Optimal Design of Energy Systems (M2794.003400)

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)

$$\mathrm{SDS} = \sum_{i=1}^{n} (\underbrace{y_i}_{\text{eqn.}} - \underbrace{Y_i}_{\text{exp.}})^2$$

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

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

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

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

(2) Average percent absolute deviation (APD)

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

(3) Goodness of fit (GOF)

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

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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

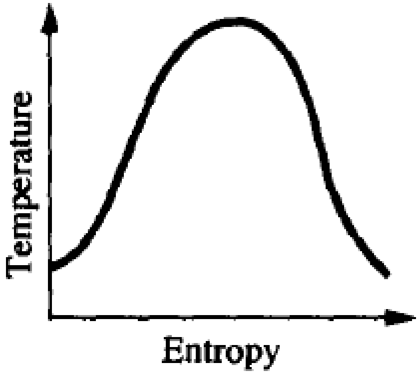
ex) $$y = ae^{bx} \rightarrow \underset{Y}{\ln y} = \underset{A}{\ln a} + bx$$

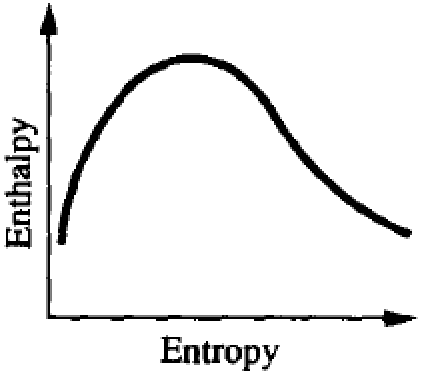
$$y = a \sin bx$$

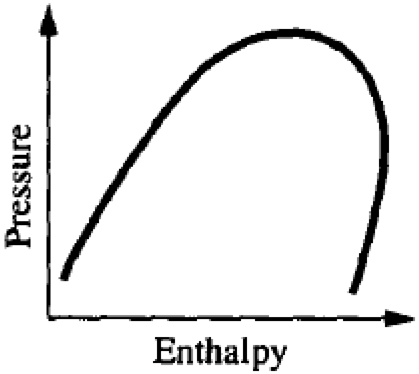
13.6 Thermodynamic properties

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. ρ_f The density of liquid







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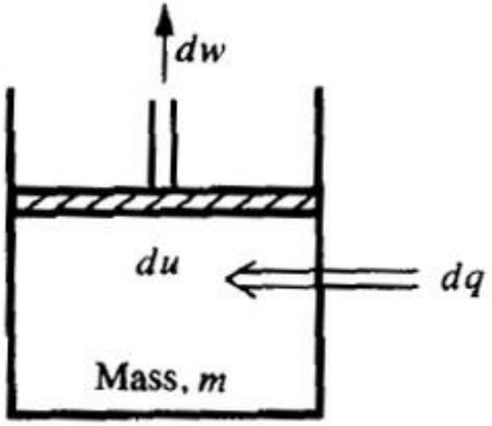
13.6 Thermodynamic properties

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

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

$$Tds = du + Pdv$$



$$du = Tds - Pdv$$

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

$$dh = Tds + vdP$$

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

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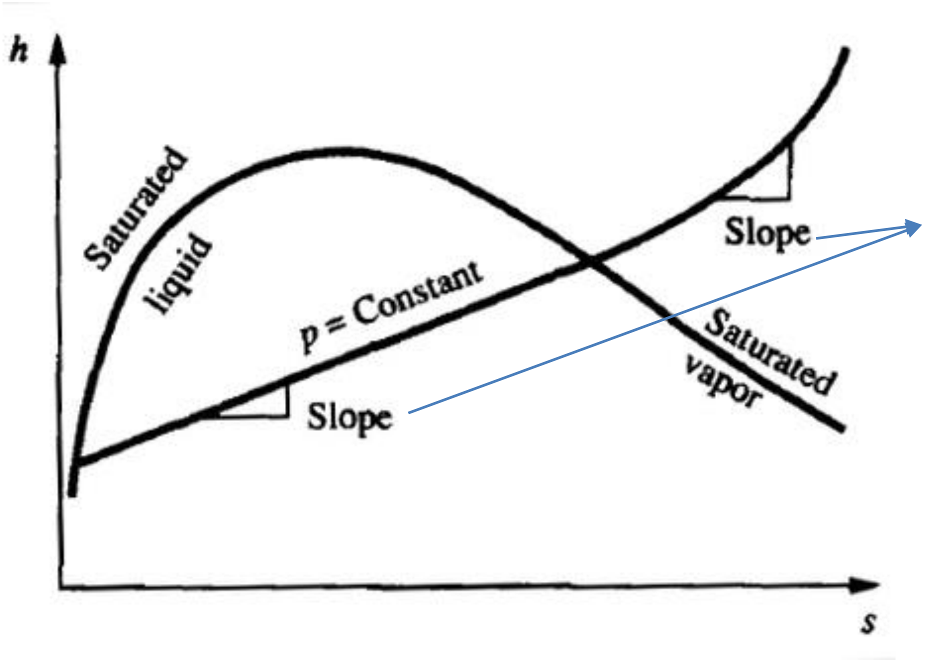
13.7 Internal energy and enthalpy



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

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13.8 The Clapeyron equation

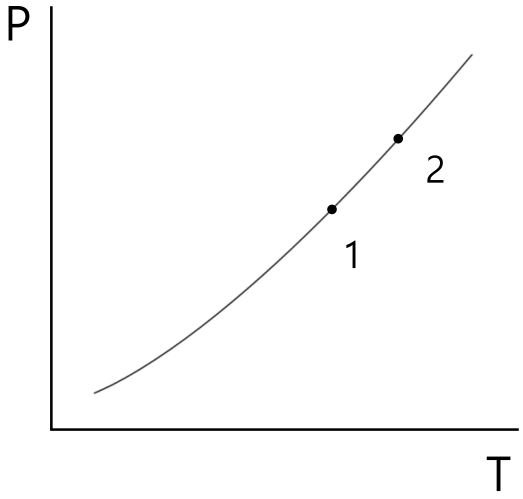
- A expression for relating some thermodynamic liquid and vapor properties **at saturated conditions**

$$G = h - Ts$$

$$dG = dh - Tds - sdT$$

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

$$= vdP - sdT$$



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

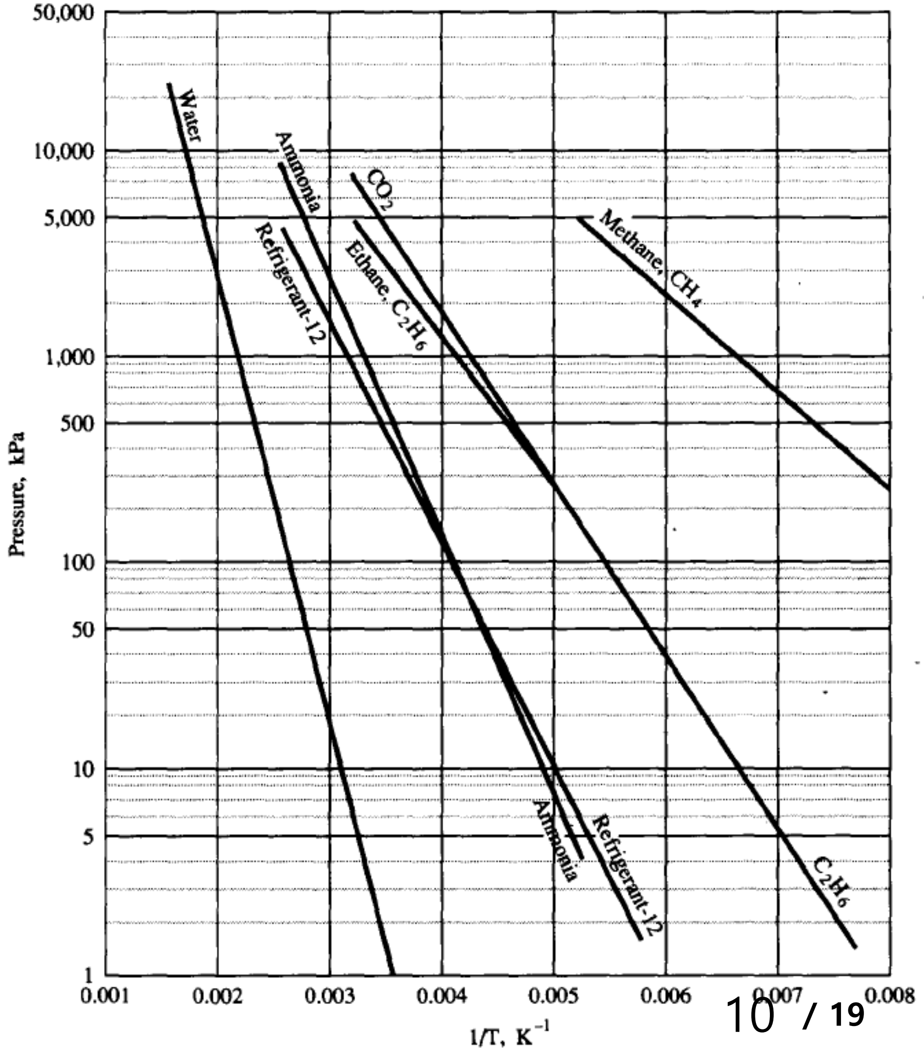
$$\frac{dP}{dT} = \frac{s_g - s_f}{v_g - v_f} = \frac{h_{fg}}{T(v_g - v_f)}$$

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

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

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

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



13.10 The Maxwell relations

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

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

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

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13.11 Specific heat

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

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

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

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

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13.12 *p-v-T* Equations

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

$$pv = ZRT$$ Compressibility, $Z = f(T, p)$

- Beattie-Bridgeman equation

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

- Van der Waals equation

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$ $a = \frac{27}{64}\frac{R^2T_c^2}{p_c}$, $b = \frac{RT_c}{8p_c}$

T_c : critical temperature [K]
p_c : critical pressure [kPa]

- Redlich-Kwong equation

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

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13.13 Building a full set of data

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

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

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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℃, the enthalpy of superheated vapor at 4000 kPa and 500℃ 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, $\ln P = 19.335 - 5416/T$.

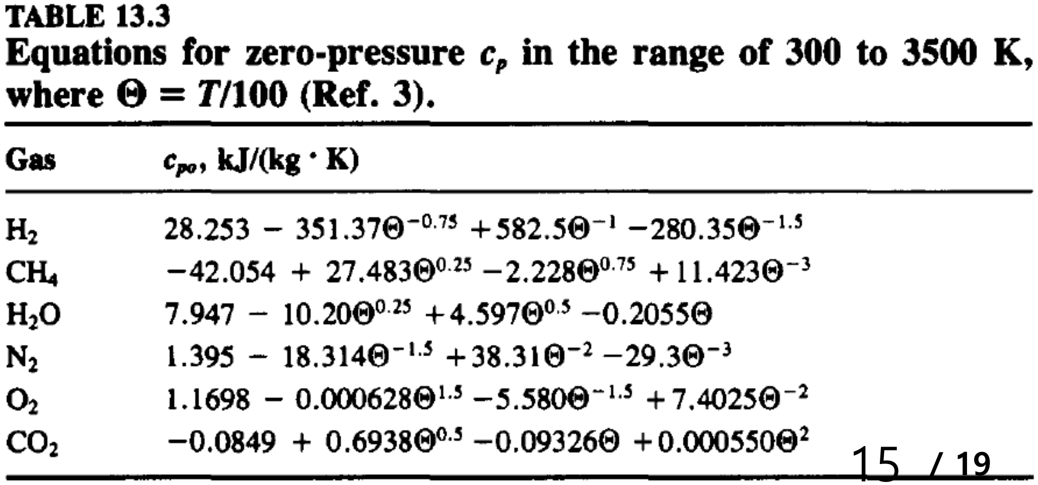

TABLE 13.3
Equations for zero-pressure c_p in the range of 300 to 3500 K, where $\Theta = T/100$ (Ref. 3).

Gas	c_{po}, kJ/(kg · K)
H_2	$28.253 - 351.37\Theta^{-0.75} + 582.5\Theta^{-1} - 280.35\Theta^{-1.5}$
CH_4	$-42.054 + 27.483\Theta^{0.25} - 2.228\Theta^{0.75} + 11.423\Theta^{-3}$
H_2O	$7.947 - 10.20\Theta^{0.25} + 4.597\Theta^{0.5} - 0.2055\Theta$
N_2	$1.395 - 18.314\Theta^{-1.5} + 38.31\Theta^{-2} - 29.3\Theta^{-3}$
O_2	$1.1698 - 0.000628\Theta^{1.5} - 5.580\Theta^{-1.5} + 7.4025\Theta^{-2}$
CO_2	$-0.0849 + 0.6938\Theta^{0.5} - 0.09326\Theta + 0.000550\Theta^2$

13.13 Building a full set of data

(solution)

$at\ 0\ [℃],\ p = 0.6108\ [\mathrm{kPa}]$

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

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

Clapeyron equation :

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

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

$\longrightarrow h_g\ at\ 0℃ = 0 + 2501.5 = 2501.5[\mathrm{kJ/kg}]$

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13.13 Building a full set of data

(solution) From Table 13.3

$$\left.\begin{aligned} c_{p0} &= 1.8703 \quad at\ 0℃ \\ c_{p0} &= 1.9603 \quad at\ 250℃ \\ c_{p0} &= 2.1319 \quad at\ 500℃ \end{aligned}\right\}$$

Equation fitting (t is in ℃)

$$c_{p0} = 1.8703 + 0.0001968t + 0.6528 \times 10^{-6}t^2$$

Integration from 0 to 500℃ at 0.6108 kPa

$$\int_{0℃}^{500℃} c_{p0}dt = 986.95$$

$$h_{500℃\ \&\ 0.6108\ \mathrm{kPa}} = 2501.5 + 986.95 = 3488.5\ [\mathrm{kJ/kg}]$$

13.13 Building a full set of data

(solution)

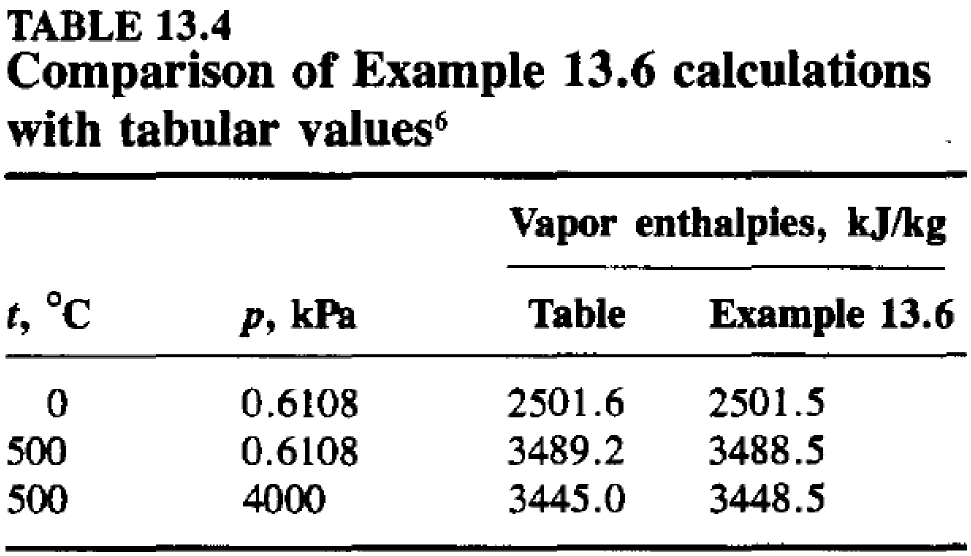

TABLE 13.4

Comparison of Example 13.6 calculations with tabular values[6]

t, °C	p, kPa	Vapor enthalpies, kJ/kg Table	Vapor enthalpies, kJ/kg Example 13.6
0	0.6108	2501.6	2501.5
500	0.6108	3489.2	3488.5
500	4000	3445.0	3448.5

13.13 Building a full set of data

(solution)

From the Redlich-Kwong equation

$$t = 499.9\ ℃, v_a = 0.08563245748$$

$$t = 500.0\ ℃, v_a = 0.085975713311$$

$$t = 500.1\ ℃, v_a = 0.085988180541$$

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

$$h_{500\ ℃\ \&\ 4000\ kPa} = dh = c_p dT + [v - T\frac{\partial v}{\partial T}\bigg|_P]dP$$

$$h_{500\ ℃\ \&\ 4000\ kPa} = 3488.5 + (-0.010) \times (4000 - 0.61) = 3448.5\ \ \mathrm{kJ/kg}$$