# Thermodynamica 2

# Thermodynamic relations of systems in equilibrium

**Thijs J.H. Vlugt**

**Engineering Thermodynamics**
**Process and Energy Department**

**Lecture 2**

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Delft University of Technology

# Today:

- Partiële afgeleiden, Maxwell relaties, min 1 regel 11.2
- Chemische potentiaal 11.9.2
- Algemene vergelijkingen voor dU en dH 11.3.1, 11.9.3

- Homework: Exercises Moran&Shapiro 11.1, 11.13, 11.16, 11.19, 11.20



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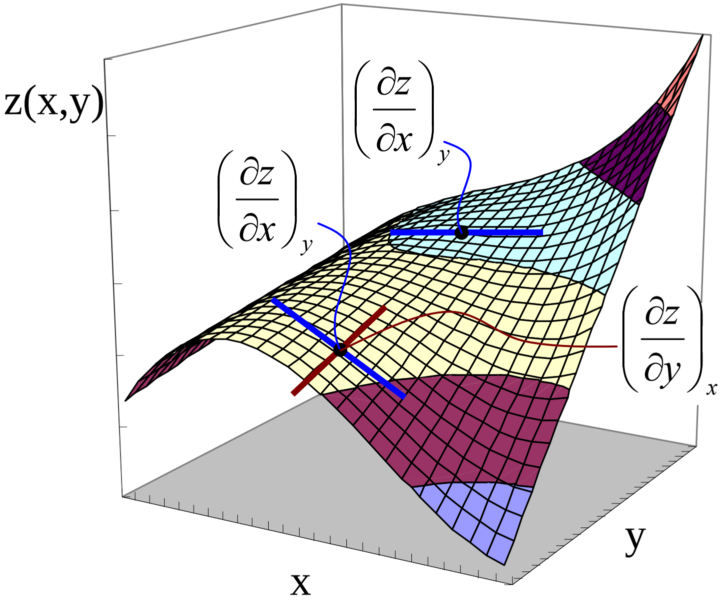
# Math: Differential relations of multivariable functions

- consider a differentiable function $z(x,y)$
- Think of $z$ as the height coordinate in the Swiss Alps, and $x$ and $y$ are the northerly direction and the westerly direction, respectively
- The total differential is

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

- $(\partial z/\partial x)_y$ is the slope with which the height changes with a change $dx$ in $x$-direction. Subscript $y$ is for: "in direction of constant $y$"
- Note, that $(\partial z/\partial x)_y$ is a function of $y$ and $x$, as seen in the illustration
- Note

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



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# Exercise 1

- Gegeven is de functie

$$f(x,y) = xy + x^2 y + 2y^2$$

- Bereken $\left(\frac{\partial f}{\partial x}\right)_y$ en $\left(\frac{\partial f}{\partial y}\right)_x$
- Laat zien dat de volgorde van differentiëren niet uitmaakt, zodat

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$$

- Dit heet een "Maxwell-Relatie"

# Exercise 2

•Coefficient of volume expansion β

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

•Isothermal compressibility κ

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$

•Question: what are β and κ for an ideal gas?

# Exercise 3: Integration

Voor een bepaalde vaste stof is de waarde van κ onafhankelijk van de druk.

123 kg van deze stof wordt gecomprimeerd van volume $V_1$ tot $V_2$ bij constante temperatuur. Leidt een formule af waarin de verandering van de druk voor dit proces kan worden uitgerekend.

Als de compressie adiabatisch zou zijn geweest, wat hadden we dan moeten doen?

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$



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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)

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

# Formulas for dU and dH

# Equations for dU and dH

$$dU = TdS - pdV + \mu dN$$

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

$$dH = TdS + Vdp + \mu dN$$

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

# Maxwell Relations

$$dU = TdS - pdV + \mu dN$$

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

$$dH = TdS + Vdp + \mu dN$$

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

# Heat capacity

$$dU = TdS - pdV + \mu dN$$

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

$$dH = TdS + Vdp + \mu dN$$

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

Note: in principle $C_p$ and $C_v$ depend on T,p and T,V respectively!!!

# Exercise 4

Een bepaalde stof wordt reversibel adiabatisch gecomprimeerd van $p_1$ naar $p_2$.

Neemt de enthalpie bij dit proces toe of af, of blijft deze gelijk? Maakt het uit of het om een ideaal gas gaat of niet?

$$dU = TdS - pdV + \mu dN$$

$$dH = TdS + Vdp + \mu dN$$

# Exercise 5

10 kg stikstof bevindt zich in een volume V bij p=1 atm en T=300K. De temperatuur wordt verhoogd naar 400K terwijl de druk constant blijft. Bereken de verandering in enthalpie en entropie. De soortelijke warmte bij constante druk is 1 kJ $kg^{-1}$ $K^{-1}$.

$$dU = TdS - pdV + \mu dN$$

$$dH = TdS + Vdp + \mu dN$$

# Antwoorden

$$\left(\frac{\partial f}{\partial x}\right)_y = y + 2xy \quad \left(\frac{\partial f}{\partial y}\right)_x = x + x^2 + 4y \quad \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = 1 + 2x$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} = \frac{nR}{pV} = \frac{nR}{nRT} = \frac{1}{T} \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{-1}{V} * \frac{-nRT}{p^2} = \frac{nRT}{pnRT} = \frac{1}{p}$$

NB dit is dus ALLEEN voor een ideaal gas

$$\frac{dV}{V} = -\kappa dp \qquad \int_{V_1}^{V_2} \frac{dV}{V} = -\kappa \int_{p_1}^{p_2} dp \qquad \ln\frac{V_2}{V_1} = -\kappa\left(p_2 - p_1\right)$$

$$\left(\frac{\partial H}{\partial p}\right)_{S,N} = V > 0$$

Dit geld voor elke stof, niet alleen voor een ideaal gas!

$$\Delta H = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_{P,N} dT = \int_{300}^{400} C_P(T) dT = C_P\left(400 - 300\right) = 1000 \text{ kJ}$$

$$\Delta S = \int_{T_1}^{T_2} \left(\frac{\partial S}{\partial T}\right)_{P,N} dT = \int_{300}^{400} \frac{C_P(T)}{T} dT = C_P \ln\frac{400}{300} = 14.5 \text{ kJ/K}$$



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