

## CHAP. 6 THERMODYNAMIC PROPERTIES OF FLUIDS.

### RECALL PHASE RULE

⇒ IF WE SPECIFY A CERTAIN NUMBER OF INTENSIVE PROPERTIES, THEN ALL OTHER PROPERTIES ARE FIXED.

NOTES: SINCE WE CAN MEASURE & CONTROL T AND P EASILY, NICE TO SET THESE AND WRITE ALL OTHER PROPERTIES IN TERMS OF T&P.

### 6.1 PROPERTY RELATIONS FOR HOMOGENEOUS PHASES

#### RECALL

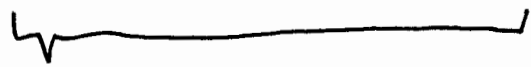
$$d(nU) = dQ_{rev} + dW_{rev}$$

→ CLOSED SYSTEM

→ REVERSIBLE PROCESS.

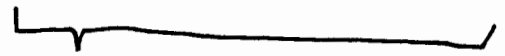
②

$$dQ_{REV} = Td(ns)$$



ENTROPY DEFINITION

$$dW_{REV} = -Pd(nV)$$



WORK (REVERSIBLE)

SUBSTITUTE:

$$d(nU) = Td(ns) - Pd(nV)$$

if unit mol ( $n=1\text{mol}$ ), then,

$$\boxed{dU = TdS - PdV}$$

CAN GET SIMILAR RELATIONS FOR H + G.

↑  
NEW ONE.

H: Enthalpy

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

Substitute for  $dU$

$$dH = TdS - PdV + PdV + VdP$$

(3)

$$\Rightarrow \boxed{dH = TdS + VdP}$$

NEW ONE: GIBBS ENERGY

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

Substitute for  $dH$ ...

$$dG = TdS + VdP - TdS - SdT$$

$$\boxed{dG = VdP - SdT}$$

Great things about Gibbs...

- 1) Parameter changes in  $P$  &  $T$  only  
(Easy to measure & control)
- 2) Can write  $V = f(P, T)$  (Egn. of State)
- 3) Can write  $S = f(P, T)$  (see example for I.G.)

$\Rightarrow$  GIBBS ENERGY VERY USEFUL,

## ENTHALPY + ENTROPY AS FUNCTIONS OF T & P:

$$dH = C_p dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

$$dS = C_p \frac{dT}{T} - \left( \frac{\partial V}{\partial T} \right)_P dP$$

### Special Case #1 IDEAL GAS

Need  $\left( \frac{\partial V}{\partial T} \right)_P \dots$

IDEAL GAS LAW:  $V = \frac{RT}{P}$

$$\left( \frac{\partial V}{\partial T} \right)_P = \frac{R}{P} \left( \frac{\partial T}{\partial T} \right)_P = \frac{R}{P}$$

$$\Rightarrow dH^{ig} = C_p^{ig} dT + \left[ V - \underbrace{T \left( \frac{R}{P} \right)}_V \right] dP$$

$$\Rightarrow \boxed{dH^{ig} = C_p^{ig} dT} \quad \leftarrow \text{JUST LIKE IN } \underline{\text{CHAP. 3}}$$

(5)

$$\Rightarrow dS^ig = C_p^{ig} \frac{dT}{T} - \frac{R}{P} dP \quad \leftarrow \text{JUST LIKE IN CHAP. 5}$$

SPECIAL CASE #2: LIQUIDS

Recall  $\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  Volume Expansivity

$$\text{So, } dH = C_p dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

$$= C_p dT + [V - T\beta V] dP$$

$$\Rightarrow dH = C_p dT + (1 - \beta T) V dP$$

$$\text{And, } dS = C_p \frac{dT}{T} - \left( \frac{\partial V}{\partial T} \right)_P dP$$

$$\Rightarrow dS = C_p \frac{dT}{T} - \beta V dP$$

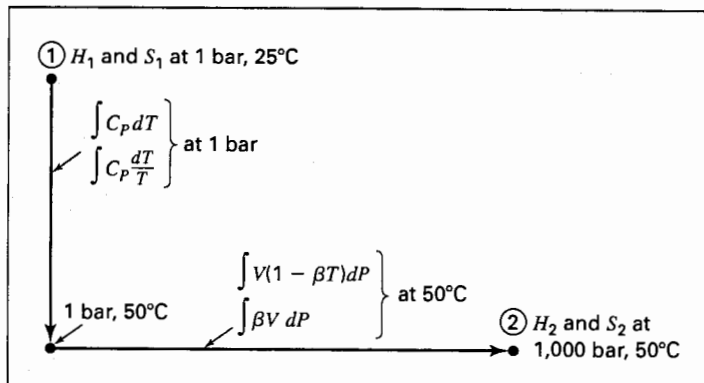
→ EXAMPLE

### Example 6.1

Determine the enthalpy and entropy changes of liquid water for a change of state from 1 bar and 25°C to 1,000 bar and 50°C. Data for water are given in the following table.

$t/^\circ\text{C}$	$P/\text{bar}$	$C_p/\text{J mol}^{-1} \text{K}^{-1}$	$V/\text{cm}^3 \text{mol}^{-1}$	$\beta/\text{K}^{-1}$
25	1	75.305	18.071	$256 \times 10^{-6}$
25	1,000	.....	18.012	$366 \times 10^{-6}$
50	1	75.314	18.234	$458 \times 10^{-6}$
50	1,000	.....	18.174	$568 \times 10^{-6}$

Figure 6.1:  
Calculational path for  
Ex. 6.1.



NOTE:  $C_p$  is weak function of  $T$  } USE  
 $V + \beta$  are weak functions of  $P$  } AVERAGE  
 VALUES.

$$\langle C_p \rangle = \frac{75.305 + 75.314}{2} = 75.310 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\langle V \rangle = \frac{18.234 + 18.174}{2} = 18.204 \frac{\text{cm}^3}{\text{mol}}$$

$$\langle \beta \rangle = \frac{458 \times 10^{-6} + 568 \times 10^{-6}}{2} = 513 \times 10^{-6} / \text{K}$$

$$\text{So, } dH = C_p dT + (1 - \beta T) V dP$$

Part 1 ( $dP=0$ )       $C_p dT$       0

Part 2 ( $dT=0$ )      0       $(1 - \beta T) V dP$

Integrate

$$\int dH = \underbrace{\int C_p dT}_{\text{Part 1 only}} + \underbrace{\int (1 - \beta T) V dP}_{\text{Part 2 only}}$$

Use Average values of  $C_p, \beta, V$

On 2nd term,  $T = 50^\circ\text{C} + 273 = 323\text{K} = T_2$   
(Part 2)

$$\Delta H = \langle C_p \rangle T \Big|_{298}^{323} + (1 - \langle \beta \rangle T_2) \langle V \rangle P \Big|_1^{1000}$$

Plug + Chug ...

(8)

$$\Delta H = \frac{75,310 \text{ J}}{\text{mol} \cdot \text{K}} (323 \text{ K} - 298 \text{ K})$$

$$+ \left( 1 - \frac{513 \times 10^{-6}}{\text{K}} \Big|_{323 \text{ K}} \right) \left| \frac{18.204 \text{ cm}^3}{\text{mol}} \right| \frac{(1000 - 1) \text{ bar}}{1}$$

$$\left| \frac{\text{mol} \cdot \text{K}}{83.14 \text{ cm}^3 \cdot \text{bar}} \right| \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}}$$

$$\Delta H = \underbrace{1,883 \frac{\text{J}}{\text{mol}}}_{\text{Due to } \Delta T} + \underbrace{1,517 \frac{\text{J}}{\text{mol}}}_{\text{Due to } \Delta P} = \boxed{3,400 \frac{\text{J}}{\text{mol}} = \Delta H}$$

Which effect is more significant?

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$$\text{Next, } \int dS = \int C_p \frac{dT}{T} - \int pV dP$$

$$\Delta S = \langle C_p \rangle \ln \left( \frac{T_2}{T_1} \right) - \langle \beta \rangle \langle V \rangle P \Big|_1^{1000}$$

Plug + Chug ...



(9)

$$\Delta S = \frac{75.310 \text{ J}}{\text{mol} \cdot \text{K}} \ln\left(\frac{323}{298}\right)$$

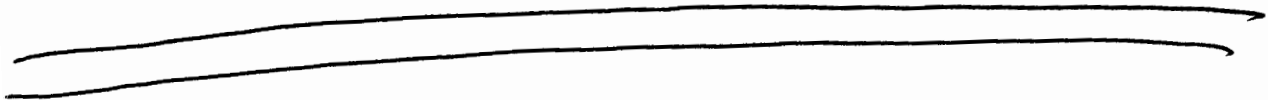
$$- \frac{513 \times 10^{-6}}{\text{K}} \left| \frac{18.204 \text{ cm}^3}{\text{mol}} \right| \frac{(1000-1) \text{ bar}}{1} \left| \frac{\text{mol} \cdot \text{K}}{83.14 \text{ cm}^3 \text{ bar}} \right|$$

$$\left| \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \right|$$

$$\Delta S = \underbrace{6.06}_{\text{Due to } \Delta T} - \underbrace{0.93}_{\text{Due to } \Delta P} = 5.13 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

Again, which is more significant?

Why is effect due to  $\Delta P < 0$ ?



CAN DO SAME TREATMENT TO INTERNAL ENERGY

$$dU = C_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV$$

$$dS = C_V \frac{dT}{T} + \left( \frac{\partial P}{\partial T} \right)_V dV$$

Special Case #1: IDEAL GAS

$$\left( \frac{\partial P}{\partial T} \right)_V = ?$$

IDEAL GAS LAW,  $P = \frac{RT}{V}$

$$\left[ \frac{\partial}{\partial T} \left( \frac{RT}{V} \right) \right]_V = \frac{R}{V} \left( \frac{\partial T}{\partial T} \right)_V = \frac{R}{V}$$

$$\text{So, } dU = C_V dT + \left[ \underbrace{\frac{TR}{V}}_P - P \right] dV$$

$\Rightarrow$   $dU^{ig} = C_V^{ig} dT$   $\leftarrow$  JUST LIKE IN CHAP. 3

AND,

$$dS^{ig} = C_V^{ig} \frac{dT}{T} + \frac{R}{V} dV$$

SPECIAL CASE #2: LIQUIDS

Recall,

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

Volume Expansivity

$$K = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

Isothermal Compressibility

FROM EQN OF STATE,  $V = f(P, T)$

So, EXACT DIFFERENTIAL,

$$dV = \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT$$

$$\frac{dV}{V} = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T dP + \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P dT$$

Put in terms of  $\beta$  +  $K$ .

$$\frac{dV}{V} = -\kappa dP + \beta dT$$

(12)

At constant volume,  $dV = 0$

$$0 = -\kappa dP + \beta dT$$

$$\frac{dP}{dT} = \frac{\beta}{\kappa} \quad (\text{but at constant } V)$$

$$\text{so } \left( \frac{\partial P}{\partial T} \right)_V = \frac{\beta}{\kappa}$$

Therefore:

$$dU = C_V dT + \left( T \frac{\beta}{\kappa} - P \right) dV$$

$$dS = C_V \frac{dT}{T} + \frac{\beta}{\kappa} dV$$

Functions of P+T only!

NEXT, A CLOSER LOOK AT GIBBS ENERGY...

$$dG = VdP - SdT$$

Recall, only easily measurable quantities changing.  
(+ easy to control  $P + T$ )

⇒ VERY USEFUL.

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT} dG + \frac{G}{R} (-1) T^{-2} dT$$

(Product Rule)

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT} dG - \frac{G}{RT^2} dT$$

Substitute for  $dG$ ...

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT} (VdP - SdT) - \frac{G}{RT^2} dT$$

$$= \frac{1}{RT} VdP - \frac{SdT}{RT} - \frac{(H - TS)}{RT^2} dT$$

$$= \frac{V}{RT} dP - \frac{SdT}{RT} - \frac{H}{RT^2} dT + \frac{SdT}{RT}$$

$$\therefore d\left(\frac{G}{RT}\right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT$$

At constant T:

$$\left[ \frac{\partial}{\partial P} \left( \frac{G}{RT} \right) \right]_T = \frac{V}{RT}$$

At constant P:

$$-T \left[ \frac{\partial}{\partial T} \left( \frac{G}{RT} \right) \right]_P = \frac{H}{RT}$$

Also,  $\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$$

⇒ If you have  $G = f(P, T)$ , you can calculate  
V, H, S, and U.

## 6.2 RESIDUAL PROPERTIES

$$M^R \equiv M - M^{ig}$$

GENERIC PROPERTY  $M$

DIFFERENCE BETWEEN ACTUAL PROPERTY ( $M$ )  
AN IDEAL PROPERTY ( $M^{ig}$ ) =  $M^R$

SO, IF IDEAL GAS

$$M^R \rightarrow 0$$

CAN WRITE RESIDUAL PROPERTIES FOR EXTENSIVE  
PROPERTIES (MOLAR VALUE)  $V, U, H, S,$  or  $G.$

$$\Rightarrow V^R = V - V^{ig} = V - \frac{RT}{P}$$

$$U^R = U - U^{ig}$$

$$S^R = S - S^{ig}$$

$$H^R = H - H^{ig}$$

$$G^R = G - G^{ig}$$

BACK TO  $\frac{G}{RT}$

$$d\left(\frac{G^{ig}}{RT}\right) = \frac{V^{ig}}{RT} dP - \frac{H^{ig}}{RT^2} dT$$

IF WE SUBTRACT THIS EQUATION FROM:

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT$$

THEN:

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT} dP - \frac{H^R}{RT^2} dT$$

Special Case: Constant T ( $dT=0$ )

$$\frac{V^R}{RT} = \left[ \frac{\partial}{\partial P} \left( \frac{G^R}{RT} \right) \right]_T$$

Special Case: Constant P ( $dP=0$ )

$$\frac{H^R}{RT} = -T \left[ \frac{\partial}{\partial T} \left( \frac{G^R}{RT} \right) \right]_P$$



$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT}$$

LOOKS VERY SIMILAR, RIGHT?

NOW JUST IN TERMS SMALL CHANGES FROM IDEAL BEHAVIOR.

TWO MORE USEFUL EQUATIONS...

$$\frac{S^R}{R} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P (Z-1) \frac{dP}{P} \quad \text{Constant } T$$

$$\frac{G^R}{RT} = \int_0^P (Z-1) \frac{dP}{P} \quad \text{Constant } T$$

Why Useful?

$$\frac{S^R}{R} + \frac{G^R}{RT} \quad \text{BOTH FUNCTIONS OF } Z, P, T$$

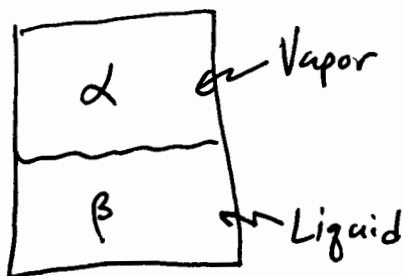
⇒ CAN USE ALL PREVIOUS EQUATIONS OF STATE TO GET  $S^R + G^R$ .

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## 6.4 Two PHASE SYSTEMS

$U$ ,  $H$ ,  $S$ , and  $V$  ALL VERY DIFFERENT  
IN GAS + LIQUID PHASES.

ANOTHER REASON  $G$  IS SPECIAL...



$$G^{\alpha} = G^{\beta}$$

@ EQUILIBRIUM

$$G^{\alpha} = G^{\beta}$$

Small changes, holds too...

$$dG^{\alpha} = dG^{\beta}$$

But,  $dG = V dP - S dT$

At Equilibrium,  $P^{\alpha} = P^{\beta} = P$

$$T^{\alpha} = T^{\beta} = T$$

So,

$$V^\alpha dP - S^\alpha dT = V^\beta dP - S^\beta dT$$

Also, at the interface between phases

$$P = P^{\text{sat}} = P^\alpha = P^\beta$$

$$\Rightarrow V^\alpha dP^{\text{sat}} - S^\alpha dT = V^\beta dP^{\text{sat}} - S^\beta dT$$

Gather terms:

$$(V^\alpha - V^\beta) dP^{\text{sat}} = (S^\alpha - S^\beta) dT$$

$$\frac{dP^{\text{sat}}}{dT} = \frac{S^\alpha - S^\beta}{V^\alpha - V^\beta} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

Next ... get rid of  $\Delta S$  ...

$$\text{Recall, } dH = TdS + VdP$$

$$\text{@ EQUILIBRIUM, } dP = 0$$

$$\int dH = \int T dS = T \int dS$$

$$\Delta H = T \Delta S \Rightarrow \Delta S = \frac{\Delta H}{T}$$

SUBSTITUTE...

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T \Delta V^{\alpha\beta}}$$

CLAPEYRON  
EQUATION

THINK  $\alpha$  (VAPOR) +  $\beta$  (LIQUID)

$\Rightarrow$  VAPOR-LIQUID EQUILIBRIUM (VLE)

$$\frac{\Delta H^{vap}}{T \Delta V^{vap}} = \frac{dP^{sat}}{dT}$$

FOR LOW PRESSURE (IDEAL GAS)

AND  $V_{(g)} \gg V_{(l)} \Rightarrow \Delta V^{vap} \approx V_{(g)}$

(21)

IDEAL GAS,

$$V(g) = \frac{RT}{p^{\text{sat}}}$$

$$\text{SO, } \frac{\Delta H^{\text{vap}}}{T \left( \frac{RT}{p^{\text{sat}}} \right)} = \frac{dp^{\text{sat}}}{dT}$$

Separate variables ( $T + p^{\text{sat}}$ )

$$\frac{\Delta H^{\text{vap}}}{R} \frac{dT}{T^2} = \frac{dp^{\text{sat}}}{p^{\text{sat}}}$$

ASIDE!

$$(1) \quad d\left(\frac{1}{T}\right) = d(T^{-1}) = (-1)T^{-2}dT = -\frac{dT}{T^2}$$

$$(2) \quad d(\ln p^{\text{sat}}) = \frac{1}{p^{\text{sat}}} dp^{\text{sat}}$$

SUBSTITUTE:

$$-\frac{\Delta H^{\text{vap}}}{R} \left( -\frac{dT}{T^2} \right) = d(\ln p^{\text{sat}})$$

$$-\frac{\Delta H^{vap}}{R} d\left(\frac{1}{T}\right) = d(\ln P^{sat})$$

$$\boxed{-\frac{\Delta H^{vap}}{R} = \frac{d(\ln P^{sat})}{d\left(\frac{1}{T}\right)}}$$

OR

$$\boxed{\Delta H^{vap} = -R \frac{d(\ln P^{sat})}{d\left(\frac{1}{T}\right)}}$$

← CLAUZIUS - CLAPEYRON EQUATION.

⇒ Plot  $\ln P^{sat}$  vs  $\frac{1}{T}$

+ Slope is proportional to  $\Delta H^{vap}$

(ONLY GOOD AT LOW PRESSURES)

Next,  $P^{sat} = f(T)$

(23)

If  $\ln P^{\text{sat}} \propto \frac{1}{T}$  (Linear or approximately linear)

⇒ EQUATION OF A LINE...

$$\ln P^{\text{sat}} = A - \frac{B}{T}$$

Slope =  $-B$

Intercept =  $A$

Good for rough estimation.

⇒ IF WE WORK IN A MORE LIMITED TEMP. RANGE...

ANTOINE EQUATION:

$$\ln P^{\text{sat}} = A - \frac{B}{T+C}$$

Values of  $A$ ,  $B$ , and  $C$  in Appendix B.

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NEXT, ONTO CHAPTER 10 (VLE)