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# **Introductory Chemical Engineering Thermodynamics**

**By J.R. Elliott and C.T. Lira**

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## The fundamental property relation

Piston+Cylinder  $\Rightarrow$  Closed system  $\Rightarrow dU=(Q+W)dt$

For the heat exchange:  $Qdt=TdS$  (macroscopic definition)

For the work  $Wdt = -PdV$  ( $W = Fdx$ )

$\Rightarrow dU = TdS - PdV$  This is the fundamental property relationship.

$H = U + PV \Rightarrow dH = dU + d(PV) = dU + PdV + VdP$

Substitution of the fundamental property relationship:

$\Rightarrow dH = (TdS - PdV) + PdV + VdP$

$\Rightarrow dH = TdS + VdP$

$dA = -SdT - PdV$

$dG = -SdT + VdP$

We can integrate these expressions to find that

$A \equiv U - TS$  **Helmholtz free energy**

$G \equiv H - TS$  **Gibbs free energy**

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## Example. Enthalpy of H<sub>2</sub>O above its saturation pressure

Determine the enthalpy of H<sub>2</sub>O at 20°C and 100 MPa. Note that values of pressure this high do not appear in the steam tables.

Solution The expression for a change in enthalpy should remind us that shaft work for an adiabatic, reversible process ( $dS=0$ ) is  $DH = \delta VdP$ . But,

$$VL \approx \text{constant} = 1.003 \text{ cm}^3/\text{g} \Rightarrow DH = 1.003(100 - 0.00234)8.314/8.314 = 100.30 \text{ J/g.}$$
$$\Rightarrow H = 83.96 + 100.30 = 184.25 \text{ J/g.}$$

NOTE:  $W = \Delta H = 100 \text{ J/g} \sim P \text{ (MPa)}$

# Maxwell's Relations

By recognizing that any variable is a function of any two other variables,

$$U = U(S, V) \Rightarrow dU = (\partial U / \partial S)_V dS + (\partial U / \partial V)_S dV$$

But the fundamental property relationship says:

$$dU = T dS - P dV$$

$$\frac{\partial^2 U(S, V)}{\partial S \partial V} = \left( \frac{\partial}{\partial S} \left( \frac{\partial U(S, V)}{\partial V} \right) \right)_V = \left( \frac{\partial}{\partial V} \left( \frac{\partial U(S, V)}{\partial S} \right) \right)_S = \frac{\partial^2 U(S, V)}{\partial V \partial S}$$

$$\frac{\partial^2 U(S, V)}{\partial S \partial V} = \left( \frac{\partial}{\partial S} (-P) \right)_V = \left( \frac{\partial}{\partial V} (T) \right)_S = \frac{\partial^2 U(S, V)}{\partial V \partial S}$$

$$dH = (\partial H / \partial S) dS + (\partial H / \partial P)_S dP = T dS + V dP$$

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S} = \left[ \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial P} \right) \right]_P = \left[ \frac{\partial}{\partial P} \left( \frac{\partial H}{\partial S} \right) \right]_S \Rightarrow \left( \frac{\partial V}{\partial S} \right)_P = \left( \frac{\partial T}{\partial P} \right)_S$$

$$dU = T dS - P dV \Rightarrow -(\partial P / \partial S)_V = (\partial T / \partial V)_S$$

$$dH = T dS + V dP \Rightarrow (\partial V / \partial S)_P = (\partial T / \partial P)_S$$

$$dA = -S dT - P dV \Rightarrow (\partial P / \partial T)_V = (\partial S / \partial V)_T$$

$$dG = -S dT + V dP \Rightarrow -(\partial V / \partial T)_P = (\partial S / \partial P)_T$$

**MAXWELL'S  
RELATIONS**

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## Example. Entropy change vs. T at constant P

Evaluate  $(\partial S/\partial T)_p$  in terms of  $C_p$ ,  $C_v$ ,  $T$ ,  $P$ , and  $V$

Solution:

Recall,  $dH = TdS + VdP$

If  $P$  is constant, then  $dP=0$ . Dividing through by  $dT$ ,

$$\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \quad \text{But, the definition of } C_p \text{ is: } C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$$

$$\text{Therefore, } \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

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## Example . Entropy change as a function of T and P

Derive a general relation for entropy changes of any fluid with respect to temperature and pressure in terms of  $C_p$ ,  $C_v$ ,  $P$ ,  $V$ ,  $T$  and their derivatives.

$dS = (\partial S/\partial T)_p dT + (\partial S/\partial P)_T dP$  but  $(\partial S/\partial T)_p = C_p/T$  as derived above, and Maxwell's Relations show that  $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ .

$$\Rightarrow dS(T,P)_p = C_p dT/T - (\partial V/\partial T)_p dP \quad (\text{eqn. 5.35, a useful, general equation})$$

Similarly

$$dS(T,V) = C_v dT/T + (\partial P/\partial T)_v dV \quad (\text{eq 5.36})$$

$$dH(T,P) = C_p dT + [V - T(\partial V/\partial T)_p] dP \quad (\text{eq 5.37})$$

$$dU(T,V) = C_v dT + [T(\partial P/\partial T)_v - P] dV \quad (\text{eq 5.38})$$

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## II. Generalized Fluid Properties

### What is so important about the variables $C_p$ , $C_v$ , $P$ , $V$ , $T$ ?

As a sample application, we can assume the ideal gas equation of state.

$$V = RT/P \Rightarrow (\partial V/\partial T)_P = R/P. \text{ Substitution } \Rightarrow \Delta S = C_p \ln(T_2/T_1) - R \ln(P_2/P_1)$$

$$\text{Applying } \Delta S = 0 \Rightarrow \ln(T_2/T_1) = R/C_p \ln(P_2/P_1) \Rightarrow (T_2/T_1) = (P_2/P_1)^{(C_p - C_v)/C_p}$$

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = \left[ \frac{P_2}{P_1} \right]^{1-1/\gamma} \Rightarrow \frac{V_2}{V_1} = \left[ \frac{P_2}{P_1} \right]^{-1/\gamma} = \left[ \frac{P_1}{P_2} \right]^{1/\gamma}$$

Once again, we arrive at this familiar relation, but this time, it is easy to recognize the necessary changes for applications to real gases. That is, we must simply replace the PVT relation by a more realistic equation of state.

e.g.  $V = RT/(P+C)$  which we may refer to as the “bogus” equation of state.

$$\Rightarrow (\partial V/\partial T)_P = R/(P+C)$$

$$\text{Substitution } \Rightarrow \Delta S = C_p \ln(T_2/T_1) - R \ln[(P_2+C)/(P_1+C)]$$

$$\text{Applying } \Delta S = 0 \Rightarrow \ln(T_2/T_1) = R/C_p \ln[(P_2+C)/(P_1+C)] \Rightarrow$$

$$(T_2/T_1) = [(P_2+C)/(P_1+C)]^{R/C_p}$$

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## II. Generalized Fluid Properties

### Triple Product Rule (a.k.a. Chain Rule)

Suppose:  $F = F(A, B)$

then  $dF = (\partial F/\partial A)_B dA + (\partial F/\partial B)_A dB$ .

Consider what happens when  $dF = 0$  (ie. at constant  $F$ ). Then,

$$0 = \left(\frac{\partial F}{\partial A}\right)_B \left(\frac{\partial A}{\partial B}\right)_F + \left(\frac{\partial F}{\partial B}\right)_A \Rightarrow \left(\frac{\partial A}{\partial B}\right)_F = -\frac{\left(\frac{\partial F}{\partial B}\right)_A}{\left(\frac{\partial F}{\partial A}\right)_B} = -\frac{\left(\frac{\partial A}{\partial F}\right)_B}{\left(\frac{\partial B}{\partial F}\right)_A}$$

But, because  $C$  is some fourth property and  $F$  is constant.

$$\left(\frac{\partial A}{\partial B}\right)_F = \frac{\left(\frac{\partial A}{\partial C}\right)_F}{\left(\frac{\partial B}{\partial C}\right)_F} = \left(\frac{\partial A}{\partial C}\right)_F \left(\frac{\partial C}{\partial B}\right)_F$$

Now the negative sign has disappeared. Did you notice the difference?



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## II. Generalized Fluid Properties

### Example. Application of the triple product relation.

Evaluate  $(\partial S/\partial V)$  in terms of  $C_p$ ,  $C_v$ ,  $T$ ,  $P$ , and  $V$ . Your answer may include absolute values of  $S$  if it not associated with a derivative.

Solution: This problem illustrates a typical situation where the triple product rule is necessary because the free energy is held constant. It is easiest to express changes in the free energies as changes in other variables.

Applying the triple product rule:  $(\partial S/\partial V)_A = -(\partial A/\partial V)_S/(\partial A/\partial S)_V$

$dA = -PdV - SdT \Rightarrow (\partial A/\partial V)_S = -P - S(\partial T/\partial V)_S$  and  $(\partial A/\partial S)_V = 0 - S(\partial T/\partial S)_V$

$$5.35 \Rightarrow (\partial T/\partial V)_S = -\frac{T}{C_v} \left( \frac{\partial P}{\partial T} \right)_V \quad \text{and} \quad \left( \frac{\partial T}{\partial S} \right)_V = \frac{T}{C_v}$$

Substitution

$$\Rightarrow \left( \frac{\partial S}{\partial V} \right)_A = \frac{-PC_v}{ST} + \left( \frac{\partial P}{\partial T} \right)_V$$