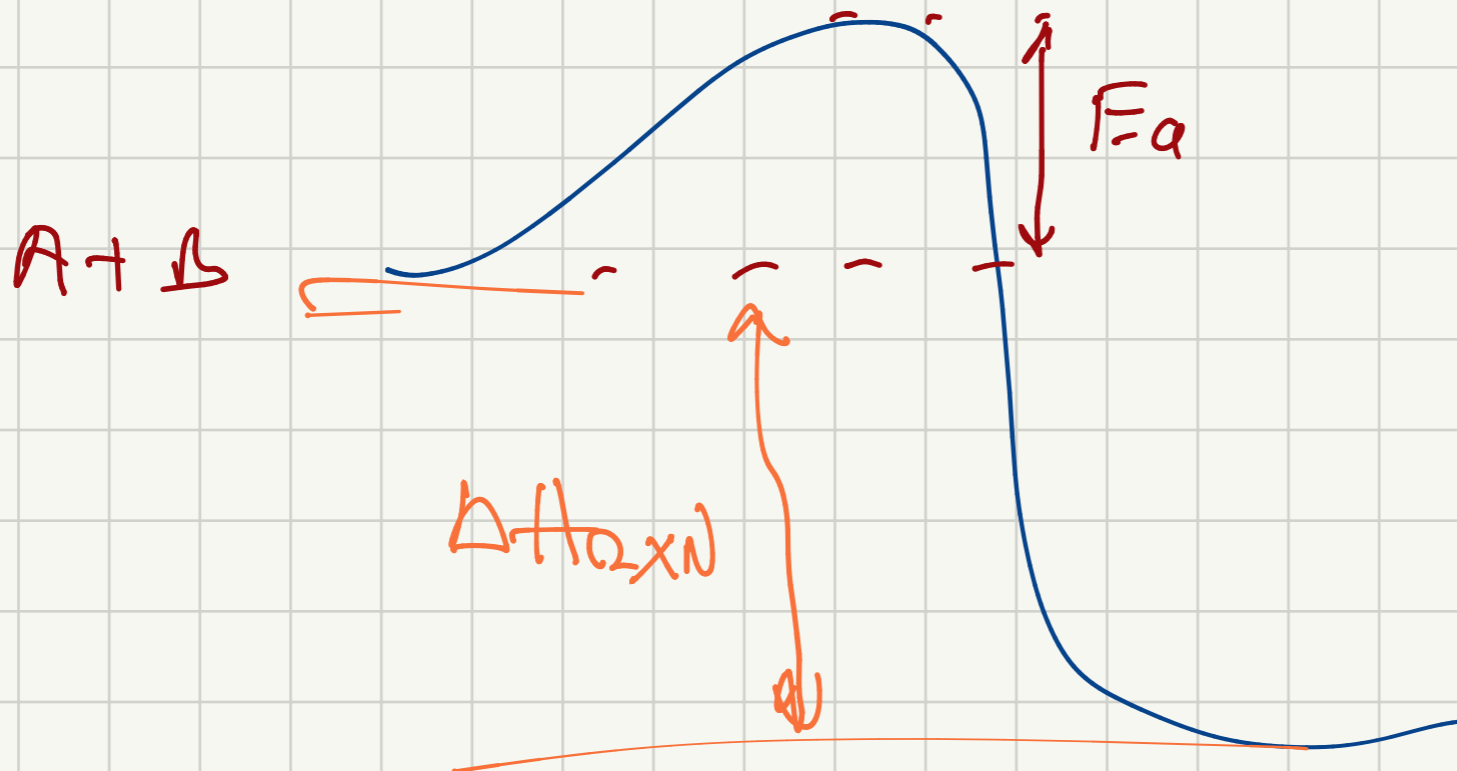
$$7 - 5 = 2$$

$$Nu \equiv \frac{hd}{k}, \quad Pe \equiv \frac{u d}{\alpha}$$

PECLET NUMBER

# CHEMICAL KINETICS

$$k = A_0 \times P \left( -\frac{E_a}{RT} \right)$$



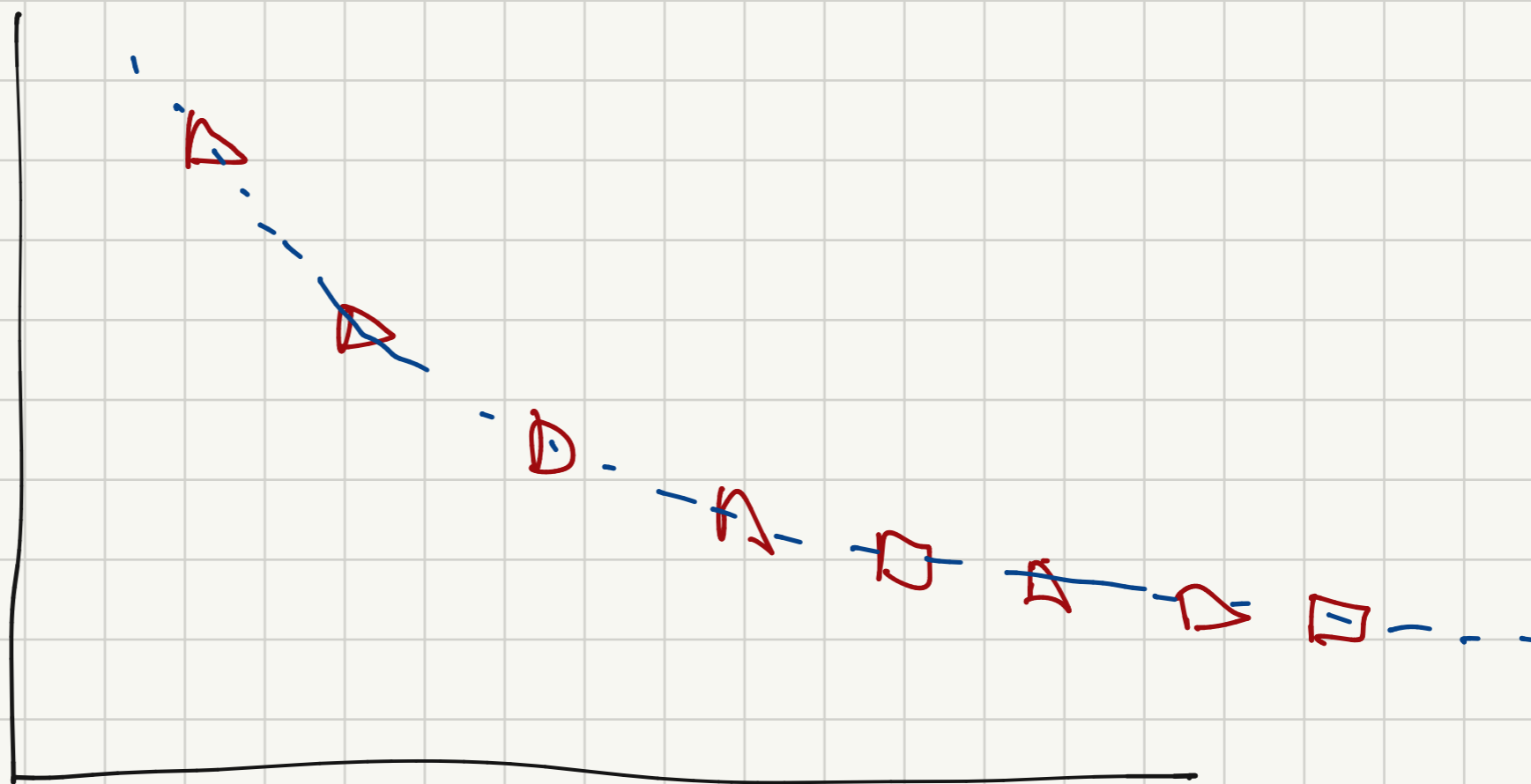
$$r = k_0$$

$$r = k C_A$$

$$r = k C_A C_B$$

$$r = \frac{k C_A C_B}{K_m + C_A}$$

# NONLINEAR FITTING



ALWAYS PLOT RAW DATA

MOST LIKELY FIT RAW DATA

(MAYBE REDUCE SCALE USING

LOG, COULD REDUCE NOISE

WITH SMOOTHING & FIT..)

