

# **Optimal Design of Energy Systems**

## **Chapter 13 Mathematical Modeling- Thermodynamic Properties**

**Min Soo KIM**

**Department of Mechanical and Aerospace Engineering  
Seoul National University**

# Chapter 13. Mathematical Modeling

---

- equation fitting  
(conversion of data to equation form)
- physical relationship
  
- complexity
- accuracy



# Chapter 13. Mathematical Modeling

---

## 13.3 Criteria for fidelity of representation

(1) Sum of the deviations squared

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

eqn. exp.

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

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

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

(2) Average percent absolute deviation

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

(3) Goodness of fit

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



# Chapter 13. Mathematical Modeling

---

## 13.4 Linear regression analysis

- Parameters appear in linear form not the variable

$$y = a + bx$$

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

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



# Chapter 13. Mathematical Modeling

---

## 13.5 Nonlinear regression analysis

- Steepest decent method – unconstrained optimization

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

$Y \qquad A$

$$y = a \sin bx$$

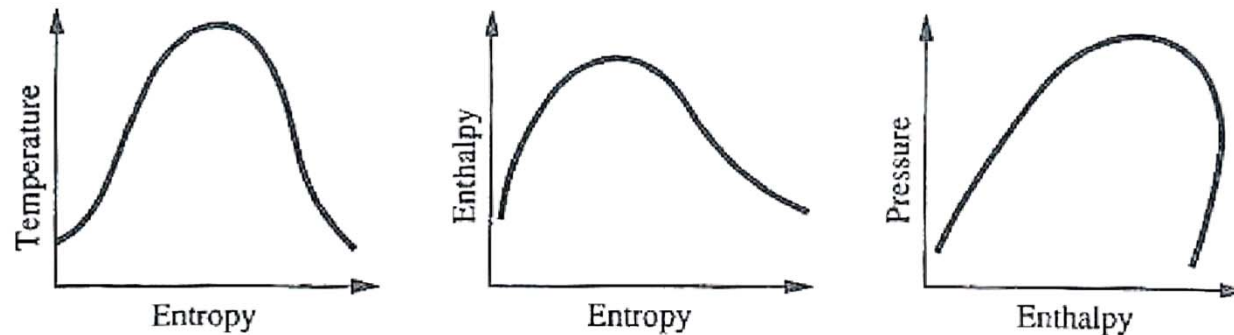


# Chapter 13. Mathematical Modeling

## 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



**FIGURE 13-3**  
Some widely used property charts.



# Chapter 13. Mathematical Modeling

## 13.7 Internal energy and enthalpy

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

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

$$Tds = du + Pdv$$

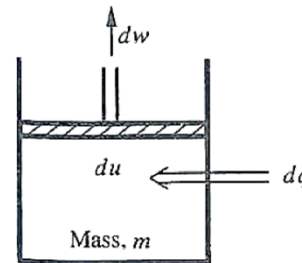


FIGURE 13-4  
Energy balance in a closed system.

$$du = Tds - Pdv$$

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

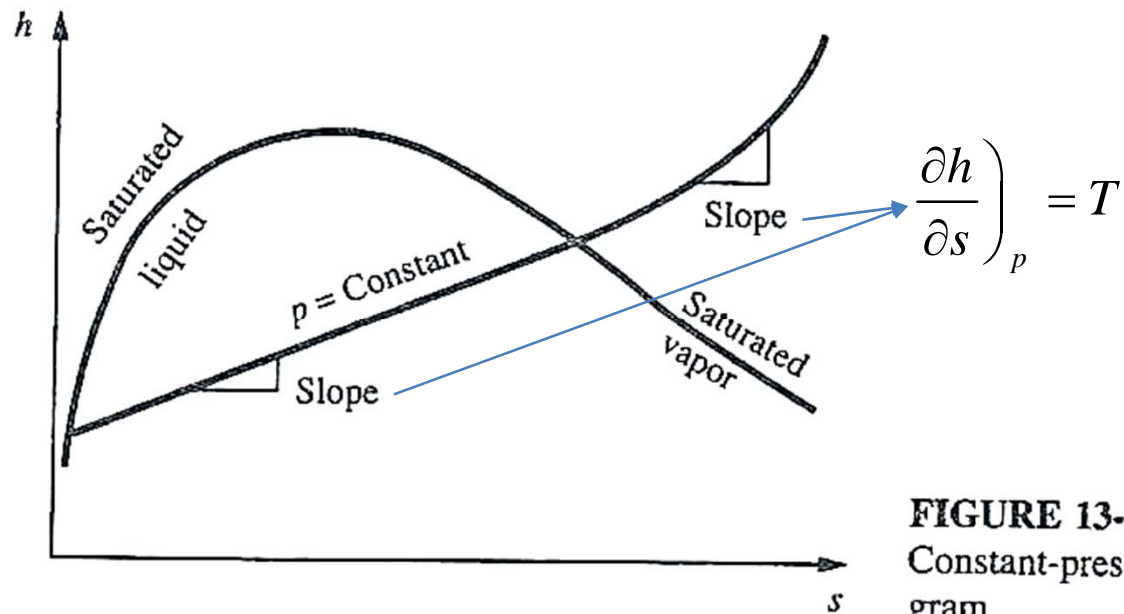
$$dh = Tds + vdP$$

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



# Chapter 13. Mathematical Modeling

## 13.7 Internal energy and enthalpy



**FIGURE 13-5**  
Constant-pressure line on an  $h$ - $s$  diagram.





# Chapter 13. Mathematical Modeling

## 13.8 Clausius-Clapeyron equation

$$G = h - Ts$$

$$dG = dh - Tds - sdT$$

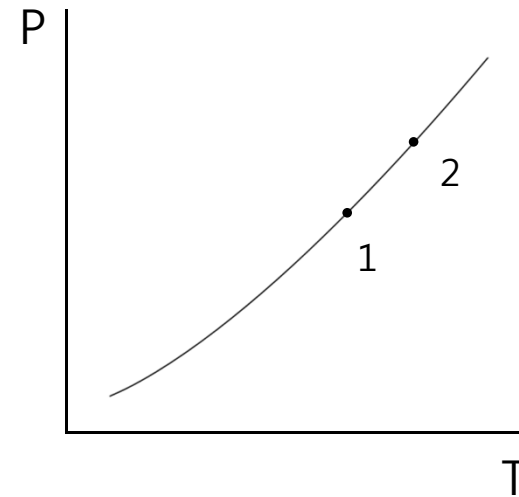
$$= du + pdv + vdP - Tds - sdT$$

$$= vdP - sdT$$

at saturation  $dG = 0$

$$G_f = G_g$$

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



# Chapter 13. Mathematical Modeling

## 13.8 Clausius-Clapeyron equation

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

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

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

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

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

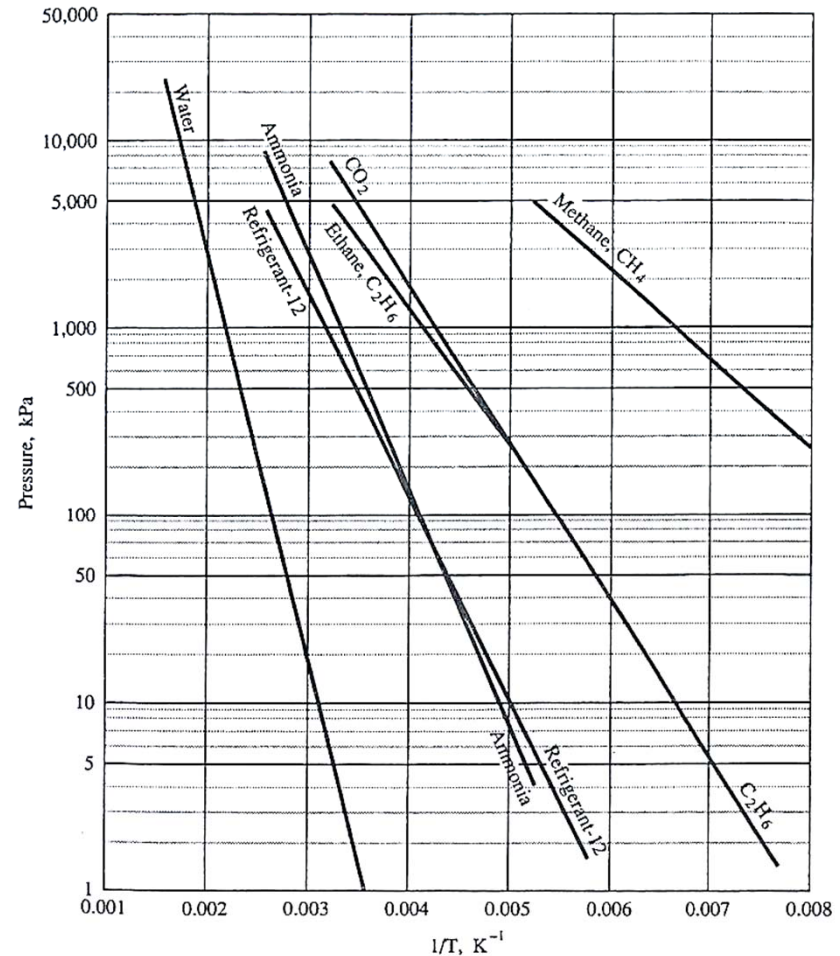


FIGURE 13-7  
Display of terms in Eq. (13.21) for several substances.



# Chapter 13. Mathematical Modeling

## 13.8 Clausius-Clapeyron equation

**Example 13.3.** At 50°C and 51°C, respectively, water has the following properties at saturated conditions,  $v_f = 0.0010121, 0.0010126 \text{ m}^3/\text{kg}$ ,  $v_g = 12.05, 11.50 \text{ m}^3/\text{kg}$ ;  $h_f = 209.26, 213.44 \text{ kJ/kg}$ ; and  $h_g = 2592.2, 2593.9 \text{ kJ/kg}$ . Use the Clapeyron equation to predict the change in saturation pressure between 50 and 51°C.

<Solution>

- calculation with Clausius-Clapeyron equation

$$\begin{aligned}\Delta P &= \Delta T \frac{h_{fg}}{T(v_g - v_f)} \\ &= (1\text{K}) \frac{(2593.1 - 211.4)}{(50.5 + 273.15)(11.775 - 0.0010124)} = 0.625 \text{ kPa}\end{aligned}$$

- calculation from steam table

$$12.961 - 12.335 = 0.626 \text{ kPa}$$



# Chapter 13. Mathematical Modeling

---

## 13.10 Maxwell Relations

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

$$\begin{array}{ll} \left. \frac{\partial T}{\partial v} \right)_s = - \left. \frac{\partial p}{\partial s} \right)_v & \left. \frac{\partial T}{\partial p} \right)_s = \left. \frac{\partial v}{\partial s} \right)_p \\ \left. \frac{\partial v}{\partial T} \right)_p = - \left. \frac{\partial s}{\partial p} \right)_T & \left. \frac{\partial p}{\partial T} \right)_v = \left. \frac{\partial s}{\partial v} \right)_T \end{array}$$




# Chapter 13. Mathematical Modeling

---

## 13.11 Specific heats

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

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

  $c_p$

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

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



# Chapter 13. Mathematical Modeling

---

## 13.12 P-v-T equations

$$pv = RT$$

$$pv = ZRT$$

$$p = \frac{RT}{v} \left( 1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \dots \right)$$

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad \text{Van der Waals}$$

$$p = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)} \quad \text{Redlich-Kwong}$$



# Chapter 13. Mathematical Modeling

---

## 13.13 Building a full set of data

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

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



# Chapter 13. Mathematical Modeling

## 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>	$-0.0849 + 0.6938\Theta^{0.5} - 0.09326\Theta + 0.000550\Theta^2$





# Chapter 13. Mathematical Modeling

---

## 13.13 Building a full set of data

<Solution>

$$\text{at } 0^\circ\text{C}, \quad p = 0.6108 \text{ kPa}$$

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

From the Redlich-Kwong equation,  $v_g = 206.54 \text{ m}^3 / \text{kg}$

Clapeyron equation :

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

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

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



# Chapter 13. Mathematical Modeling

---

## 13.13 Building a full set of data

<Solution> From Table 13.3

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

Integration from 0 to 500°C at 0.6108 kPa

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

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



# Chapter 13. Mathematical Modeling

## 13.13 Building a full set of data

<Solution>

From the Redlich-Kwong equation

$$t = 499.9^\circ C \quad v_a = 0.085963245748$$

$$t = 500.0^\circ C \quad v_b = 0.085975713311$$

$$t = 500.1^\circ C \quad v_c = 0.085988180541$$

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

$$\begin{aligned} h_{500^\circ C \text{ \& } 4000 \text{ kPa}} &= dh = c_p dT + \left[ v - T \frac{\partial v}{\partial T} \right)_p ] dp \\ &= 3488.5 + (-0.010) \times (4000 - 0.61) = 3448.5 \text{ kJ / kg} \end{aligned}$$



# Chapter 13. Mathematical Modeling

## 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

