

**Chapter 13. MATHEMATICAL MODELING-  
THERMODYNAMIC PROPERTIES**

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# Chapter 13. Mathematical modeling – Thermodynamic properties

## 13.1 Need for Mathematical modeling

- Mathematical modeling : the conversion of data to equation form

- ┌ equation fitting (ch.4)
- └ (conversion of data to equation form)
- ┌ physical relationship (ch.5)
- └
- ┌ complexity
- └ accuracy

## 13.2 The form of the equation

- Choice of equation from that gives a good representation with a simple equation. → Art of equation fitting (ch.4)

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## 13.3 Criteria for fidelity of representation

(1) Sum of the deviations squared (SDS)

$$SDS = \sum_{i=1}^n (y_i - Y_i)^2$$

eqn. exp.

$y_i$  : variable computed from the equation  
 $Y_i$  : variable from the original data  
 $n$  : total number of data points

(2) Average percent absolute deviation (APD)

$$APD = \frac{100}{n} \sum_{i=1}^n \sqrt{\left(\frac{Y_i - y_i}{Y_i}\right)^2}$$

$$RMS = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - Y_i)^2}$$

$$Bias = \frac{1}{n} \sum_{i=1}^n (y_i - Y_i)$$

$$AAD = \frac{1}{n} \sum_{i=1}^n |y_i - Y_i|$$

(3) Goodness of fit (GOF)

$$GOF = 100 \sqrt{1 - \frac{SDS}{G}} \quad [\%], \quad G = \sum_{i=1}^n (Y_i - y_{\text{mean}})^2$$

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## 13.4 Linear regression analysis

- Parameters appear in linear form not the variable

$$y = a + bx$$

$$y = a + be^x + c \ln x$$

$$y = a \sin x + b \cos 2x$$

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## 13.5 Nonlinear regression analysis

- Steepest decent method – unconstrained optimization

$$\text{ex) } y = ae^{bx} \rightarrow \ln y = \ln a + bx$$

$Y \qquad A$

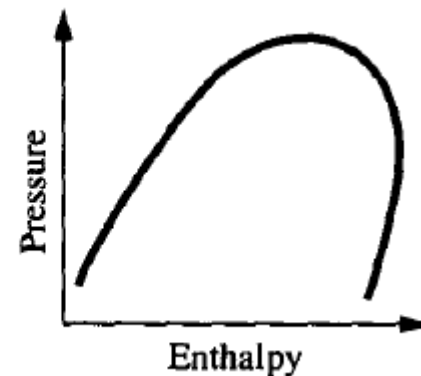
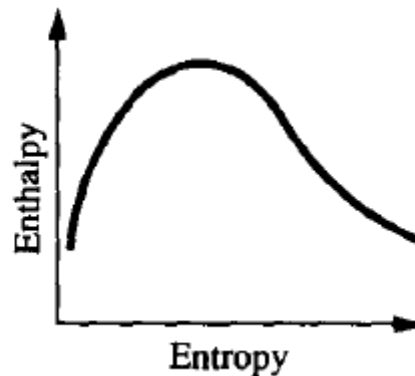
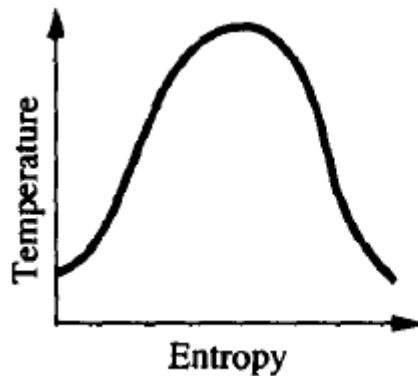
$$y = a \sin bx$$

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## 13.6 Thermodynamic properties

Property equations

1.  $P - v - T$  Equations for vapor
2.  $c_p^o$  The specific heat at zero pressure
3.  $P - T$  Relation for saturated conditions
4.  $\rho_f$  The density of liquid



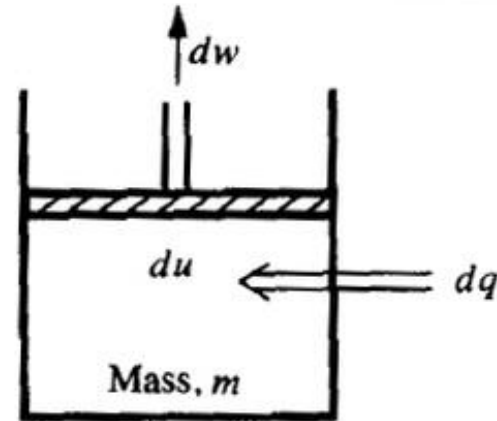
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## 13.6 Thermodynamic properties

$$\delta q = du + \delta w$$

$$\delta q)_{rev} = Tds, \delta w)_{rev} = Pdv$$

$$Tds = du + Pdv$$



$$du = Tds - Pdv$$

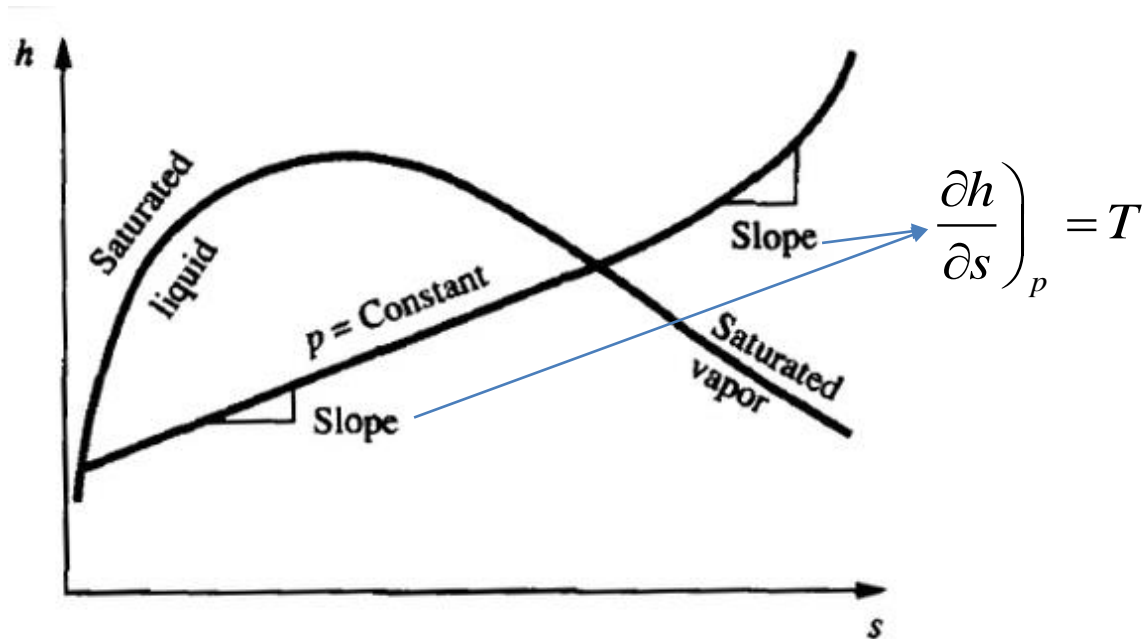
$$\left. \frac{\partial u}{\partial s} \right)_v = T, \left. \frac{\partial u}{\partial v} \right)_s = -P$$

$$dh = Tds + vdP$$

$$\left. \frac{\partial h}{\partial s} \right)_p = T, \left. \frac{\partial h}{\partial P} \right)_s = v$$

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## 13.7 Internal energy and enthalpy





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## 13.8 The Clapeyron equation

- A expression for relating some thermodynamic liquid and vapor properties **at saturated conditions**

$$G = h - Ts$$

$$dG = dh - Tds - sdT$$

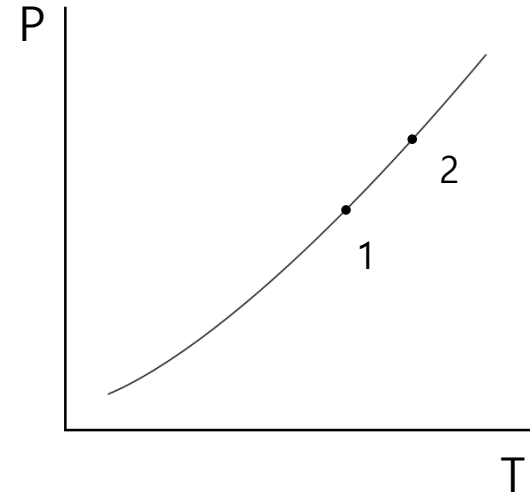
$$= du + pdv + vdP - Tds - sdT$$

$$= vdP - sdT$$

at saturation  $dG = 0$

$$G_f = G_g$$

$$v_f dP - s_f dT = v_g dP - s_g dT$$



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## 13.9 Pressure-temperature relationships at saturated conditions

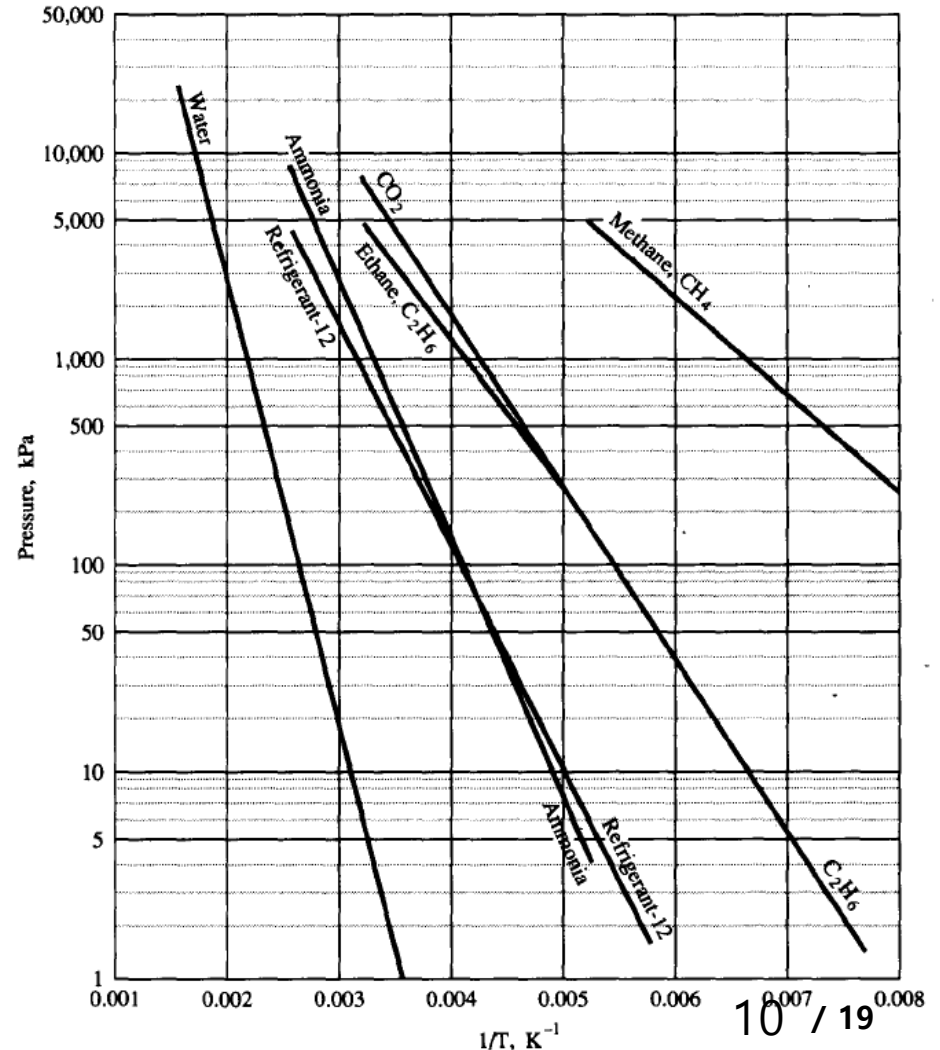
$$\frac{dP}{dT} = \frac{s_g - s_f}{v_g - v_f} = \frac{h_{fg}}{T(v_g - v_f)}$$

$$\approx \frac{h_{fg}}{Tv_g} \quad (v_g \gg v_f, \quad v_g = \frac{RT}{P})$$

$$\frac{dP}{dT} \approx \frac{Ph_{fg}}{RT^2}$$

$$\ln P = -\frac{h_{fg}}{RT} + C$$

$$\ln P = A + \frac{B}{T}$$



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## 13.10 The Maxwell relations

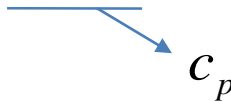
$$\frac{\partial(P, v)}{\partial(T, s)} = 1 \quad Tds = du + Pdv \quad Tds = dh - vdP$$
$$-sdT = df + Pdv \quad -sdT = dg - vdP$$

$$\left. \frac{\partial T}{\partial v} \right)_s = - \left. \frac{\partial p}{\partial s} \right)_v \quad \left. \frac{\partial T}{\partial p} \right)_s = \left. \frac{\partial v}{\partial s} \right)_p$$
$$\left. \frac{\partial v}{\partial T} \right)_p = - \left. \frac{\partial s}{\partial p} \right)_T \quad \left. \frac{\partial p}{\partial T} \right)_v = \left. \frac{\partial s}{\partial v} \right)_T$$

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## 13.11 Specific heat

$$c_v = \left. \frac{\partial u}{\partial T} \right)_v \quad c_p = \left. \frac{\partial h}{\partial T} \right)_p$$

$$\left. \frac{1}{T} \frac{\partial h}{\partial T} \right)_p = \left. \frac{\partial s}{\partial T} \right)_p$$


$c_p$

$$\left. \frac{1}{T} \frac{\partial c_p}{\partial p} \right)_T = \frac{\partial^2 s}{\partial p \partial T} = \frac{\partial}{\partial T} \left[ \left. \left( \frac{\partial s}{\partial p} \right)_T \right]_p = - \frac{\partial^2 v}{\partial T^2}$$

$$\text{If ideal gas : } pv = RT, \quad \left. \frac{\partial c_p}{\partial p} \right)_T = -T \frac{\partial^2 v}{\partial T^2} = 0$$

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## 13.12 $p$ - $v$ - $T$ Equations

$$pv = RT \quad \text{Universal gas constant, } R = 8.314 \left[ \frac{\text{kJ}}{\text{kg}\cdot\text{K}} \right]$$

$$pv = ZRT \quad \text{Compressibility, } Z = f(T, p)$$

- Beattie-Bridgeman equation

$$p = \frac{RT}{v} + \frac{\alpha}{v^2} + \frac{\beta}{v^3} + \frac{\gamma}{v^4} \quad \alpha, \beta, \gamma : \text{determined from experimental data}$$

- Van der Waals equation

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \quad a = \frac{27}{64} \frac{R^2 T_c^2}{p_c}, \quad b = \frac{RT_c}{8p_c} \quad \begin{array}{l} T_c : \text{critical temperature [K]} \\ p_c : \text{critical pressure [kPa]} \end{array}$$

- Redlich-Kwong equation

$$p = \frac{RT}{v - b} - \frac{a}{T^{0.5} v(v + b)} \quad a = 0.42748 \frac{R^2 T_c^{5/2}}{p_c}, \quad b = 0.08664 \frac{RT_c}{p_c}$$

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## 13.13 Building a full set of data

$$dh = \underbrace{\left. \frac{\partial h}{\partial T} \right)_p}_{c_p} dT + \underbrace{\left. \frac{\partial h}{\partial p} \right)_T}_{v + T \left. \frac{\partial s}{\partial p} \right)_T} dp = v - T \left. \frac{\partial v}{\partial T} \right)_P$$

$$ds = \underbrace{\left. \frac{\partial s}{\partial T} \right)_p}_{\frac{c_p}{T}} dT + \underbrace{\left. \frac{\partial s}{\partial p} \right)_T}_{-\left. \frac{\partial v}{\partial T} \right)_P} dp$$

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## 13.13 Building a full set of data

### (Example 13.6)

Starting with a base enthalpy of  $h = 0$  kJ/kg for saturated liquid water at  $0^\circ\text{C}$ , the enthalpy of superheated vapor at 4000 kPa and  $500^\circ\text{C}$  using the following equations: (1) Redlich-Kwong equation of state ( $a=43.951$ ,  $b=0.001171$ ), (2)  $c_{p0}$  from Table 13.3 and (3) the p-T equation for saturation conditions at low pressure,  $\ln P = 19.335 - 5416/T$ .

**TABLE 13.3**  
**Equations for zero-pressure  $c_p$  in the range of 300 to 3500 K,**  
**where  $\Theta = T/100$  (Ref. 3).**

Gas	$c_{p0}$ , kJ/(kg · K)
H <sub>2</sub>	$28.253 - 351.37\Theta^{-0.75} + 582.5\Theta^{-1} - 280.35\Theta^{-1.5}$
CH <sub>4</sub>	$-42.054 + 27.483\Theta^{0.25} - 2.228\Theta^{0.75} + 11.423\Theta^{-3}$
H <sub>2</sub> O	$7.947 - 10.20\Theta^{0.25} + 4.597\Theta^{0.5} - 0.2055\Theta$
N <sub>2</sub>	$1.395 - 18.314\Theta^{-1.5} + 38.31\Theta^{-2} - 29.3\Theta^{-3}$
O <sub>2</sub>	$1.1698 - 0.000628\Theta^{1.5} - 5.580\Theta^{-1.5} + 7.4025\Theta^{-2}$
CO <sub>2</sub>	$-0.0849 + 0.6938\Theta^{0.5} - 0.09326\Theta + 0.000550\Theta^2$

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## 13.13 Building a full set of data

(solution)

at 0 [°C],  $p = 0.6108$  [kPa]

$$\frac{dp}{dT} = p \frac{5416}{T^2} = 0.04434 \text{ [kPa/K]}$$

From the Redlich-Kwong equation,  $v_g = 206.54$  [m<sup>3</sup>/kg]

Clapeyron equation :

$$\frac{dp}{dT} = \frac{h_{fg}}{T(v_g - v_f)} \approx \frac{h_{fg}}{Tv_g}$$

$$\longrightarrow h_{fg} = 0.0434 \times 273.15 \times 206.54 = 2501.5 \text{ [kJ/kg]}$$

$$\longrightarrow h_g \text{ at } 0^\circ\text{C} = 0 + 2501.5 = 2501.5 \text{ [kJ/kg]}$$



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## 13.13 Building a full set of data

(solution) From Table 13.3

$$\left. \begin{array}{l} c_{p0} = 1.8703 \quad \text{at } 0^\circ\text{C} \\ c_{p0} = 1.9603 \quad \text{at } 250^\circ\text{C} \\ c_{p0} = 2.1319 \quad \text{at } 500^\circ\text{C} \end{array} \right\} \begin{array}{l} \text{Equation fitting (} t \text{ is in } ^\circ\text{C)} \\ c_{p0} = 1.8703 + 0.0001968t + 0.6528 \times 10^{-6}t^2 \end{array}$$

Integration from 0 to 500°C at 0.6108 kPa

$$\int_{0^\circ\text{C}}^{500^\circ\text{C}} c_{p0} dt = 986.95$$

$$h_{500^\circ\text{C} \& 0.6108 \text{ kPa}} = 2501.5 + 986.95 = 3488.5 \text{ [kJ/kg]}$$

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## 13.13 Building a full set of data

(solution)

**TABLE 13.4**  
**Comparison of Example 13.6 calculations**  
**with tabular values<sup>6</sup>**

$t, ^\circ\text{C}$	$p, \text{kPa}$	Vapor enthalpies, kJ/kg	
		Table	Example 13.6
0	0.6108	2501.6	2501.5
500	0.6108	3489.2	3488.5
500	4000	3445.0	3448.5

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## 13.13 Building a full set of data

(solution)

From the Redlich-Kwong equation

$$t = 499.9 \text{ }^\circ\text{C}, v_a = 0.08563245748$$

$$t = 500.0 \text{ }^\circ\text{C}, v_a = 0.085975713311$$

$$t = 500.1 \text{ }^\circ\text{C}, v_a = 0.085988180541$$

$$v - T \left. \frac{\partial v}{\partial T} \right|_p = v_b - \frac{773.15 \times (v_c - v_a)}{0.2} = -0.010 \text{ m}^3/\text{kg}$$

$$h_{500 \text{ }^\circ\text{C} \ \& \ 4000 \text{ kPa}} = dh = c_p dT + \left[ v - T \left. \frac{\partial v}{\partial T} \right|_P \right] dP$$

$$h_{500 \text{ }^\circ\text{C} \ \& \ 4000 \text{ kPa}} = 3488.5 + (-0.010) \times (4000 - 0.61) = 3448.5 \text{ kJ/kg}$$