] THE 2" LAW AND STABILITY

AS IN A RECENT EXAMPLE, CONSIDER A BODY IN THERMAL CONTACT WITH A LARGE RESERVOIR THAT CAN ABORBS WITS OF ENERGY WITHOUT STENIFICANT CHANGE IN TEMPERATURE.

ARE THE SAME AND FIXED. TEMPERATURE OF THE BODY AND RESERVOER

FOR BODY dH = TdS (Space dP=0)

FOR RESERVOIR { dHR = - dH (BY ENERGY CONSERVATION)

TdSR - TdS

So TOTAL ENTROPY CHANGE IS

O & dSTOTAL = dS + dSe = dS + (- \frac{1}{7} dH)

200 AD = -\frac{1}{7} (dH - TdS)

BUT GIBBS FREE ENERGY IS G = H-TS => dG = dH-TdS-SdT == dH-TdS

SO O & STOTAL = - + dq (ISOTHERMAL, ISOBARIC)

THAT IS TO SAY, WHILE ENTROPY ALWAYS TENDS TO

INCREASE, THE GIBBS FREE ENERGY ALWAYS TENDS

TO DECREASE.

A SYSTEM WILL ALWAYS EVOLUE TO MINIM; ZE G.

IF G IS NOT AT ITS MINIMUM IT IS "UNSTABLE".

2] VAN DER CHARLS EQ" REVISITED

RECALL (P + 9 N/2) (V-bN) = NKT FOR LIQUID & GAS GIDGALIZED) WITH CRITICAL POINT AT VE=36N, KT = 8 0 , Pc= 27 62 IN NON-DIMENSIONAL FORM WITH P=P, V=V, T=TE GET

IF T(1, THE FLUTD CAN EXIST 0.6 4 2 TILL WITH 3 POSSIBLE VOLUMES IF P IS

IN A CERTAIN RANGE (C.g. 0.55 \$ 50.7 ABOVE). DETERMINE THE STABILITY OF EACH STATE USING GIBBS FREE ENERGY

Along Isotherm T, dG = -SdT + VdP = VdP $\Rightarrow (\frac{\partial G}{\partial V})_{T} = V(\frac{\partial P}{\partial V})_{T} = \frac{\partial G}{\partial V} = \frac{247}{(3\tilde{V}-1)^{2}}\tilde{V} + \frac{G}{\tilde{V}^{2}}$ Use $(\frac{\partial G}{\partial V})_{T} = \frac{1}{V_{2}}(\frac{\partial G}{\partial V})_{T}$ AND INTEGRATE BOTH STDES WITT \tilde{V}

 $\Rightarrow G = P_{c}V_{c}\left[\int \frac{-24\tilde{T}\tilde{V}}{(3\tilde{V}-1)^{2}} + \frac{6}{\tilde{V}^{1}} d\tilde{V}\right] \qquad \text{Temperature - Dep. } \\ \Rightarrow G = P_{c}V_{c}\left[-\frac{8\tilde{I}}{3} \ln(3\tilde{V}-1) + \frac{8\tilde{I}}{3} \frac{1}{(3\tilde{V}-1)} - \tilde{V} + \frac{2}{V}\right] 2$

Numbertically at least, one can use () to recast $G(T,\tilde{V})$ as $G(T,\tilde{P})$ in (2).

For $\tilde{T}(1)$, a typical pot is:

BUT WE HAVE SEEN G ALWAYS TENDS TO ITS MINIMUM VALUE WITH T, P FIXED. So THE SYSTEM WILL EVOLUE STRATUT FROM STATE 2006, SKIPPING 3,4,5 etc

DURING PRASE CHANGE dT=dP=0 => dG=-SdT+VdP=0 So 0 = S2+3+4+5+6 = S2+-+6(2G) dP = SVdP So IN PV-DIAGRAM ARGA 12-3-41 = AREA 14-5-61 [MANNEW'S CONSTRUCTION]

To Find constant, we know $T = T_B \approx 373 \text{ K}$ P = Po = LATM

P(T) \approx Po EXP[$\frac{l_v}{R_v}(\frac{1}{T_B} - \frac{1}{T})$]

THE VAPOUR PRESSURE EQUATION

(GOOD, ASSUMING (& CONSTANT)

3] (cont'd)

EXAMPLE: AT WHAT TEMPERATURE DOES WATER BOIL AS YOU GO TO HIGHER ALTITUDES?

SOLM

IGNORING STORM SYSTEMS, etc., WE WILL RELATE ALTITUDE TO PRESSURE USING HYDROSTATIC BALANCE: P=Poe-Z/Hp
IN WHICH WE WILL TAKE Hp=8km.

INVERTING THE VAROUR PRESSURE EQUATION TO WRITE T

$$T(P) \simeq \left[\frac{1}{T_B} - \frac{R_V}{\ell_V} \ln \left(\frac{P}{P_0} \right) \right]^{-1}$$

$$\simeq \left[\frac{1}{T_B} + \frac{R_V}{\ell_V} \frac{Z}{H_P} \right]^{-1}$$

 $\Rightarrow T() = T_3 (1 + \frac{3}{4})^{-1}$

IN WHICH) $t = H_p l_v / (R_v T_B)$ $\simeq (8000 m)(2.26 \times 10^6 \frac{J}{kg}) / [(462 \frac{J}{kg})(373 K)]$ $\simeq 1.05 \times 10^5 m \simeq 105 km$

EVEN GOING UP TO THE TOP OF EVEREST ZKZ.

$$\Rightarrow$$
 $T(z) \simeq T_B (1 - \frac{z}{H}) \simeq (373 \text{ K}) [1 - \frac{z}{105 \text{ km}}] /$

#N PARTICULAR, IN JASPER (~ 1000 M ABOUR SEA LEVEL)
WATER BOILS AT 373 (1-105) = 369 K = 96°C
(So THINGS TAKE A LITTLE LONGER TO GOOK.)

4] VAPOUR PRESSURE OF WATER IN AIR.

THE CLAUSIUS - CLAPETRON EQUATION CAN ALSO BE APPLIED FOR MIXTURES OF WATER VAPOUR AND AIR.

LET $V = \frac{\#}{molecules} \frac{H_{20}}{H_{20}} + AJR$ BE THE "Volume mixING RATIO"

DEFINE C = VP TO BE THE "PARTIAL PRESSURE" OF WATER VAPOUR, I.e. THE PART OF PRESSURE DUE TO H_{20} .

LET C3 BE THE "SATURATION VAPOUR PRESSURE", WHICH MEASURES
THE MOST AMOUNT OF WATER NAPOUR THAT ATTR CAN HOLD AT PRESSURE, P.
AS WITH PURE H2O, C3 SATISFIES THE CLAUSIES-CLAPETRON EQ":

$$\frac{de_s}{dT} = \frac{l_v}{R_v} \frac{e_s}{T^2} \Rightarrow \left[e_s(T) = e_o \, Exp \left[\frac{l_v}{R_v} \left(\frac{1}{T_o} - \frac{1}{T} \right) \right] \right]$$

IN WHICH CO 9 TO ARE DETERMEND BY MEASUREMENTS.

E.g. AT $T_0 = 273 \,\text{K}$ $C_0 = C_5(T_0) \simeq 6.11 \,\text{mbar}$.

GRAPHING (1) GIVES 60+

40+

FOR TROCK

C3(MBB)
60
40
FOR
20
-40 -20 0 20 40

T (°C)

(NOTE ATR CAN HOLD MUCH MORE WATER VAROUR AT HIGH TEMPERATURES)

KNOWERLE CS FROM (), WE CAN DEFINE THE "RELATIVE HUMIDIT"

R. H. = C/Cs = V/Vs = (#MOLECOLES HZO)/(#MOLECOLES HZO AT SATURATION)

IF My IS MASS OF VAPOUR IN MASS MY OF DRY AIR, ITS "MIXING

RATIO" IS $W = \frac{m_d}{m_d}$.

The terms of Partiel Pressure: $C = VP = \frac{m_d/M_{ARR} + m_d/M_{Hzo}}{m_d/M_{ARR} + m_d/M_{Hzo}}P = \frac{w}{w+\epsilon}P \approx \frac{w}{\epsilon}P$ Where $E = \frac{M_{Hzo}}{M_{ARR}} \approx \frac{18.02}{28.41} \approx 0.622$, AND USED WKE (TYP. $W \sim \frac{19}{k_0} \frac{hzo}{k_0}$)

DEW POINT OCCURS AT TEMP To wim R.H.=1 => W=Ws= FC EXP[RV (To - To)]



4] (cont'd)

Example (1):

AIR CONTAINS WATER VAPOUR WITH A MIXENY RATIO OF W=5.5g/kg AND THE PRESSURE IS 1026.8 hPa AND T = 20°C.
WHAT IS THE VAPOUR PRESSURE AND RELATIVE HUMIDITY?

 $S2^{n}$ $C = VP = \left(\frac{5.5 \times 10^{-3}}{5.5 \times 10^{-3} + 0.622}\right) \left(1026.8 \text{ hPa}\right) \approx 9.0 \text{ hPa} \left(9.0 \text{ mByz}\right)$

AT 20°C, SATURATION VAPOUR PRESSURE IS $C_s \simeq (6.11 \text{ mBar}) \text{ EXP} \left[\frac{2.50 \times 10^6 \text{ J/kg}}{462 \text{ J/kg/k}} \left(\frac{1}{273 \text{ K}} - \frac{1}{293 \text{ K}} \right) \right] \simeq 23.6 \text{ mBar}$ $C_s = C_s(0^\circ c)$ So relative humidity is $C_s \simeq \frac{9.0}{23.7} \simeq 0.38$ i.e. 38% humidity

Example (2)1

FOR THE ABOVE PROBLEM, WHAT IS THE DEW POINT?

SOLY

WANT To Such that $W = W_0 \text{ EXP} \left[\frac{l_V}{R_V} \left(\frac{1}{T_0} - \frac{1}{T_0} \right) \right]$ WHERE $W_0 = \frac{\mathcal{E}}{P} e_0$ is mixing ratio at $T = T_0$

 $T_{1} = \left[\frac{1}{7_{0}} - \frac{R_{V}}{\ell_{V}} L_{n}(\frac{W}{W_{0}})\right]^{-1} = \frac{0.0055}{0.00370}$ $= \left[\frac{1}{273 \text{ K}} - \frac{462 \frac{J}{4R}}{2.50 \times 10^{6} \frac{J}{k_{3}}} L_{n}(\frac{0.0055}{(0.622)(6.11 \text{ mBAR})/(1026.8 \text{ mB/R})})\right]^{-1}$ $= 273 \text{ K} \left[1 - 5.48 \times 10^{-2} L_{n}(1.49)\right]^{-1}$ $= 273 \text{ K} \left[1.02\right]$ = 279 K

So DEW POINT IS ~6°C/

(63)

5] EQUIVALENT POTENTIAL TEMPERATURE

AS MOISTURE-LADEN. AIR RISES AND COOLS, SOME OF THE WATER VAPOUR CONDENSES (FORMENG CLOUDS) WHICH RELEASES HEAT INTO THE AIR. IF THE DROPS ARE SO MINUTE THAT THEY CONTINUE TO RISE WITH THE AIR, THE PROCESS IS ADIABATIC. BUT IF THE DROPS LITERALLY RAIN OUT, THE PROCESS IS PSEUDOADIABATIC.

HOW THE TEMPERATURE OF A SATURATED (1006 HOMIDITY) AIR PARCEL CHANGES AS IT MOVES THROUGH DECREASING DRESSURE ALL THE WHILE LOSING MOISTURE IS GIVEN BY THE EQUIVALENT POTENTIAL TEMPERATURE, OR

USE $S = C_P L n \theta$ AND $dS = \frac{89}{T} = \frac{1}{T} \left(-l_V \frac{d m_V}{m_{ATR}} \right) \approx \frac{1}{T} \left(-l_V d w_s \right)$ IN WHICH $W_S \left(= W_0 \exp \left[\frac{l_V}{R_V} \left(\frac{1}{1_0} - \frac{1}{T_0} \right) \right] \right)$ IS SATURATION MIXTUGINATION. MJ

So dln0 = - It ly dws = d(-lyws) - lyws 1 dT

NOW ASSUME RELATIVE CHANGE OF TEMPERATURE IS TINY COMPARED TO RELATIVE CHANGE OF Ws: \$\frac{dT}{T} \ll \frac{dws}{Ws}\$

=> d Ln 8 = d (- PVWs)

=> Ln (0/0e) = - evws/(cpT) WHERE De IS INTEGRATION CONSTANT

=> Oe = O EXP[Q, Ws]

OF AIR AFTER ALL THE WATER VAPOUR HAS CONDENSED AND THE SATURATION MIXING RATIO (W) IS ZERO.

5] (contid)

TO ELUCIDATE THE TWEERPRETATION OF De, CONSIDER THE FOLLOWING 3 SCENARIOS

- POTENTIAL TEMPERATURE O. THIS MEASUS IS IT T=0, ? WILL HAVE TEMPERATURE T'=0 WHEN BROUGHT TO THE GROUND.
- 2) A PARCEL OF SATURATE AIR (WITH W=Ws) HAS

 POTENTIAL TEMPERATURE O. AS ABONE, IF T.P II WS III

 BROUGHT STRAIGHT TO GROUND ITS TEMPERATURE T'=0 III W:WS W:OIT T''

 WILL BE T'=O (NO CONSUSATION, SO NO HEAT RELEASE).

 HOWEVER, IF BROUGHT UPWARDS UNTIL IT DRYS OUT, ITS

 POTENTIAL TEMPERATURE BECOMES OE = O EXP[GIT] > 0. IF

 THE PARCEL THEN DESCENDS TO GROUND REMAINING DRY,

 ITS TEMPERATURE WILL BE T"=Oe > O = T'.

 (LATENT HEAT RELEASE HAS WARMED THE AIR)
 - 3) A PARCEL OF MOIST (BUT UNSATURATED) HAS

 POTENTIAL TEMPERATURE &. IT IS BROUGHT

 UPWARDS UNTIL IT HAS COOLED TO

 TEMPERATURE To AT WHICH IT IS SATURATED

 (W=W). THEN IT CONTINUES TO RESE UNTIL ALL THE MOISTURE

 CONDENSES AND RATINS OUT. DURING THIS PROCESS THE POTENTIAL

 TEMPERATURE INCREASES TO GE. IF BROUGHT TO GROUND

 THE TEMPERATURE WILL BE T"= Q= Q EXP[QTS] > Q.

 [NOTE TS, NOT STARTING TEMPERATURE T IN EXPONENTIAL]

THE LAST SCENARIO GIVES A PARTIAL EXPLANATION FOR THE WARMING OF CHINCOK WINDS. AS MOISTURE LADEN AIR FROM WEST IS RUSHED UPWARD OVER MOUNTAINS, RAIN FALLSONT. WHEN DESCENDENT ON THE OTHER SIDE, THE AIR IS RELATIVELY WARMER.

5] (cont'd)

EXAMPLE (1): AIR AT 1:14°C AND 1:950 MBAR HAS A MIXING RATIO OF W=89/kg. It rises adiabatically until IT BECOMES SATURATED. FIND AN IMPLICIT EQUATION FOR THE TEMPERATURE, Ts, AT SATURATION.

SOLY

FIRST NOTE THAT THE SATURATION VAPOUR PRESSURE IS $C_{S,1} = C_0 \text{ EXP} \left[\frac{e_V}{R_V} \left(\frac{1}{T_0} - \frac{1}{T_1} \right) \right]$ $\simeq \left(6.11 \text{ mBAR} \right) \text{ EXP} \left[\frac{2.50 \times 10^6 \text{ J/kg/k}}{462 \text{ J/kg/k}} \left(\frac{1}{273 \text{ K}} - \frac{1}{287 \text{ K}} \right) \right]$

= 14.6 MBAR

So the mixture ratio at saturation for $T_1 = 14^\circ c$ and $P_2 = 950$ more is $W_{S1} = \frac{E}{P_1} e_{S1} \simeq \frac{0.622}{950 \, \text{mbar}} \cdot 14.6 \, \text{mbar} \simeq 9.59 \times 10^{-3}$ $\Rightarrow W_{S1} = 9.59 \, 9 \, \text{kg}$ at initial height of parcel Since $W_{S1} > W_1 = 89 \, \text{kg}$ the parcel is indeed unsaturated.

AS PARCEL RISES, ITS POTENTIAL TEMPERATURE. IS CONSTANT UP TO BECOMING SATURATED: $\theta = T_1 \left(\frac{P_1}{P_0}\right)^{-X} = T\left(\frac{P}{P_0}\right)^{-X}$ $\Rightarrow p = p_1 \left(T/T_1\right)^{1/X} \tag{4}$

AT SATURATION $W_1 = W_S = \frac{\mathcal{E}}{P} \mathcal{C}_S = \frac{\mathcal{E}}{P} \mathcal{C}_S = \frac{\mathcal{E}}{P} \mathcal{C}_S = \frac{\mathcal{E}}{W_1} \mathcal{C}_S =$

EQUATING (#) + (**) GIVES AN IMPLICIT EQUATION FOR $T = T_s$ $P_1 \left(T_s / T_1 \right)^{1/\chi} = \frac{\varepsilon}{W_1} \, e_0 \, \exp \left[\frac{\ell_V}{R_V} \left(\frac{1}{T_0} - \frac{1}{T_s} \right) \right]$

THE PRACTISE THIS MOST BE SOLVED NUMERICALLY. (FIND IS - 8C AT PS-80MBM)
HOWEVER, ATMOSPHERIC SCIENTISTS OFTEN TAKE A SHOPT-CUT
BOX FINDING INTERSECTIONS OF LINES OF LOGPT. /. WE CONST

CONSTANT & AND SATURATION MIXING RATIO WS
ON A "SKEW T-LAP" CHART OR A "TEPHIDIAGRAM"

Wy = CAUST

5] (ani'd)

EXAMPLE (2): A SATURATED ATR PARCEL AT 950 MBAR HAS
A TEMPERATURE OF 5°C. FIND ITS POTENTIAL TEMPERATURE
AND ITS EQUIVALENT POTENTIAL TEMPERATURE.

Solv

THE POTENTIAL TEMPERATURE IS

 $\theta = T (P/P_0)^{-x}$ $\approx (278 \text{ K}) \left[\frac{950 \text{ mBar}}{1000 \text{ mBAR}} \right]^{-2/7}$

⇒ 0 ~ 282 K

(SO AIR WILL HAVE TEMPERATURE ~ 9°C IF BROUGHT TO GROUD.)

FOR Θ_e , NEED TO FIND W_s $W_s \simeq \frac{\mathcal{E}}{\mathcal{P}} C_s \simeq \frac{\mathcal{E}}{\mathcal{P}} C_o \, \text{EXP} \left[\frac{l_v}{R_v} \left(\frac{1}{l_o} - \frac{1}{T} \right) \right]$ $\simeq \frac{0.622}{950 \, \text{mBAR}} \left[\left(6.11 \, \text{mBAR} \right) \, \text{EXP} \left[\frac{2.2 \, \text{x} \, 106}{462} \left(\frac{1}{273} - \frac{1}{278} \right) \right]$ $\simeq \frac{0.622}{950 \, \text{mBAR}} \, \left[8.73 \, \text{mBAR} \right] \simeq 0.00572$ (i.e. $W_s \approx 5.72 \, 9/kg$)

So $\theta_e = \theta \exp\left[\frac{\ell_V W_S}{c_P T}\right]$ $\simeq (282 \text{ K}) \exp\left[\frac{2.56 \times 10^6 \text{ J/ks}}{278 \text{ K}}, \frac{0.00572}{278 \text{ K}}\right]$ $\simeq 282 \text{ K} \exp\left[0.0463\right]$ $\Rightarrow \left[\theta_e \approx 295 \text{ K}\right]$

(SO IF ALL THE MOISTURE CONDENSES AND RAINS OUT,
THE AIR TEMPERATURE WOULD BE 22°C IF
BROUGHT TO THE GROUND. THE LATENT HEAT
RELEASE AMOUNTS TO A 13°C RISE IN TEMPERATURE.)