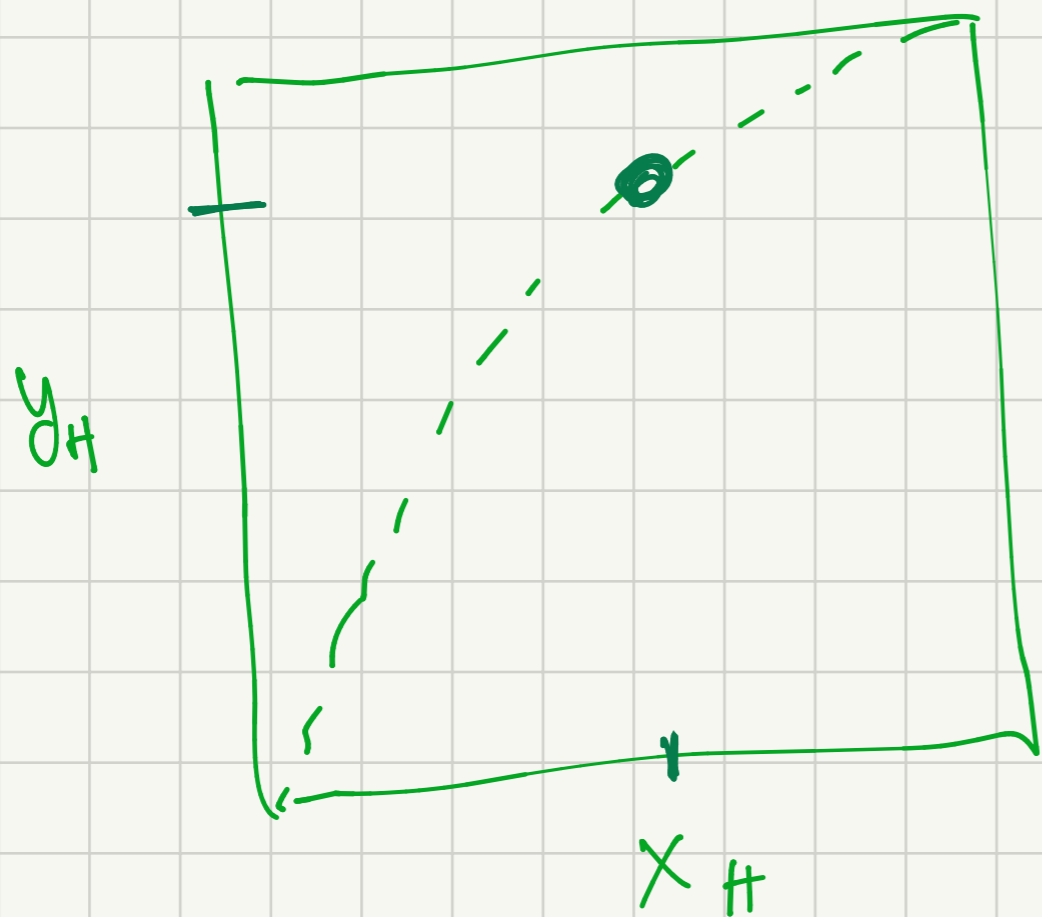
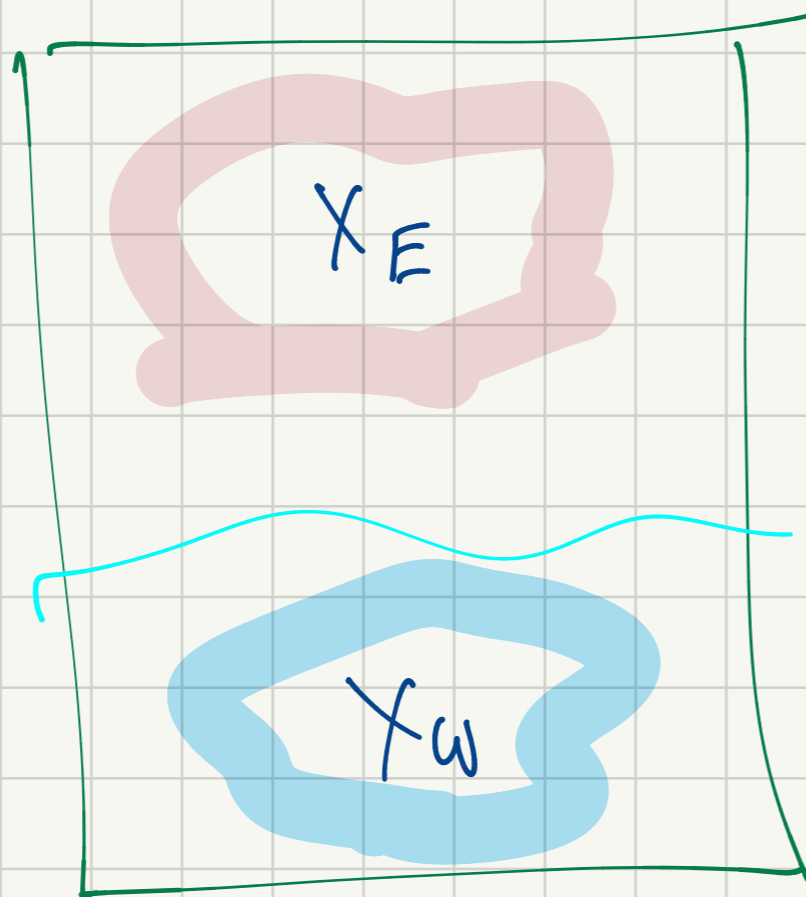


THERMODYNAMICS OF PHASE EQUILIBRIA

WE JUST USED RESULTS FROM
PHASE EQUILIBRIA

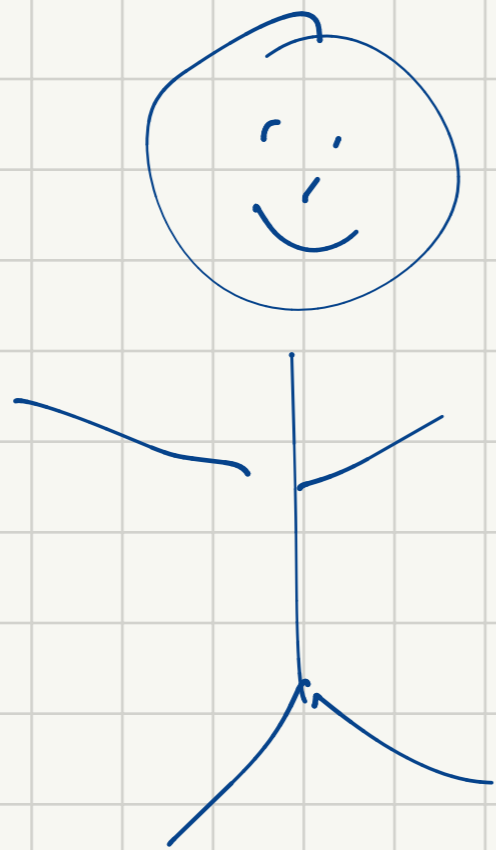


HEXANE ENHANCED
IN VAPOR PHASE



$$x_E = m x_W$$

A SELECT
COMPONENT
PARTIONS INTO
ETHER PHASE



A PHARMACEUTICAL
COMPOUND COULD
PARTITION PREFERENTIAL
INTO "LIPID-PHASE"
AND EVEN MAKE
IT INACTIVE WHILE
IT IS THERE.

E.G.: ANESTHESIA

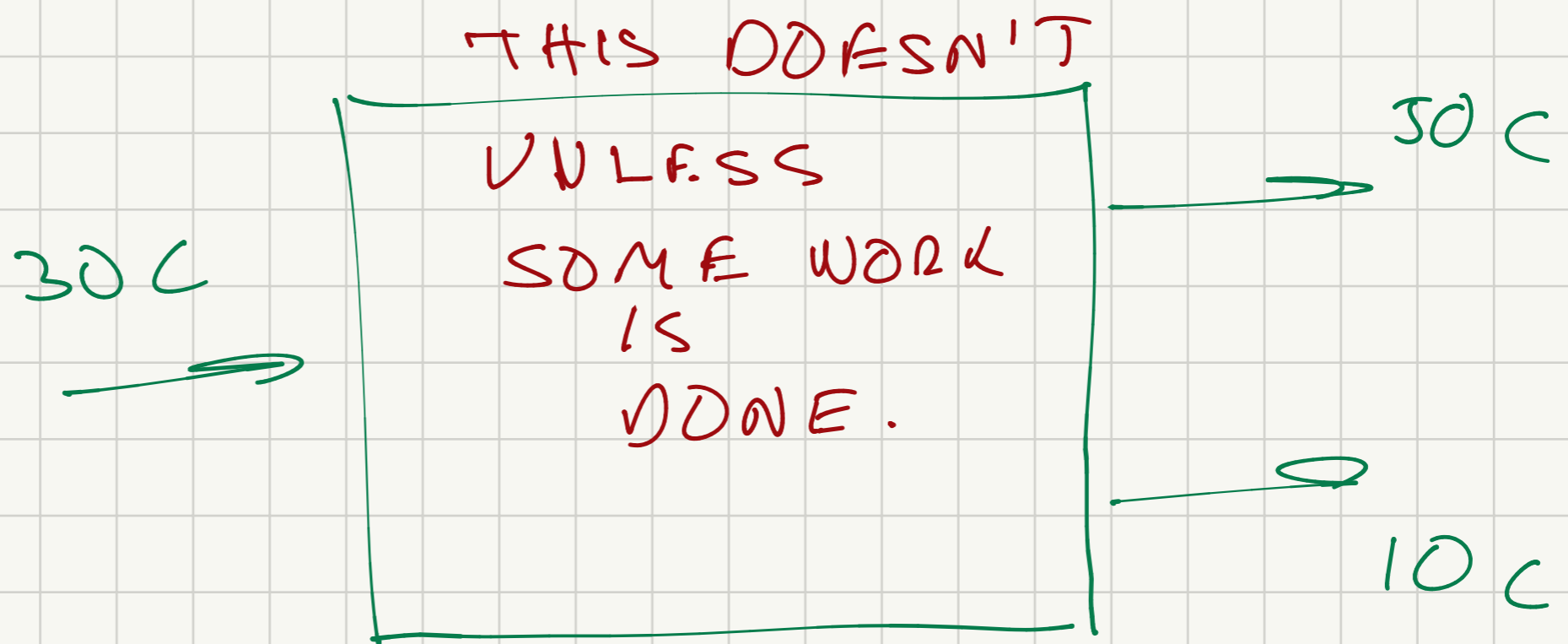
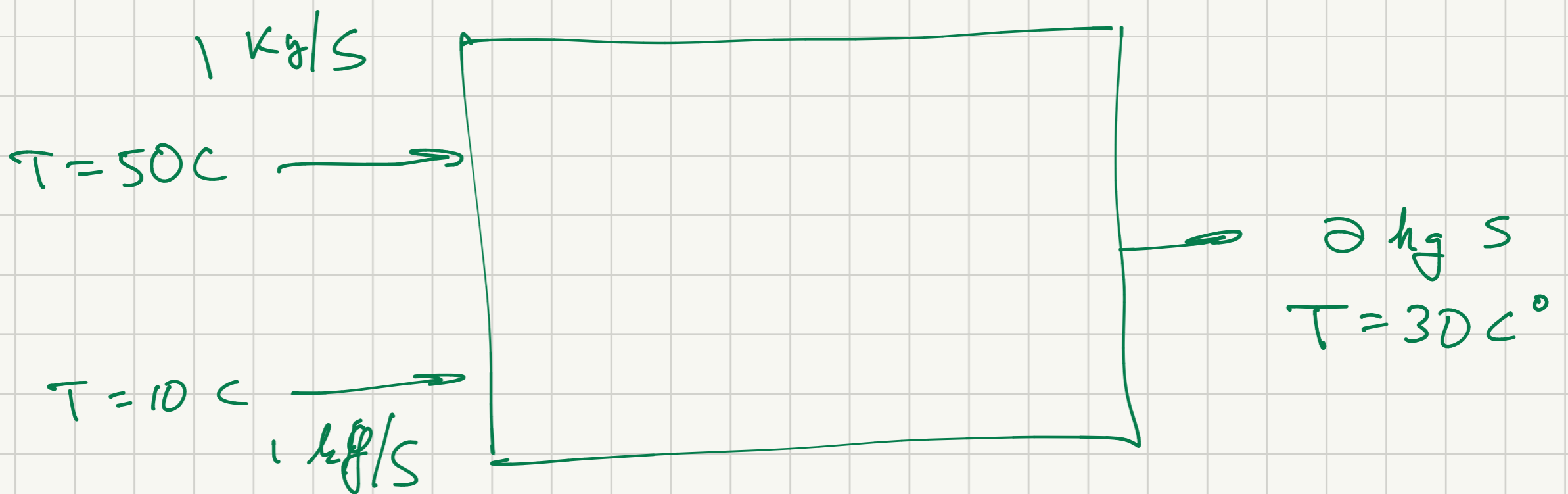
WHAT CONTROLS THE COMPOSITIONS
OF THE PHASES → HOW DO WE
MODEL IT ?

FOR HEXANE - OCTANE YOU MIGHT BE
TEMPTED TO WRITE :

$$x_H P_H^{\text{SAT}} = y_H P$$

THIS MIGHT WORK WELL ... BUT
WHERE DOES IT COME FROM ?

THIS WORKS



NATURE HAS DIRECTIONALITY !!

SOME PROCESSES ARE
SPONTANEOUS . . .

OTHERS ARE NOT

WE HYPOTHESIZE EXISTENCE
OF AN ADDITIONAL STATE
PROPERTY Θ , THAT IS NOT
CONSERVED

FOR ANY SPONTANEOUS CHANGE

$$\frac{d\Theta}{dt} > 0$$

AT EQUILIBRIUM

$$\frac{d\Theta}{dt} = 0, \quad \Theta = \text{CONST}$$

WITH SOME FURTHER COGITATION
WE WOULD CONCLUDE THAT

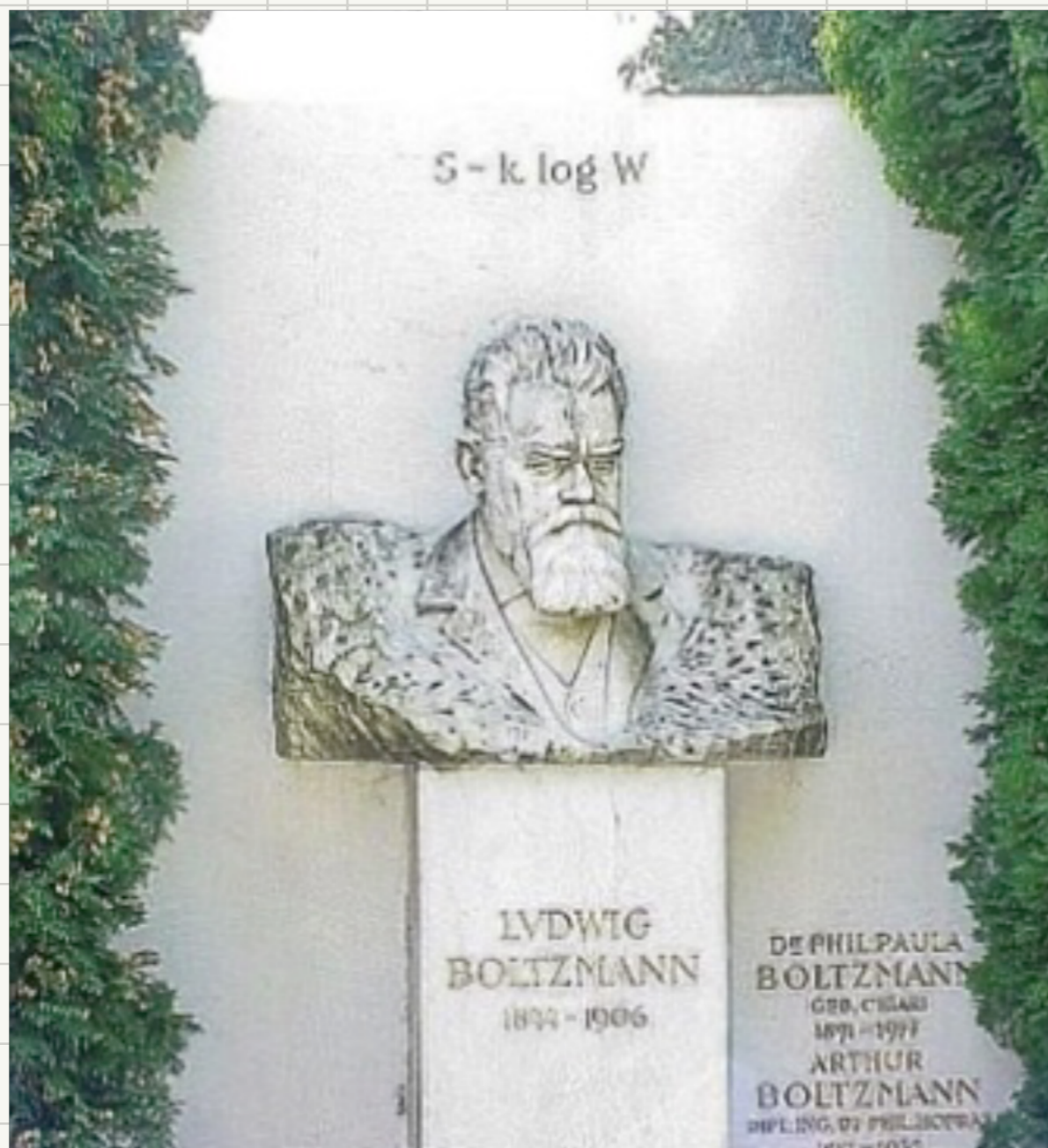
$$dS \geq \frac{Q}{T}, \quad \text{BUT THAT WORK}$$

DOES NOT CHANGE VALUE OF S .

$$\frac{dS}{dt} = \sum_{k=1}^N \dot{m}_k \hat{S}_k + \frac{\dot{Q}}{T} + \dot{S}_{\text{GEN}}$$

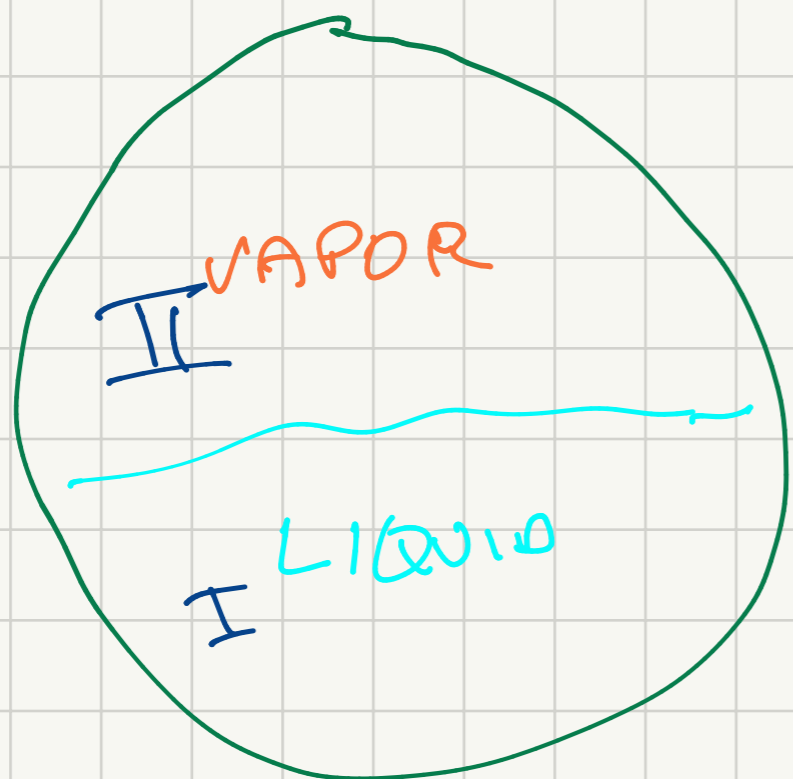
IF YOU START WITH THE
MOLECULAR NATURE OF
MATTER & INQUIRE ABOUT
NUMBER OF POSSIBLE
CONFIGURATIONS OF PARTICLES
IN A GIVEN SYSTEM

JUST NEED TO FIND
THE CORRECT "TOMBSTONE"
TO GET AN ANSWER.



$$S = k \ln W$$

↑ CONFIGURATION STATES OF SYSTEM



SYSTEM WILL
BE IN EQUILIBRIUM

WHEN S IS

MAXIMIZED

WITH $T^I = T^II$

$$P^I = P^II$$

$$\underline{G}^I = \underline{G}^II$$

$$\left\{ \begin{array}{l} dG = 0 \\ \underline{G} \Rightarrow \text{MINIMUM} \\ \text{IF } T, P \\ \text{ARE HELD FIXED} \end{array} \right.$$

FOR A PURE SUBSTANCE

$$\underline{G}^I = \underline{G}^II$$

$$\mu^I = \mu^II$$

MOLAR GIBBS FREE
ENERGY

CHEMICAL POTENTIAL

$$\mu_i = \left. \frac{\partial U}{\partial N_i} \right|_{S, V}$$

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

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

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

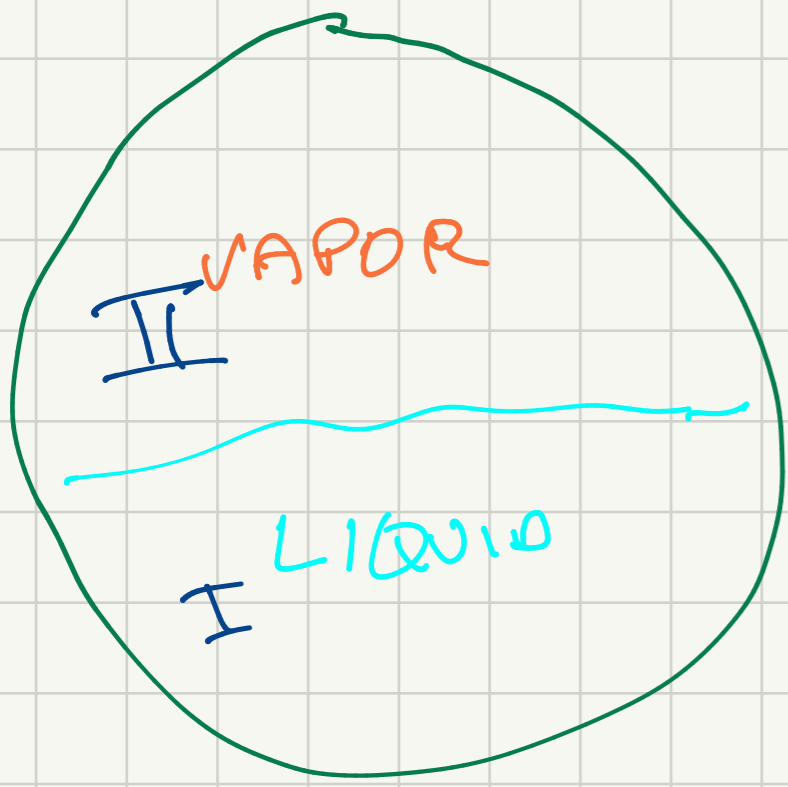
UNITS OF PRESSURE REAL GAS OR LIQUID IDEAL GAS

* 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

$$f^L = f^V$$

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

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

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

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

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

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

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

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

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

BACK TO RAOULT'S LAW

I WROTE:

$$x_H p_H^{\text{SAT}} = y_H p^{\text{TOTAL}}$$

THIS FOLLOWS FROM SOMETHING
WE KNOW FOR SURE!

$$p_H^{\text{SAT}} = p^{\text{TOTAL}}$$

$$\text{IF } x_H = y_H = 1$$

THUS RAOULT'S LAW IS A RATIONAL
SIMPLIFICATION OF FUNDAMENTAL
THERMODYNAMICS

$$f^L = f^V$$

AS WELL AS INTUITIVELY

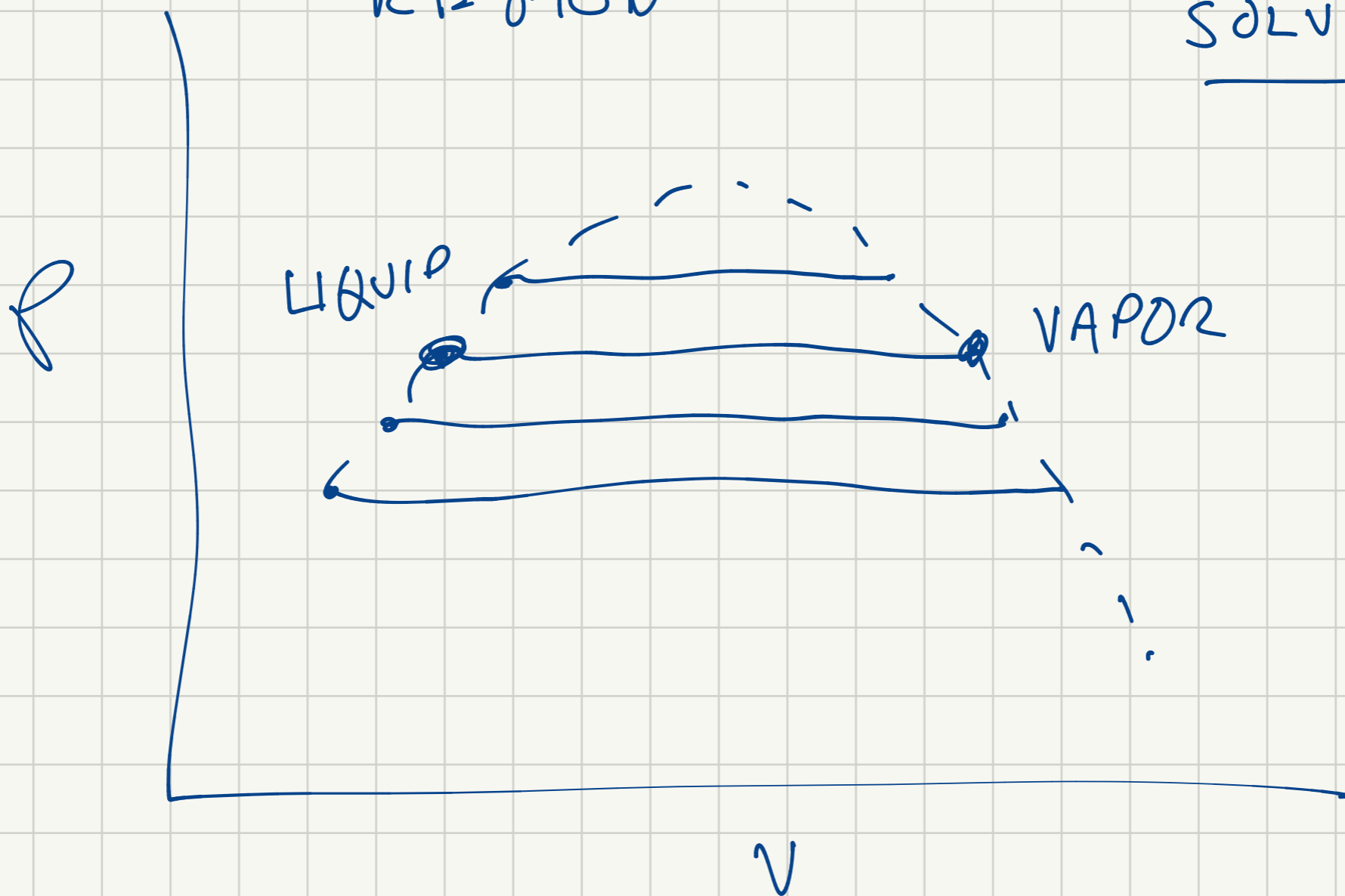
SATISFYING FROM EXPERIMENT!!

PHASE EQUILIBRIUM CALCULATIONS

1) PURE COMPONENT

⇒ USE EQUATION OF STATE TO
CALCULATE TWO-PHASE
REGION

SOLVE P, V, T



MIXTURES

$$x_i P_i^{\text{VAP}} = y_i P$$

BUT IF NONE IDEAL

$$x_i \gamma_i P_i^{\text{VAP}} = y_i P$$

↑

DEVELOP ACTIVITY COEFFICIENT

MODELS TO PREDICT BEHAVIOR

→ VARIOUS DEGREES OF "CHEMISTRY"
ARE INCLUDED

→ SOME ARE PURELY PREDICTIVE
"GROUP CONTRIBUTION METHODS"

→ GETTING MULTICOMPONENT
BEHAVIOR FROM BINARY PAIRS
IS VERY COMMON &
IMPORTANT.

3) CAN ALSO DO PHASE

EQUILIBRIA FOR MULTICOMPONENT
MIXTURES

$$x_i \phi_i^L P = y_i \phi_i^V P$$

"CUBIC" EQUATIONS OF STATE

VAN der Waals :

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

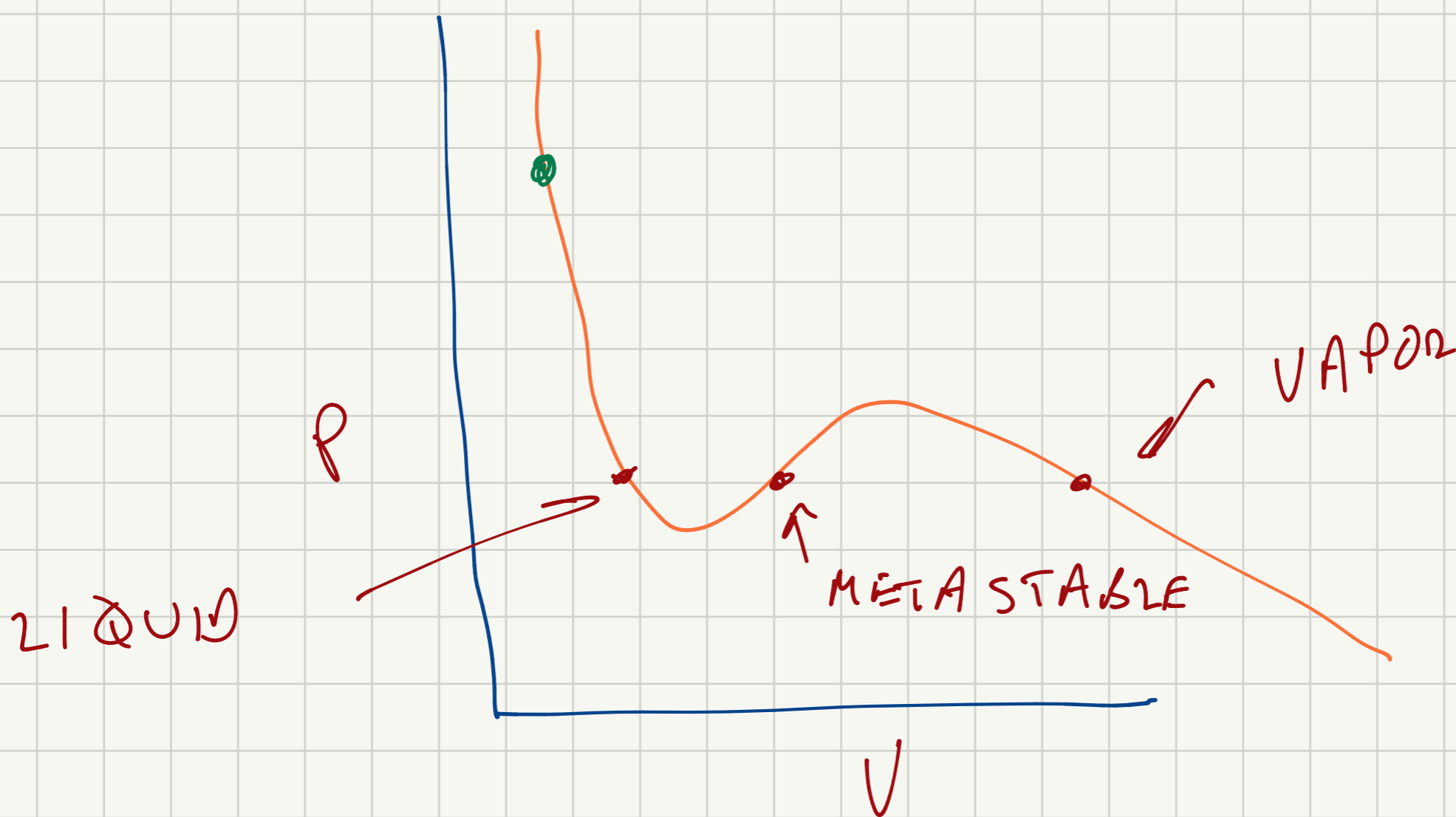
↙ ATTRACTION

↗ EXCLUDED VOLUME

IF YOU PICK T, P
3 ROOTS FOR V

1 REAL — 2 COMPLEX CONJUGATE

3 — REAL

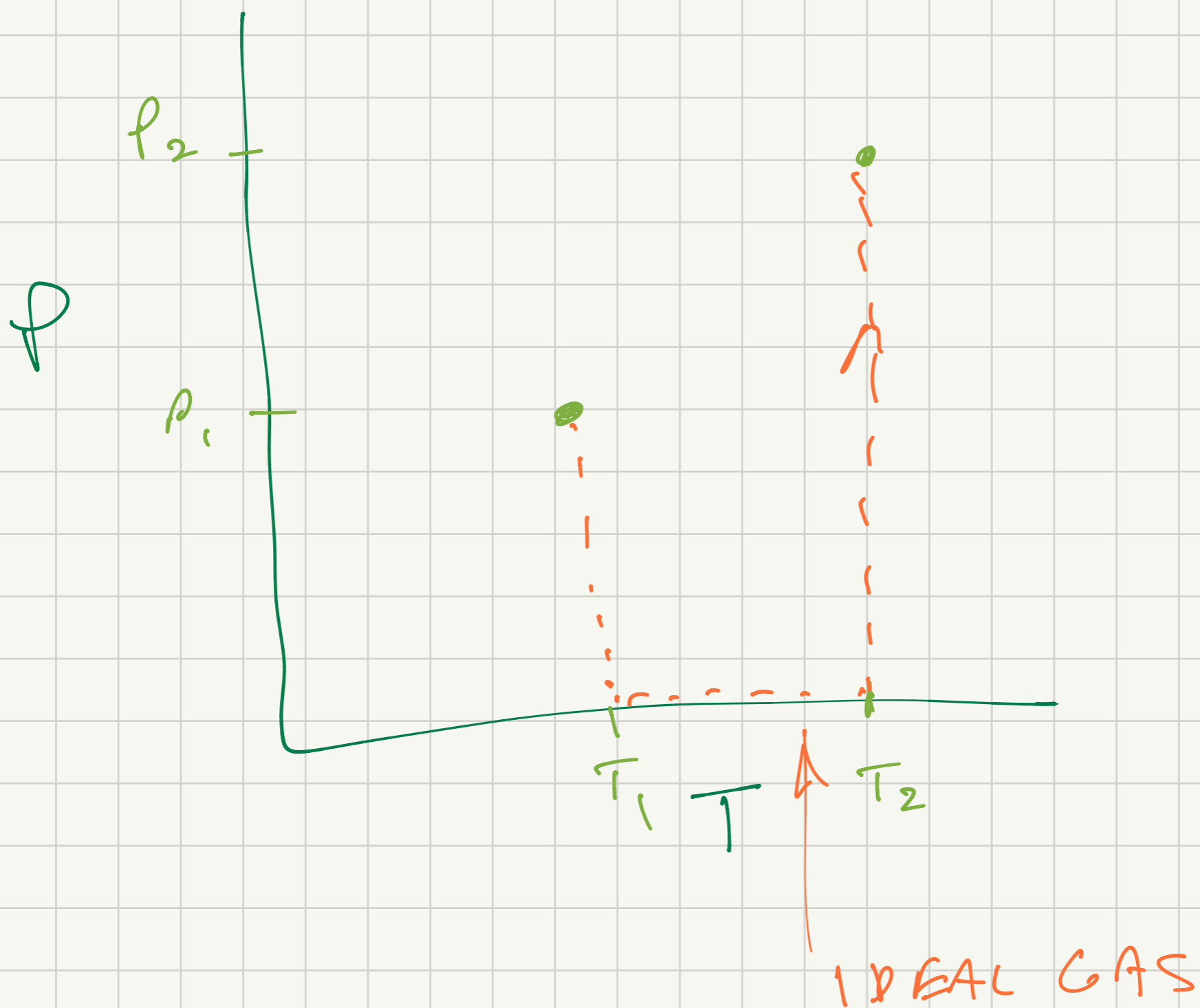


VAN DER WAALS DOES NOT
WORK VERY WELL BUT
PENG-ROBINSON (1976)

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

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 TO FOR
AN IDEAL GAS \rightarrow THEN INCREASE
 P TO FINAL VALUE.



FOR P-R EQ.

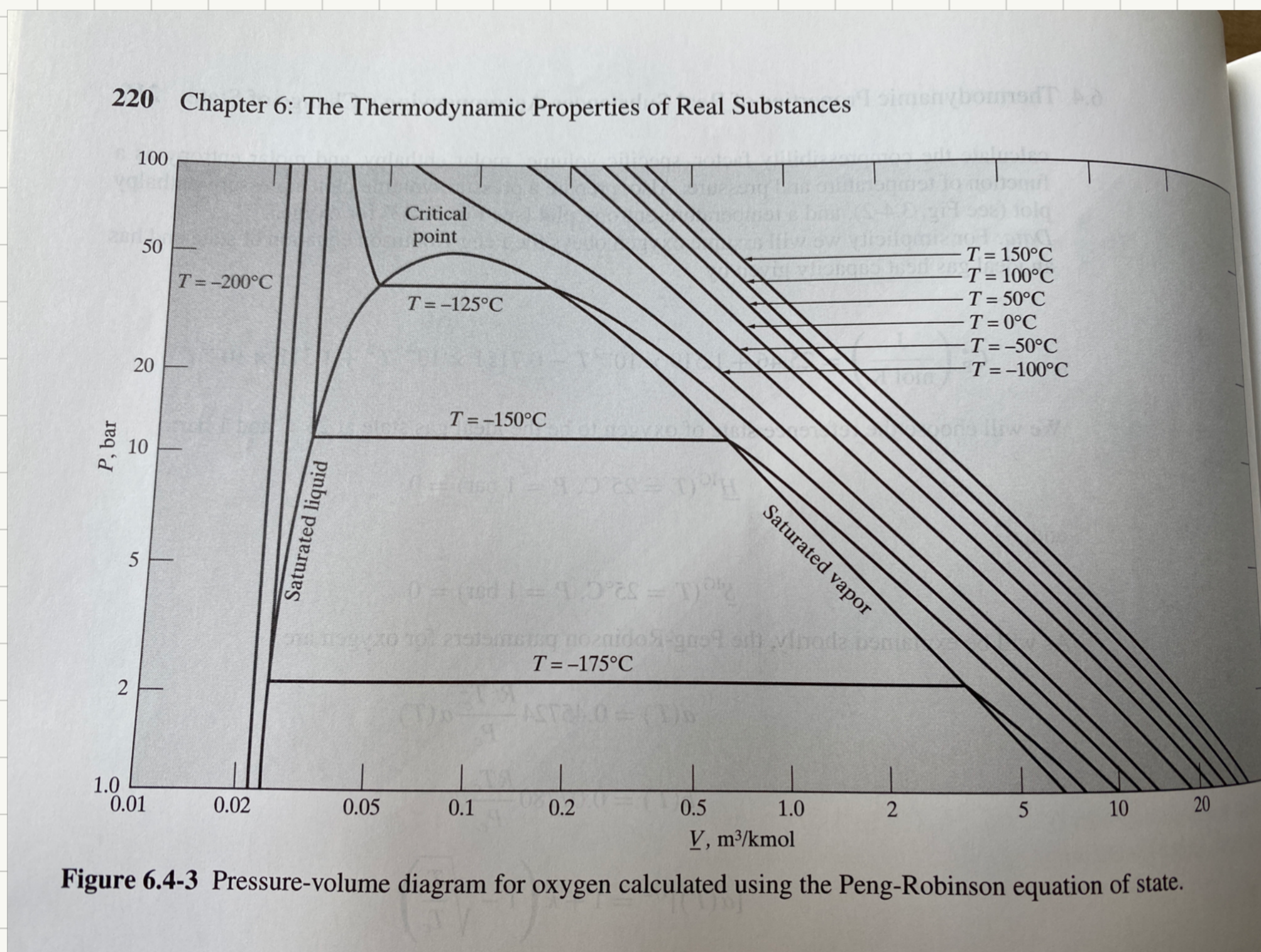
$$\underline{H}(T, P) - \underline{H}^{lb.}(T, P) = RT(z-1) + \frac{T \left(\frac{da}{dT} \right) - a}{2\sqrt{2}b}$$

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

$$z \equiv \frac{PV}{RT}$$

$$B \equiv \frac{Pb}{RT}$$

FROM FORMALISM WE CAN
CALCULATE FLUID PROPERTY
DIAGRAMS



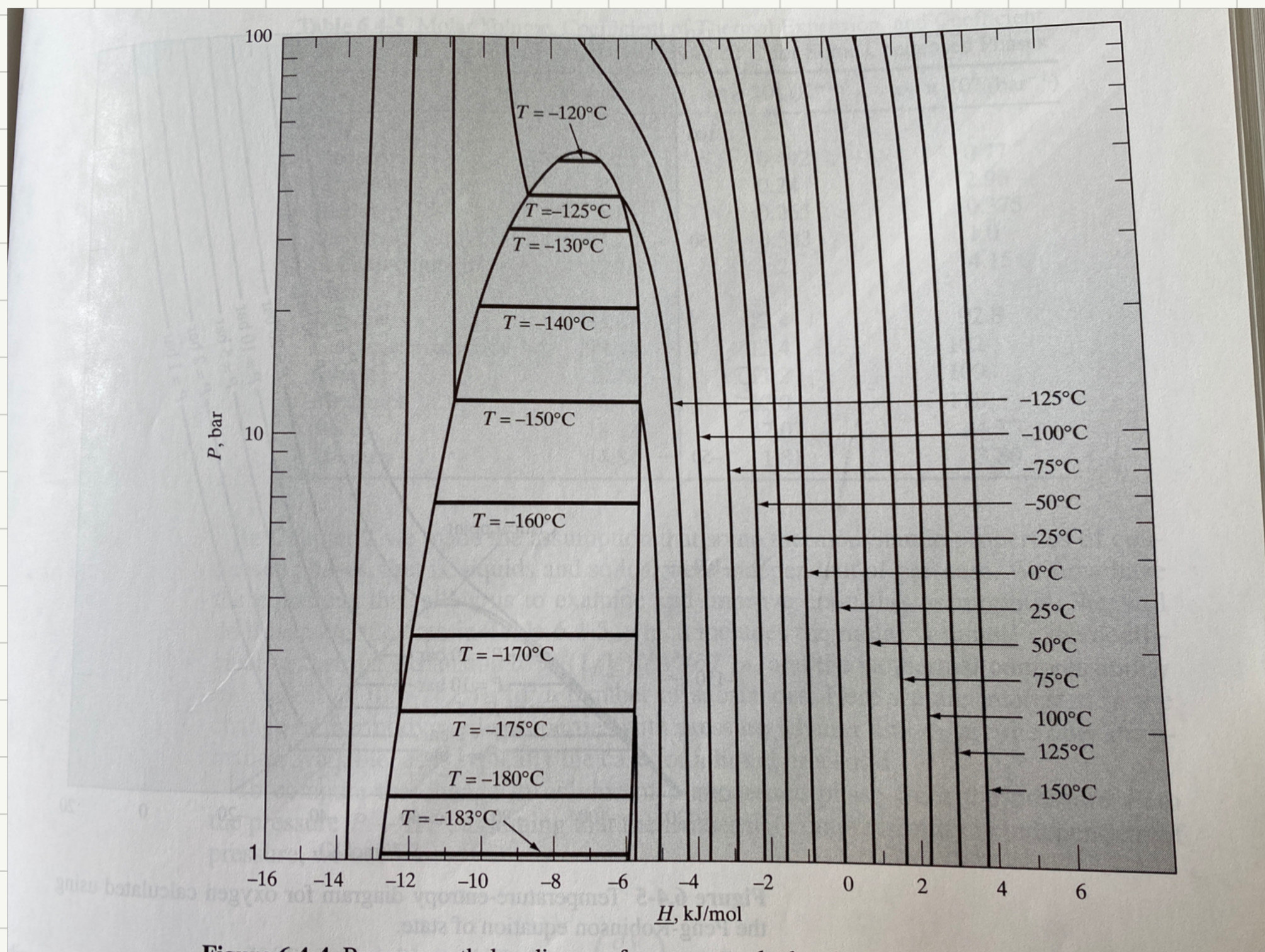


Figure 6.4.4. Pressure-enthalpy diagram for water.