

Thermodynamica 2

Thermodynamic relations of systems in equilibrium

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Lecture 5

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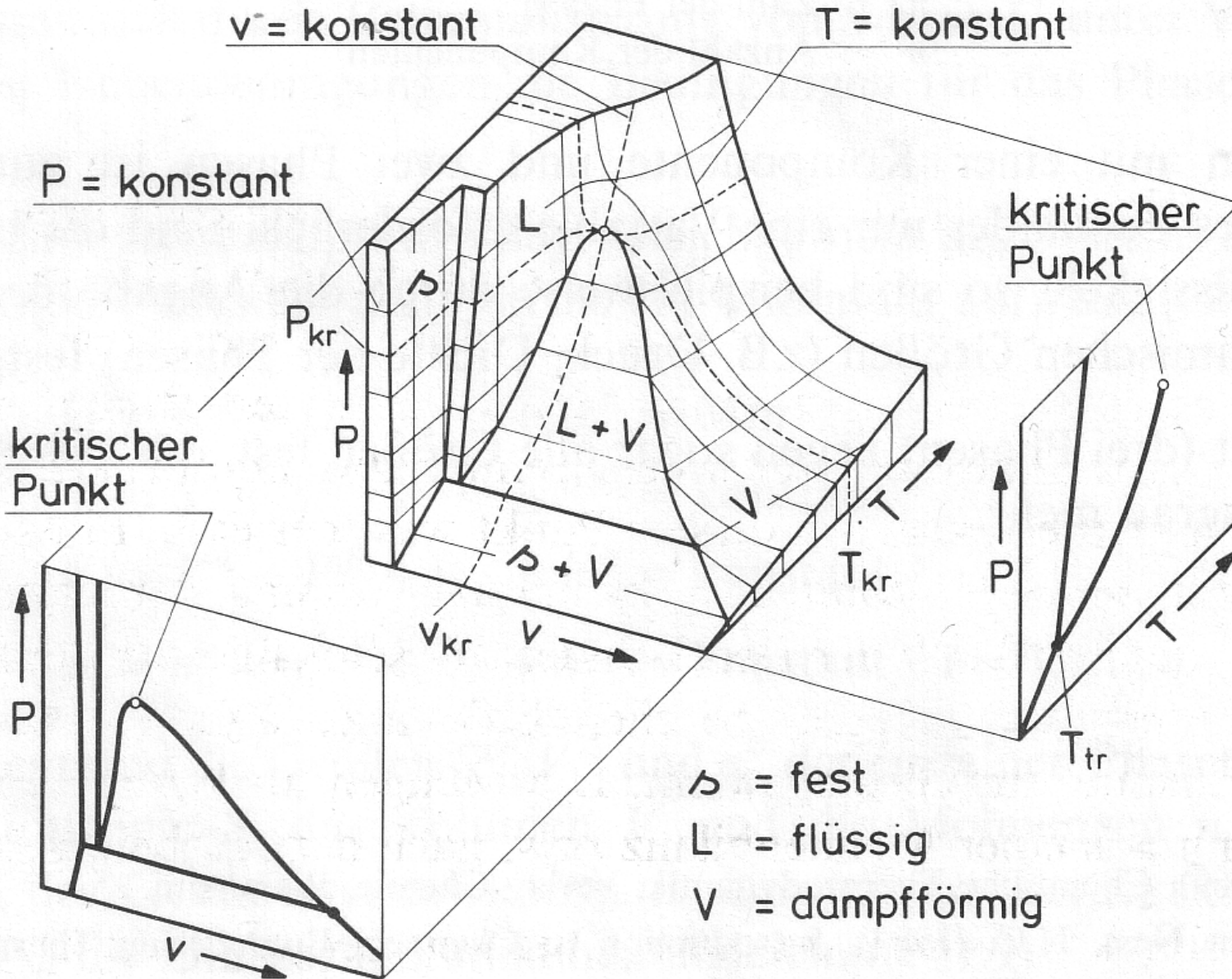
Today:

- Equation of state 11.1
- Departure functions 11.7

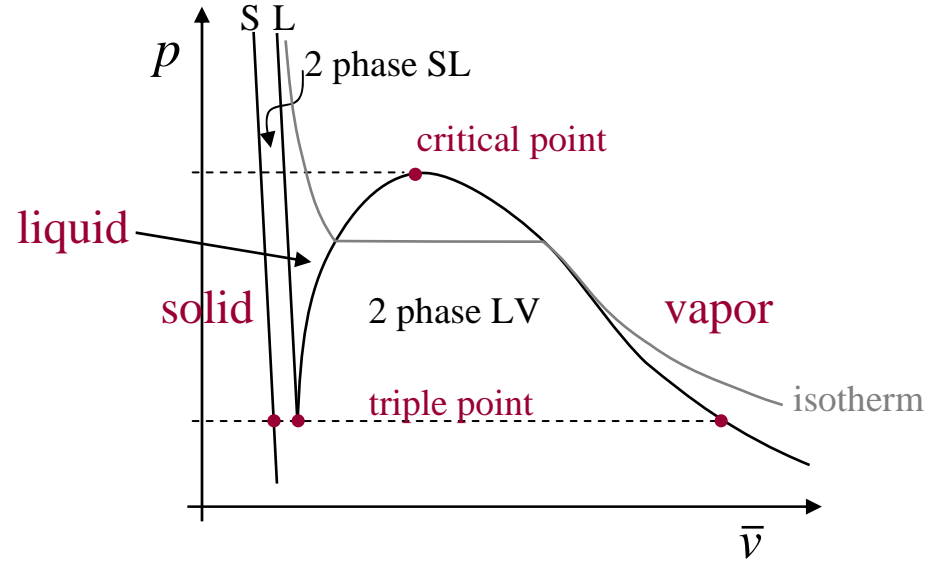
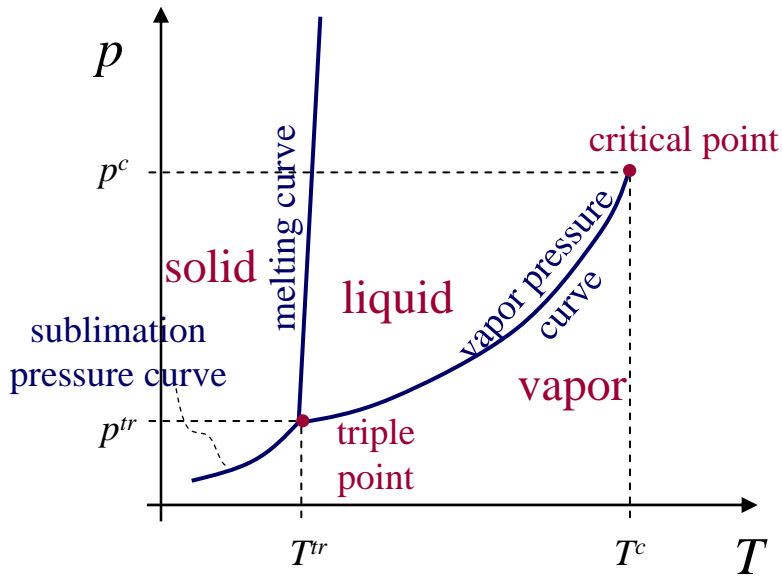
- Homework: Moran&Shapiro 11.68, 11.69, 11.70
- Homework: extra opgaven 3 en 9

- Next lecture: I will answer your questions. Please let me know by email which questions you would like me to answer

Pure component behavior – pVT diagrams



Phase behavior of pure substances



Examples of equations of state

- Ideal gas equation of state

$$Z = \frac{pV}{nRT} = 1$$

- Virial equation of state (for non-ideal gasses)

$$Z = \frac{pV}{nRT} = 1 + B(T)p + C(T)p^2 + D(T)p^3 + \dots$$

- Van der Waals equation of state (for non-ideal gasses)

$$\left(p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

The Van der Waals equation of state



The first EOS able to describe vapor and liquids was proposed 1873 by Johannes Diderik van der Waals (Nobel price 1910)

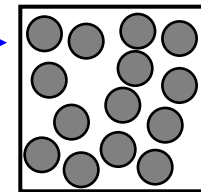
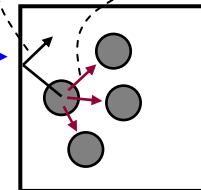
$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

(a 2-parameter EOS: a, b)

pressure of a real fluid is reduced by the attraction of molecules among each other

the volume accessible to molecules is reduced by b , the volume occupied by molecules

pressure attraction

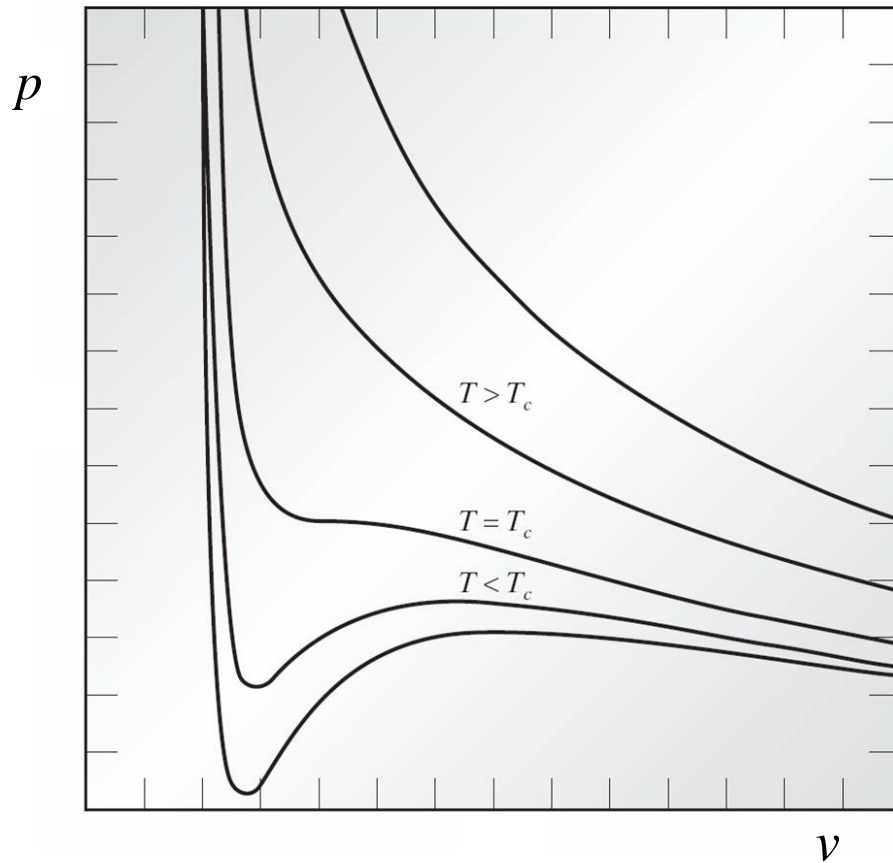


volume occupied per mole = b

free volume = $v - b$

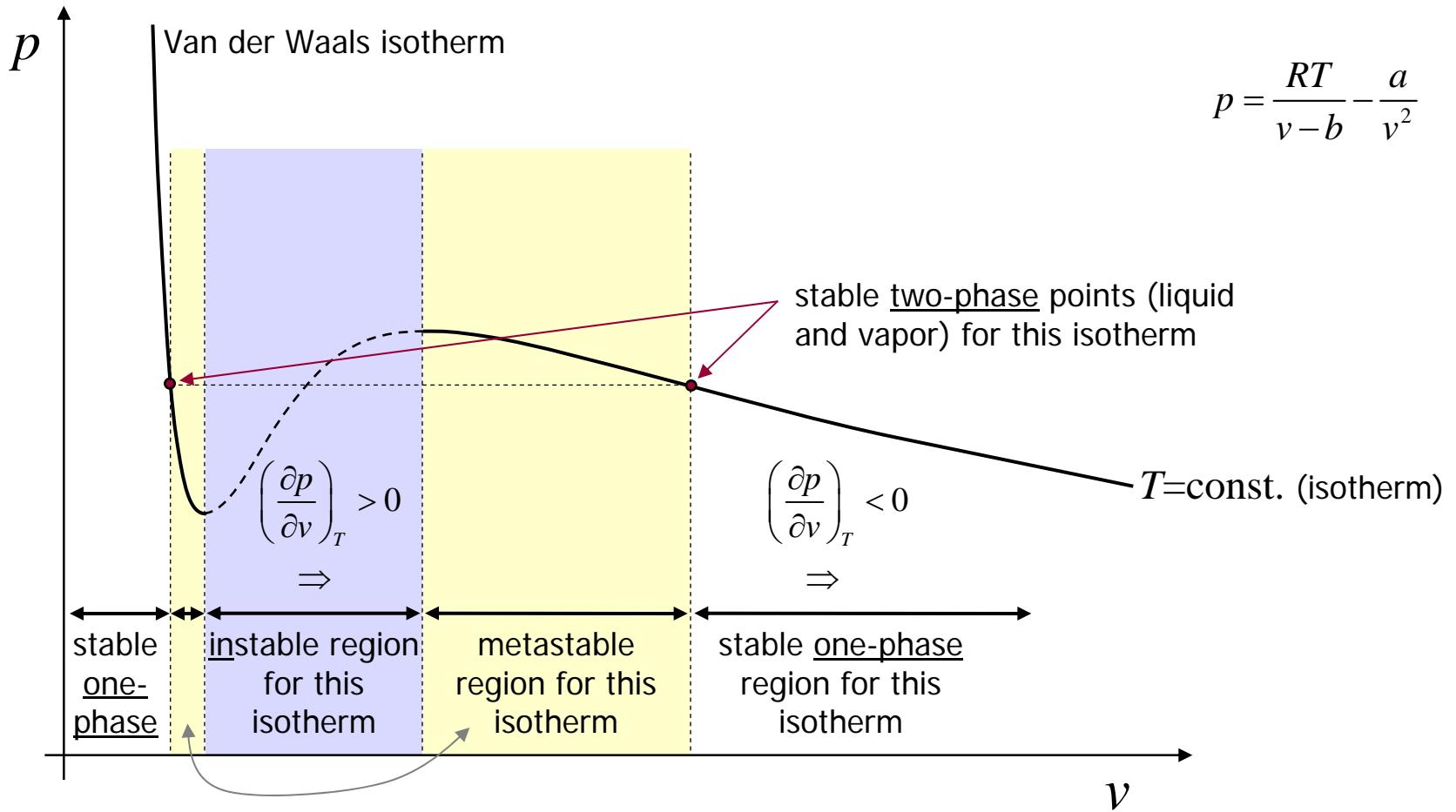
- Parameter a and b can be determined by fitting the EOS to exp. data, or, more commonly, from critical point data (T_c, p_c)
- The **VdW** EOS self is not accurate and is merely of historical interest

Van der Waals isotherms



$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

Stable, metastable and unstable regions



The principle of corresponding states

Van der Waals parameter a and b can be determined from critical point data (T_c, p_c)

→ Starting from the conditions for the critical point

$$\left. \begin{array}{l} \left(\frac{\partial p}{\partial v} \right)_T = 0 \\ \left(\frac{\partial^2 p}{\partial v^2} \right)_T = 0 \end{array} \right\} \text{with } p = \frac{RT}{v-b} - \frac{a}{v^2} \Rightarrow \left\{ \begin{array}{l} \left(\frac{\partial p}{\partial v} \right)_T = 0 = -\frac{RT}{(v_c-b)^2} + \frac{2a}{v_c^3} \\ \left(\frac{\partial^2 p}{\partial v^2} \right)_T = 0 = +\frac{2RT}{(v_c-b)^3} - \frac{6a}{v_c^4} \end{array} \right\} \Rightarrow \left\{ \begin{array}{l} a = \frac{27}{64} \frac{R^2 T_c^2}{p_c} \\ b = \frac{1}{8} \frac{RT_c}{p_c} \end{array} \right.$$

⇒ The 2 parameters a and b are then defined in terms of (T_c, p_c)

A generalized form of the VdW EOS can then be formulated

$$p_R = \frac{T_R}{v_R' - 1/8} - \frac{27/64}{v_R'^2}$$

where reduced variables are defined as

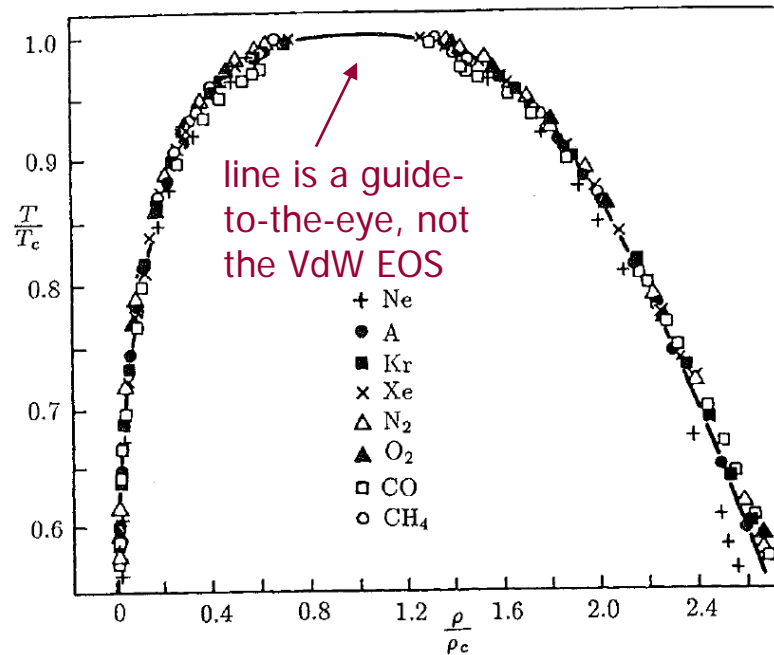
$$T_R = T/T_c$$

$$p_R = p/p_c$$

$$v_R' = p_c v / RT_c$$

The principle of corresponding states

The corresponding states principle can be visualized in diagrams given in terms of the reduced variables



Redlich-Kwong EOS

- The Redlich-Kwong EOS is an empirical modification of the VdW EOS
- It improves the description of real components
- It is also a 2-parameter EOS (with parameters a and b)

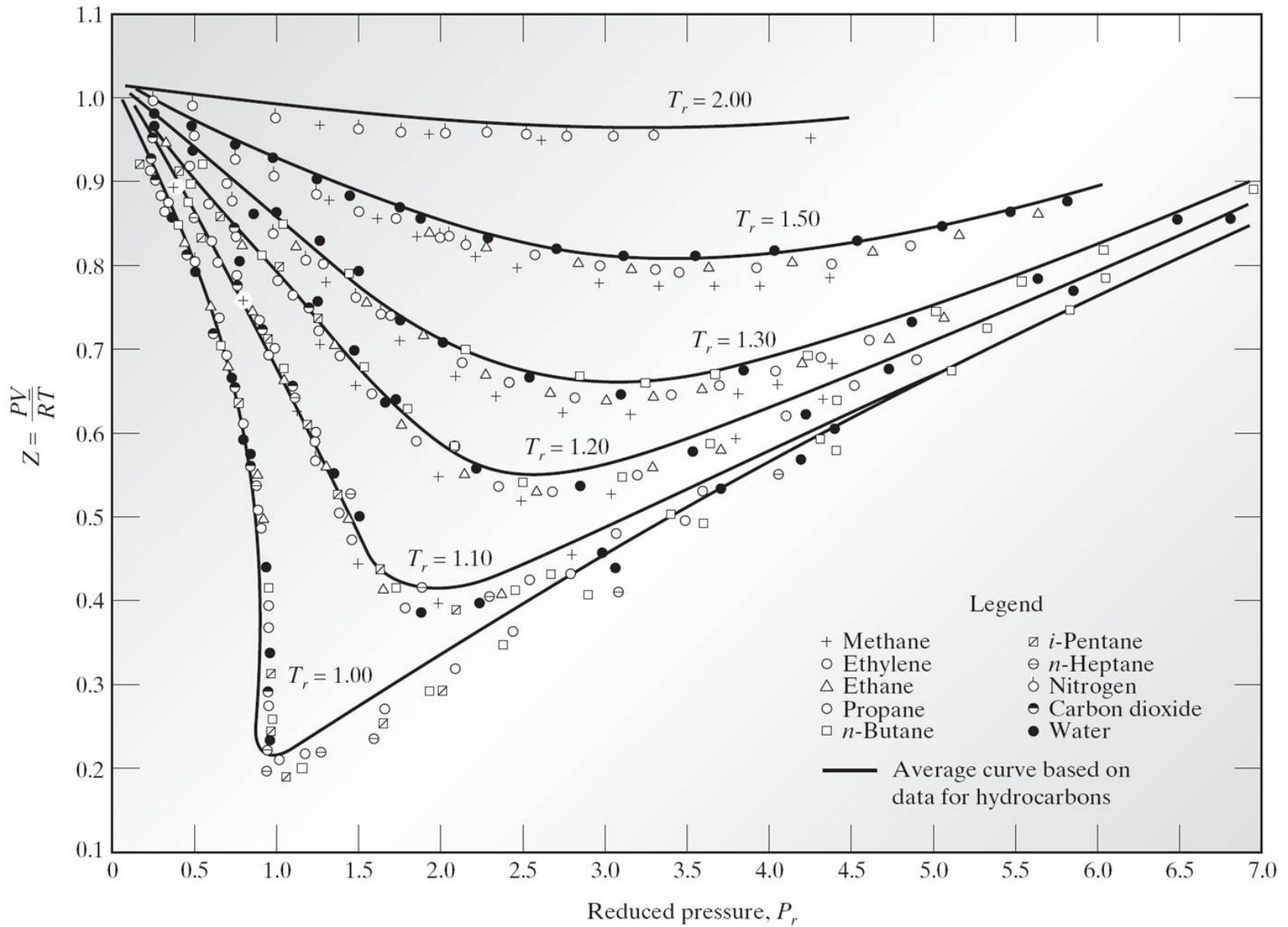
$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)\sqrt{T}}$$

- a and b of real substances follow from the critical point data (T_c, p_c)

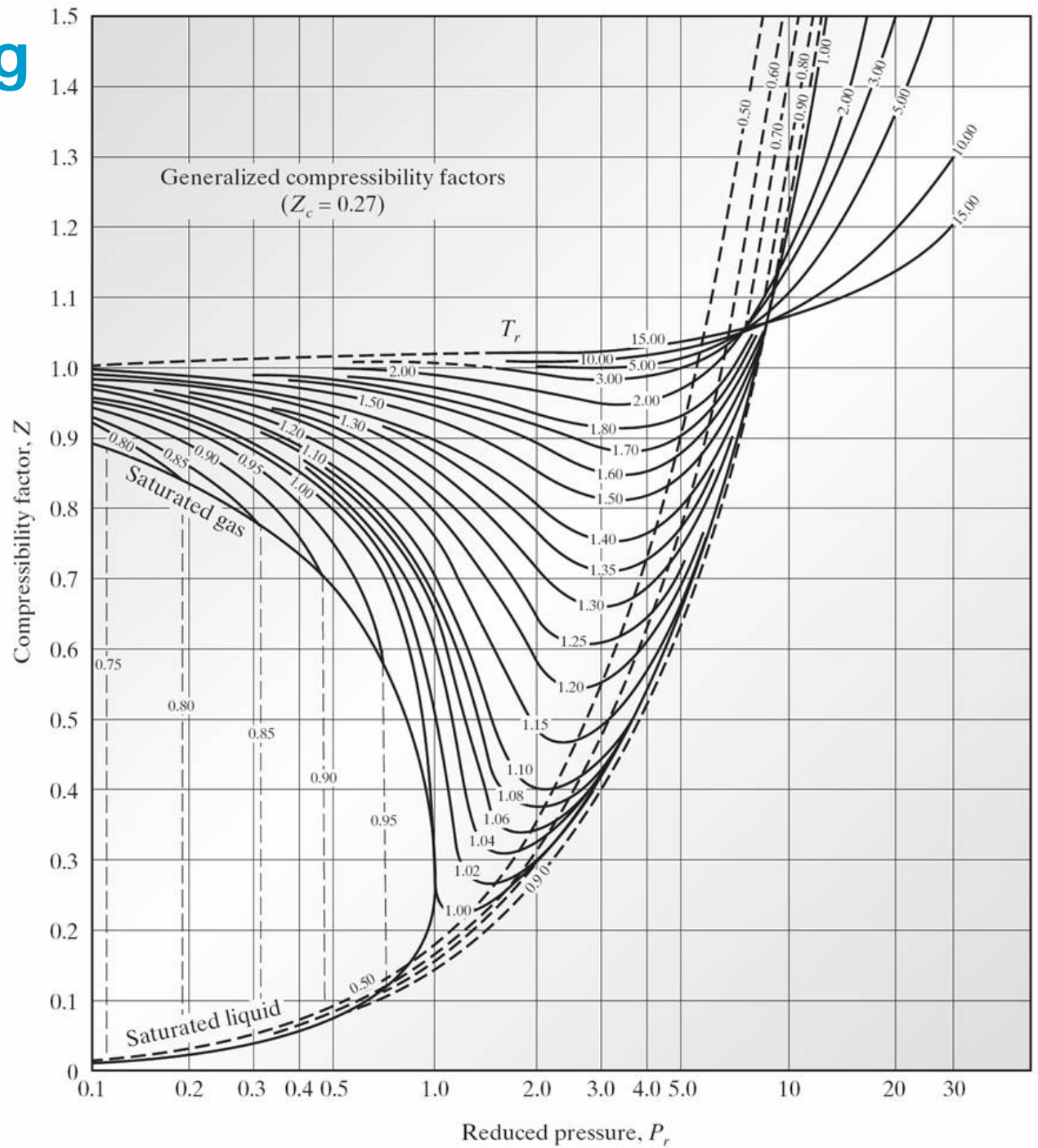
$$a = 0.42748 \frac{R^2 T_c^{5/2}}{p_c}$$

$$b = 0.08664 \frac{RT_c}{p_c}$$

The principle of corresponding states



Corresponding states



Changes of S and H with T and p

$$\left(\frac{\partial S}{\partial T}\right)_{p,N} =$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} =$$

$$\left(\frac{\partial H}{\partial T}\right)_{p,N} =$$

$$\left(\frac{\partial H}{\partial p}\right)_{T,N} =$$

Changes of S and H with T and p

$$\left(\frac{\partial S}{\partial T}\right)_{p,N} = \frac{C_p}{T}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

$$\left(\frac{\partial H}{\partial T}\right)_{p,N} = C_p$$

$$\left(\frac{\partial H}{\partial p}\right)_{T,N} = V - T\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

De afleiding van de onderste formule \rightarrow zie de laatste slide

Enthalpy departure

$$\left(\frac{\partial h}{\partial p}\right)_{T,N} = v - T \left(\frac{\partial v}{\partial T}\right)_{p,N}$$

voor een ideaal gas: $\left(\frac{\partial h}{\partial p}\right)_{T,N} = 0$

dus: $h(T, p) - h^{IG}(T) = \int_0^p \left[v - T \left(\frac{\partial v}{\partial T}\right)_{p,N} \right] dp$

$h^{IG}(T)$ is de enthalpie die het systeem zou hebben als het een ideaal gas zou zijn

dus $h^{IG}(T)$ hangt dus NIET van de druk af !!!

Corresponding state principle for departure functions

Combining the principle of corresponding states with the concept of departure functions gives dimensionless charts, that are easy to use for specified T and p

See table A-4 (Moran & Shapiro) for $\left(\frac{\bar{h} - \bar{h}^{ig}}{\bar{R}T_c}\right)$ as a function of (p_R, T_R)

See table A-5 (Moran & Shapiro) for $\left(\frac{\bar{s} - \bar{s}^{ig}}{\bar{R}}\right)$ as a function of (p_R, T_R)

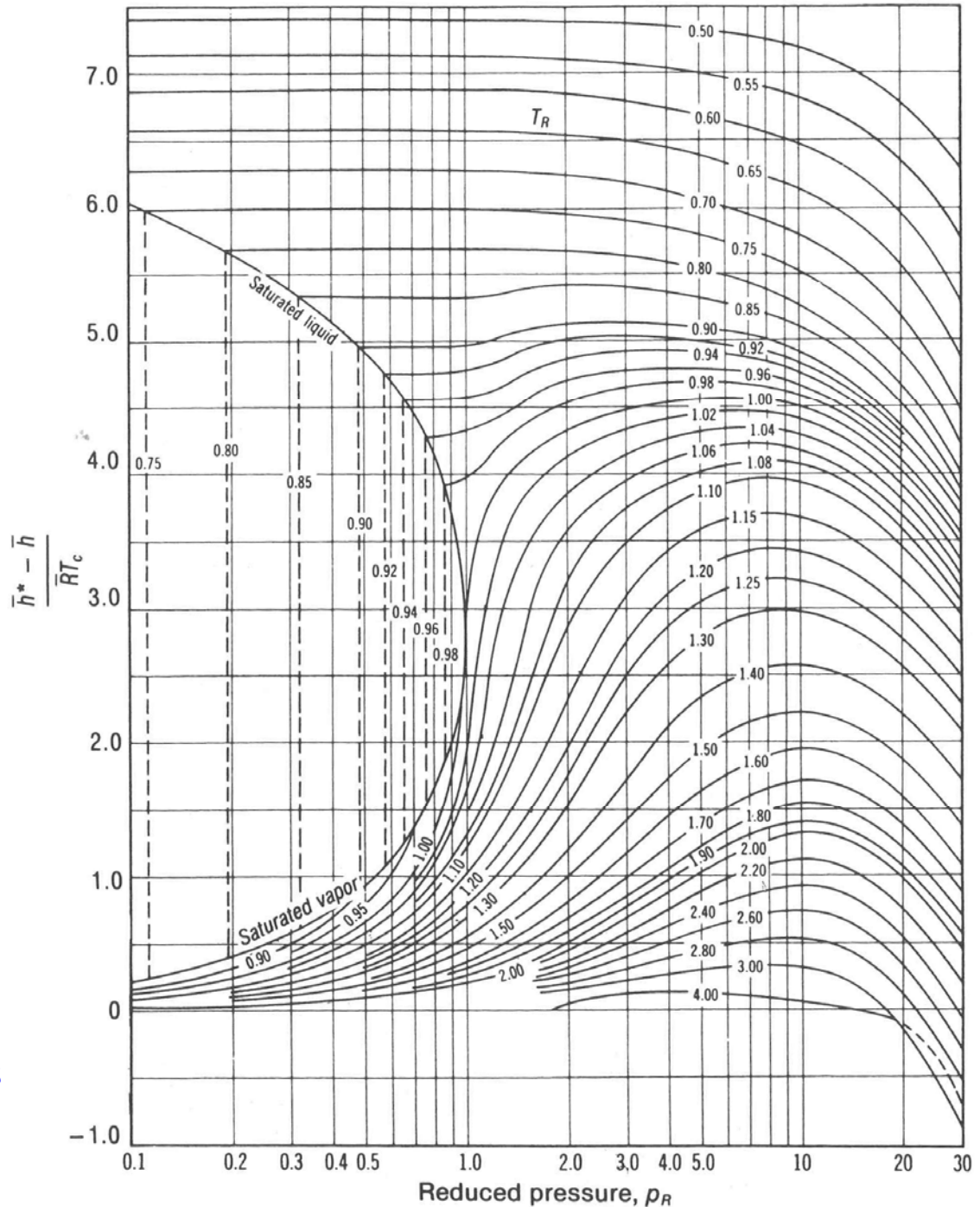
\downarrow
 $T_R = \frac{T}{T_c}$
 \downarrow
 $p_R = \frac{p}{p_c}$

Enthalpy departure in corresponding states

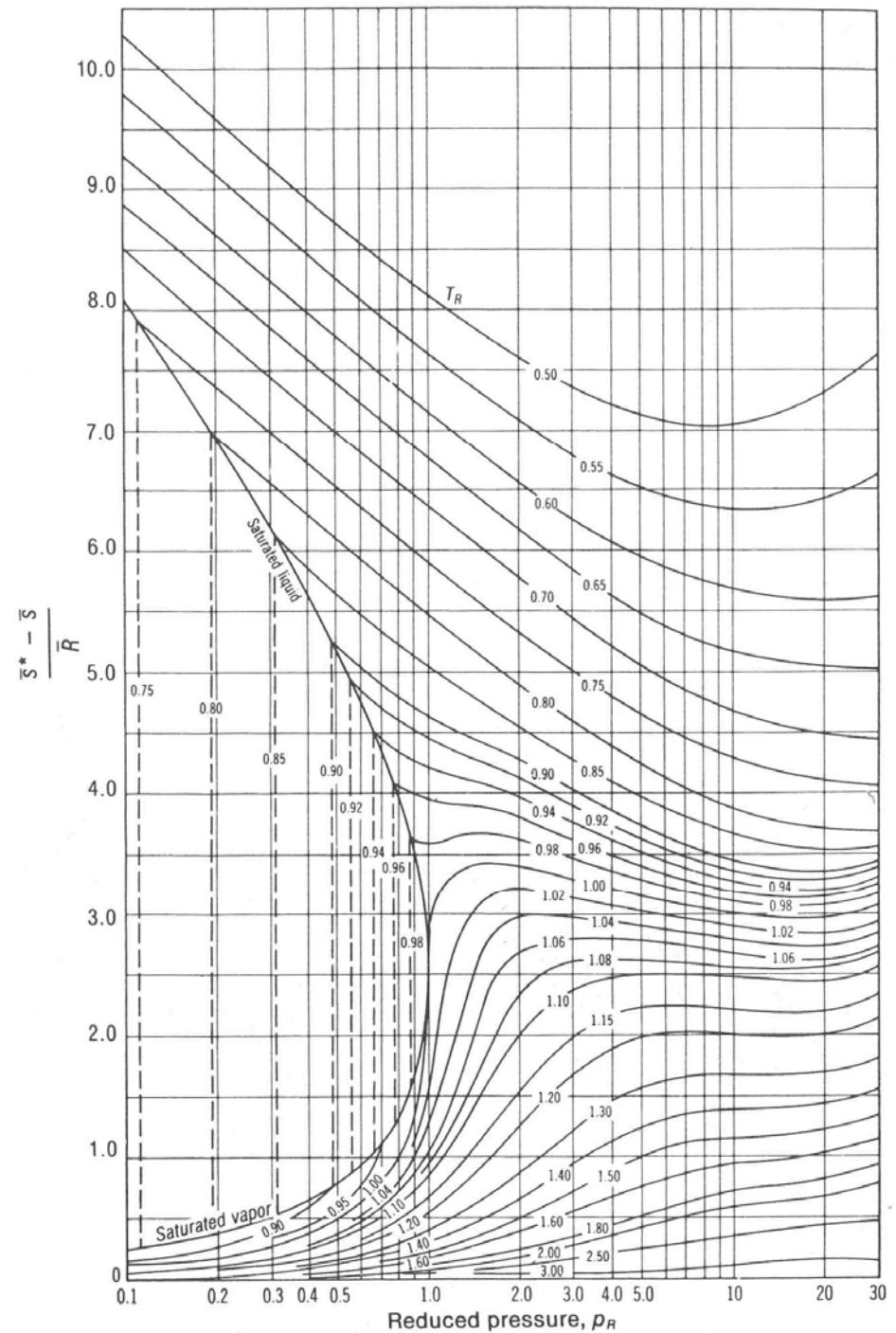
caution

$\left(\frac{\bar{h} - \bar{h}^{ig}}{\bar{R}T_c} \right)$ is equal to minus the values from this table

asterisk * (just as *ig*) is for ideal gas



Entropy-departure in corresponding states



Exercise

• Stikstof komt een turbine binnen bij 100bar en 300K en komt de turbine uit bij 40bar en 245K. Er vindt geen warmteuitwisseling plaats met de omgeving. Gegeven is dat $T_c=126K$ en $p_c=33.9$ bar. De c_p van stikstof is $28 \text{ J mol}^{-1} \text{ K}^{-1}$. Bereken de geleverde arbeid in kJ/kmol en de entropieproductie in kJ/(kmol K) met behulp van de departure grafieken.

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) - \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right)$$

$$\frac{dS_{cv}}{dt} = \frac{\dot{Q}_{cv}}{T_{trans}} + \dot{m}_i s_i - \dot{m}_e s_e + \dot{\sigma}_{cv} \quad \text{met} \quad \dot{\sigma}_{cv} \geq 0$$

$$\frac{\dot{W}_{CV}}{\dot{m}} = h_1 - h_2 \quad \text{en} \quad \frac{\dot{\sigma}_{CV}}{\dot{m}} = s_2 - s_1$$

$$h_1^{IG} - h_2^{IG} = -\int_{T_1}^{T_2} \left(\frac{\partial h}{\partial T} \right)_{p,N} dT = -\int_{T_1}^{T_2} c_p dT = 28 \cdot (300 - 245) \text{ J/mol} = 1540 \text{ J/mol}$$

$$T_{R1} = \frac{300}{126} = 2.38 \quad p_{R1} = \frac{100}{33.9} = 2.95 \quad T_{R2} = \frac{245}{126} = 1.94 \quad p_{R1} = \frac{40}{33.9} = 1.18$$

$$\text{met behulp van de tabellen:} \quad \left(\frac{h^{IG} - h}{RT_c} \right)_1 = 0.5 \quad \left(\frac{h^{IG} - h}{RT_c} \right)_2 = 0.31$$

$$\text{en} \quad \left(\frac{s^{IG} - s}{R} \right)_1 = 0.21 \quad \left(\frac{s^{IG} - s}{R} \right)_2 = 0.14$$

$$\text{dus} \quad \frac{\dot{W}_{CV}}{\dot{m}} = \left(1540 \frac{\text{J}}{\text{mol}} - \left(8.31 \frac{\text{J}}{\text{mol K}} \right) (126 \text{K}) (0.5 - 0.31) \right) = 1341 \frac{\text{J}}{\text{mol}}$$

$$s_2^{IG} - s_1^{IG} = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T} \right)_{p,N} dT + \int_{p_1}^{p_2} \left(\frac{\partial S}{\partial p} \right)_{T,N} dp = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T} \right)_{p,N} dp = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1} = \left[28 \ln \frac{245}{300} - 8.31 \ln \frac{40}{100} \right] \frac{\text{J}}{\text{mol K}} = 1.94 \frac{\text{J}}{\text{mol K}}$$

$$\text{dus} \quad \frac{\dot{\sigma}_{CV}}{\dot{m}} = 1.94 \frac{\text{J}}{\text{mol K}} - 8.31 \frac{\text{J}}{\text{mol K}} (0.14 - 0.21) = 2.5 \frac{\text{J}}{\text{mol K}}$$

Voor een ideaal gas:

$$\begin{aligned} s_2^{IG}(T_2, p_2) - s_1^{IG}(T_1, p_1) &= \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T} \right)_{p,N} dT + \int_{p_1}^{p_2} \left(\frac{\partial S}{\partial p} \right)_{T,N} dp \\ &= \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T} \right)_{p,N} dp \quad \leftarrow \text{Voor elk ideaal gas} \\ &= c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1} \end{aligned}$$

Alleen voor ideaal gas met c_p onafhankelijk van de temperatuur

Verandering van H met p

$$G = U - TS + pV = H - TS$$

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = \left(\frac{\partial H}{\partial p}\right)_{T,N} - T \left(\frac{\partial S}{\partial p}\right)_{T,N}$$

$$V = \left(\frac{\partial H}{\partial p}\right)_{T,N} + T \left(\frac{\partial V}{\partial T}\right)_{p,N}$$

$$\left(\frac{\partial H}{\partial p}\right)_{T,N} = V - T \left(\frac{\partial V}{\partial T}\right)_{p,N}$$