Thermodynamica 2

Thermodynamic relations of systems in equilibrium

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Lecture 4

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Today:

- meetbare grootheden: C_p C_v 11.4,11.5
- Uitzettingscoefficient, compressibiliteit 11.5
- Veranderingen van U, H, A, G met V, P, T 11.6, 11.7

- Homework: Exercises Moran&Shapiro 11.36, 11.37, 11.50 en extra opgaven 2,5,7,8 (zie blackboard)

- Print de laatste 2 slides uit en neem ze mee naar het volgende college

- Volgende week: 11.1, 11.7

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Summary

- Partial derivatives

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = Mdx + Ndy \quad \text{so} \quad M = \left(\frac{\partial f}{\partial x}\right)_y \quad \text{en} \quad N = \left(\frac{\partial f}{\partial y}\right)_x$$

- Maxwell Relations

$$\text{If} \quad df = Mdx + Ndy \quad \text{then} \quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \text{in other words} \quad \frac{\partial}{\partial x}\left[\left(\frac{\partial f}{\partial y}\right)_x\right]_y = \frac{\partial}{\partial y}\left[\left(\frac{\partial f}{\partial x}\right)_y\right]_x$$

- Integration

$$f(x_2, y_1) = f(x_1, y_1) + \int_{x_1}^{x_2} \left(\frac{\partial f}{\partial x}\right)_y dx$$

- Minus 1 rule (Moran&Shapiro page 495)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

Sommetje vorige week

•Laat zien dat voor een ideaal gas, *U* niet afhangt van *V*, maar dat voor een van der Waals gas *U* wel afhangt van *V*

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

ideaal gas: $\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{nR}{V}$ dus $\left(\frac{\partial U}{\partial V}\right)_{T,N} = -p + \frac{nRT}{V} = 0$

van der Waals gas: $\left(p + \frac{n^2 a}{V^2}\right)\left(V - nb\right) = nRT$ oftewel $p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$

invullen: $\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{nR}{V - nb}$ dus $\left(\frac{\partial U}{\partial V}\right)_{T,N} = -p + \frac{nRT}{V - nb} = \frac{n^2 a}{V^2}$

NB indien $V \to \infty$ krijgen we hetzelfde resultaat als voor het ideale gas

Exercise 1

Gegeven is de van der Waals equation of state. Hangt C_V af van het volume?

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

$$dU = TdS - pdV + \mu dN$$
$$dH = TdS + Vdp + \mu dN$$
$$dA = -SdT - pdV + \mu dN$$
$$dG = -SdT + Vdp + \mu dN$$

Exercise 1

Voor elke stof geldig

$$\left(\frac{\partial C_V}{\partial V}\right)_{T,N} = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_{V,N}\right)_{T,N} = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_{T,N}\right)_{V,N} = \left(\frac{\partial}{\partial T}\left[-p + T\left(\frac{\partial p}{\partial T}\right)_{V,N}\right]\right)_{V,N} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_{V,N}$$

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{R}{v-b} \quad \text{en} \quad \left(\frac{\partial^2 p}{\partial T^2}\right)_{V,N} = 0 \quad \text{dus} \quad \left(\frac{\partial C_V}{\partial V}\right)_{T,N} = 0$$

Invullen voor het systeem dat we bekijken

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Partial derivatives of *U*

$$\left(\frac{\partial U}{\partial T}\right)_{V,N} = C_V$$

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

maar wat doen we als we $\left(\frac{\partial U}{\partial p}\right)_{T,N}$ willen weten ?????

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Exercise 2

Leid een algemene uitdrukking af voor C_p-C_v als functie van meetbare grootheden.
Bepaal C_p-C_v voor een gas met de volgende toestandsvergelijking:
$v=RT/p - A/T + B$

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Exercise 2 (.....continued)

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

$H = U + pV$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV$$

$U(T,V)$

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

$V(T,p)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} \left(\frac{\partial V}{\partial T}\right)_{p,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} \left(\frac{\partial V}{\partial p}\right)_{T,N} dp$$

invullen

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

p constant ($dp = 0$) en delen door dT

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

eerder afgeleid

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

uiteindelijke resultaat, geldig voor ieder systeem

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Exercise 2

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

Geldig voor elk systeem

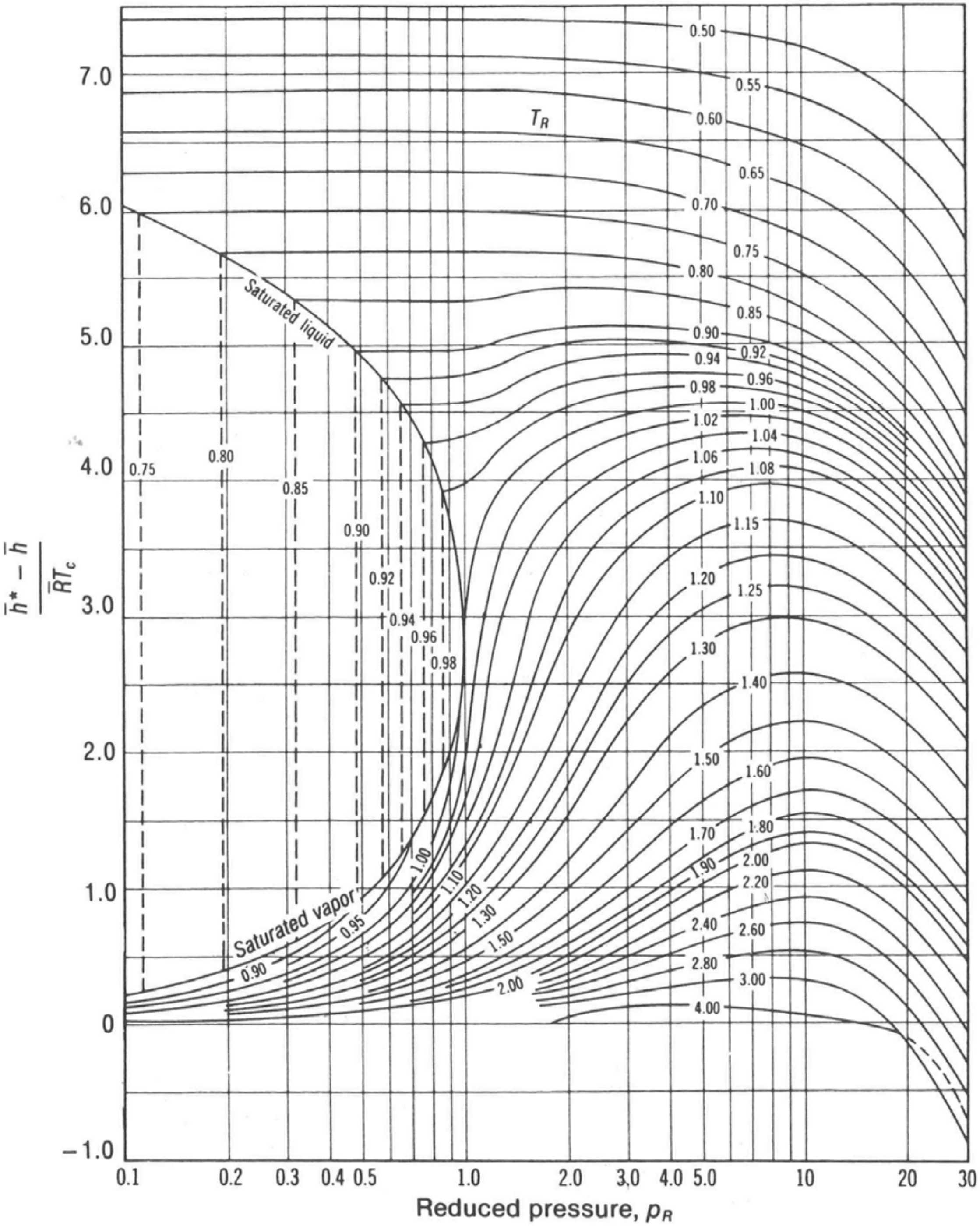
$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{R(V-B)+\dfrac{2RA}{T}}{\left(V+\dfrac{A}{T}-B\right)^2}$$

Invullen voor het gevraagde systeem

$$\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{R}{p}+\frac{A}{T^2}$$

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_{V,N}\left(\frac{\partial V}{\partial T}\right)_{p,N} = T\left[\frac{R}{p}+\frac{A}{T^2}\right]\left[\frac{R(V-B)+\dfrac{2RA}{T}}{\left(V+\dfrac{A}{T}-B\right)^2}\right]$$

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