Physical Chemistry I. practice

Gyula Samu

I.: Calculus overview

gysamu@mail.bme.hu

http://oktatas.ch.bme.hu/oktatas/konyvek/fizkem
/PysChemBSC1/Requirements.pdf
http://oktatas.ch.bme.hu/oktatas/konyvek/fizkem
/PysChemBSC1/Important_dates.pdf

Derivatives of functions of a single variable

Rules:

[notation: $\frac{\mathrm{d}f(x)}{\mathrm{d}x} = f'(x)$]

$$\frac{\mathrm{d}x^n}{\mathrm{d}x} = n \cdot x^{n-1}$$

$$\frac{\mathrm{d}[f(x) \cdot g(x)]}{\mathrm{d}x} = f'(x) \cdot g(x) + f(x) \cdot g'(x)$$

$$\frac{\mathrm{d}e^x}{\mathrm{d}x} = e^x$$

$$\frac{\mathrm{d}}{\mathrm{d}x} \cdot \left(\frac{f(x)}{g(x)} \right) = \frac{f'(x) \cdot g(x) - f(x) \cdot g'(x)}{[g(x)]^2}$$

$$\frac{\mathrm{d}ln(x)}{\mathrm{d}x} = \frac{1}{x}$$

$$\frac{\mathrm{d}f[g(x)]}{\mathrm{d}x} = \frac{\mathrm{d}f[g(x)]}{\mathrm{d}g(x)} \cdot \frac{\mathrm{d}g(x)}{\mathrm{d}x}$$

$f'(x) = ?$

a) $f(x) = 2x^3 - \frac{1}{\sqrt{x}} + 2$

b) $f(x) = (x+2) \cdot (x^2 - 2)$

c) $f(x) = \frac{e^{2x-1}}{x+2}$

d) $f(x) = (x-1) \cdot e^{(2x-3)^2}$

Derivatives of functions of a single variable

a) $f(x) = 2x^3 - \dfrac{1}{\sqrt{x}} + 2$

b) $f(x) = (x+2)\cdot(x^2-2)$

c) $f(x) = \dfrac{e^{2x-1}}{x+2}$

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a) $f'(x) = 6x^2 + \dfrac{1}{2}x^{-\frac{3}{2}}$

b) $f'(x) = (x^2-2) + (x+2)\cdot 2x$

c) $f'(x) = \dfrac{2e^{2x-1}\cdot(x+2) - e^{2x-1}}{(x+2)^2}$

d) $f'(x) = e^{(2x-3)^2} + (x-1)\cdot e^{(2x-3)^2}\cdot 2(2x-3)\cdot 2$

Derivatives of functions of a single variable

a) Where is the extremum of $\boxed{f(x) = ln(x) \cdot x^2}$ for $x > 0$?

b) What kind of extremum is it (min., max., inflection)?

[a) At which x is $f'(x) = 0$?

b) What is the sign of $f''(x)$ at this x?

$+$: minimum; -: maximum; 0: inflection]

Derivatives of functions of a single variable

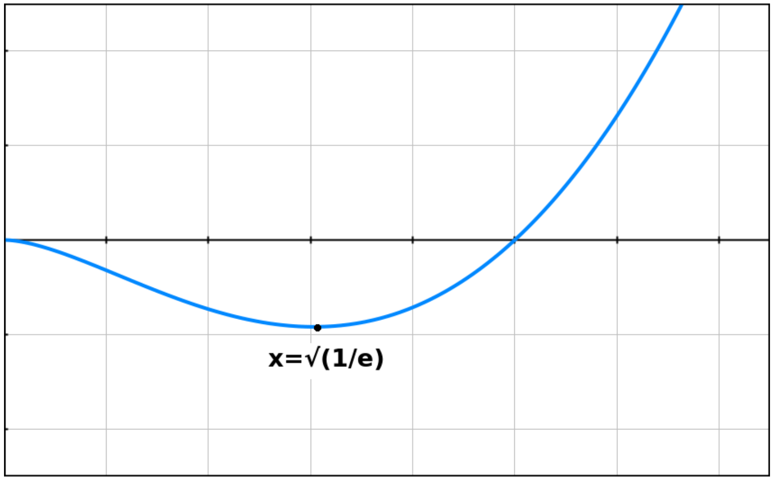
Where is the extremum of $\boxed{f(x) = ln(x) \cdot x^2}$ for $x > 0$?

$$f'(x) = 0 = x + ln(x) \cdot 2x$$

$$ln(x) = -\frac{1}{2}$$

$$x = e^{-\frac{1}{2}} = \frac{1}{\sqrt{e}}$$

What kind of extremum is it?

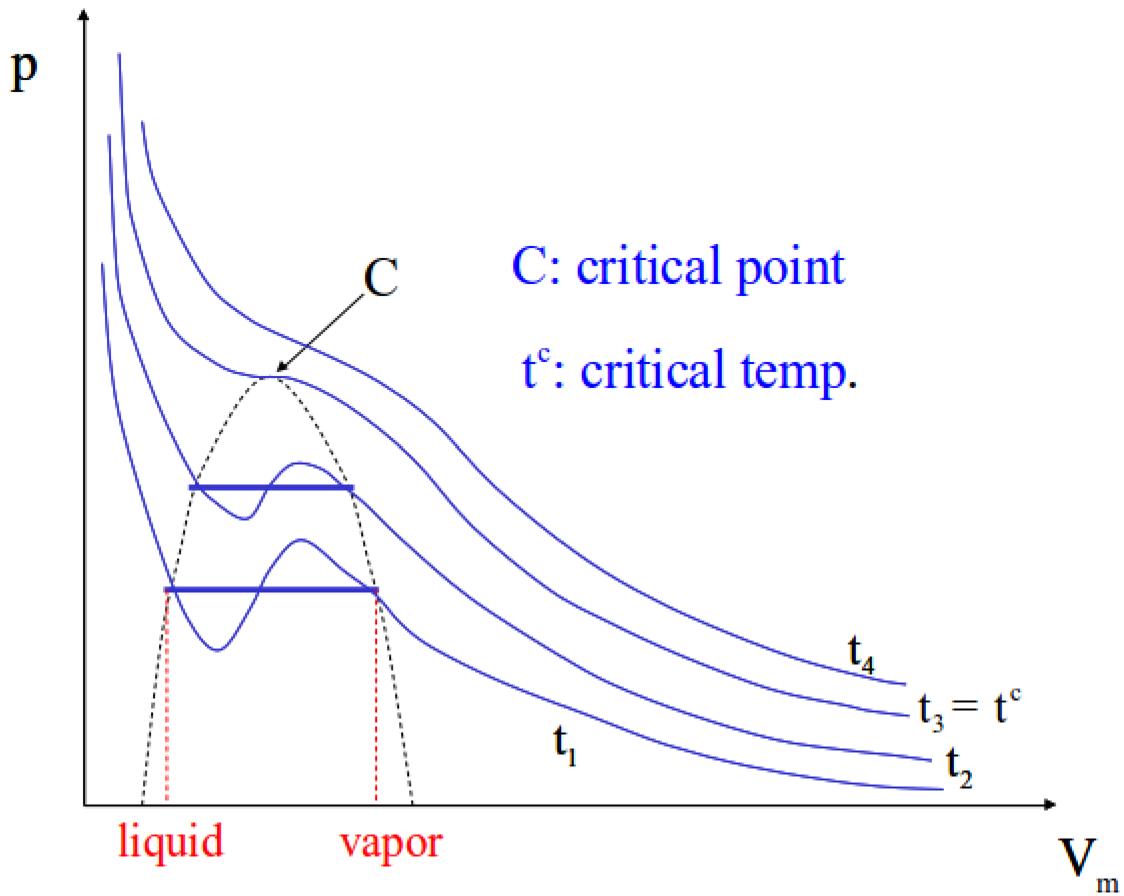


$$f''(x) = 3 + ln(x) \cdot 2$$

$$f''(e^{-\frac{1}{2}}) = 2 \rightarrow \text{minimum}$$

Derivatives of functions of a single variable

Application: Determine the critical point of water from the van der Waals equation of state



$$p(V_m) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Inflection point at the critical point:

$$p'(V_m^c) = p''(V_m^c) = 0$$

$$p^c = ?\ V_m^c = ?\ T^c = ?$$

Derivatives of functions of a single variable

Application: Determine the critical point of water from the van der Waals equation of state

$$p(V_m) = \frac{RT}{V_m - b} - \frac{a}{(V_m)^2}$$

At the critical point:

$$p'(V_m^c) = 0 = -\frac{RT^c}{(V_m^c - b)^2} + \frac{2a}{(V_m^c)^3} \rightarrow \frac{RT^c}{(V_m^c - b)^2} = \frac{2a}{(V_m^c)^3}$$

$$p''(V_m^c) = 0 = 2\frac{RT^c}{(V_m^c - b)^3} - \frac{6a}{(V_m^c)^4} \rightarrow 2\frac{RT^c}{(V_m^c - b)^3} = \frac{6a}{(V_m^c)^4}$$

Express V_m^c and T^c in terms of constants (a, b, R)

Derivatives of functions of a single variable

$$\frac{RT^c}{(V_m^c - b)^2} = \frac{2a}{(V_m^c)^3}$$ substitute it into $\rightarrow$ $$2\frac{RT^c}{(V_m^c - b)^3} = \frac{6a}{(V_m^c)^4}$$

$$\frac{RT^c}{(V_m^c - b)^2} \cdot \frac{2}{V_m^c - b} = \frac{4a}{(V_m^c)^4 - b(V_m^c)^3} = \frac{6a}{(V_m^c)^4}$$

$$4a \cdot (V_m^c)^4 = 6a \cdot (V_m^c)^4 - 6ab \cdot (V_m^c)^3 \quad , \quad V_m^c > 0$$

$$\boxed{V_m^c = 3b}$$

$$\frac{RT^c}{(2b)^2} = \frac{2a}{(3b)^3}$$

$$\boxed{T^c = \frac{8a}{27Rb}}$$

$$p^c = p(V_m^c) = p(3b) = \frac{R\frac{8a}{27Rb}}{2b} - \frac{a}{(3b)^2}$$

$$\cdots \rightarrow \boxed{p^c = \frac{a}{27b^2}}$$

Partial derivatives of multivariable functions

$$\frac{\partial f(x,y)}{\partial x} = ? \quad , \quad \frac{\partial f(x,y)}{\partial y} = ?$$

a) $f(x,y) = x^2 \cdot y + 2x + 2y + 4$

b) $f(x,y) = e^x \cdot x \cdot y + y^2 + 2$

c) $f(x,y) = \dfrac{x^2}{y}$

d) Check Young's theorem $\left(\dfrac{\partial^2 f}{\partial x \partial y} = \dfrac{\partial^2 f}{\partial y \partial x}\right)$ for b)

Partial derivatives of multivariable functions

a) $f(x, y) = x^2 \cdot y + 2x + 2y + 4$

b) $f(x, y) = e^x \cdot x \cdot y + y^2 + 2$

c) $f(x, y) = \dfrac{x^2}{y}$

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a) $\dfrac{\partial f}{\partial x} = 2x \cdot y + 2$ $\quad$ $\dfrac{\partial f}{\partial y} = x^2 + 2$

b) $\dfrac{\partial f}{\partial x} = e^x \cdot x \cdot y + e^x \cdot y$ $\quad$ $\dfrac{\partial f}{\partial y} = e^x \cdot x + 2y$

c) $\dfrac{\partial f}{\partial x} = \dfrac{2x}{y}$ $\quad$ $\dfrac{\partial f}{\partial y} = -\dfrac{x^2}{y^2}$

d) $\dfrac{\partial^2 f}{\partial y \partial x} = e^x \cdot x + e^x$ $\quad$ $\dfrac{\partial^2 f}{\partial x \partial y} = e^x \cdot x + e^x$

Partial derivatives of multivariable functions

Application: exact differential of $p(V,T)$

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

$$p(V,T) = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2}$$

$$\mathrm{d}p(V,T) = \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T = \ ?$$

Partial derivatives of multivariable functions

Application: exact differential of $p(V,T)$

$$p(V,T) = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{nRT}{(V-nb)^2} + \frac{2n^2a}{V^3}$$

$$\mathrm{d}p(V,T) = \left(-\frac{nRT}{(V-nb)^2} + \frac{2n^2a}{V^3}\right)\mathrm{d}V + \left(\frac{nR}{V-nb}\right)\mathrm{d}T$$

Partial derivatives of multivariable functions

Application: isothermal compressibility (κ_T) and thermal expansion coefficient (α)

$$p(V,T) = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

How do we make $\left(\frac{\partial V}{\partial p}\right)_T$ appear from $p(V,T)$?

Trick: $$\frac{\partial f(x)}{\partial g(x)} \cdot \frac{\partial g(x)}{\partial f(x)} = 1$$

Partial derivatives of multivariable functions

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \quad ? \quad , \qquad p(V,T) = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2}$$

$$\left(\frac{\partial p}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial p}\right)_T = 1 \quad \rightarrow \quad \left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{nRT}{(V-nb)^2} + \frac{2n^2 a}{V^3}$$

$$\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{-\frac{nRT}{(V-nb)^2} + \frac{2n^2 a}{V^3}} \rightarrow \kappa_T = -\frac{1}{V}\frac{1}{-\frac{nRT}{(V-nb)^2} + \frac{2n^2 a}{V^3}}$$

Partial derivatives of multivariable functions

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \quad ? \qquad , \qquad p(V,T) = \frac{nRT}{V-nb} - \frac{n^2 a}{V^2}$$

$$\left(\frac{\partial T}{\partial V}\right)_p \cdot \left(\frac{\partial V}{\partial T}\right)_p = 1 \quad \rightarrow \quad \left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_p}$$

$$p(V,T) \;\rightarrow\; T(p,V) = \frac{\left(p + \frac{n^2 a}{V^2}\right)\cdot(V-nb)}{nR}$$

$$\left(\frac{\partial T}{\partial V}\right)_p = -\frac{\left(-\frac{2n^2 a}{V^3}\right)\cdot(V-nb) + \left(p + \frac{n^2 a}{V^2}\right)}{nR}$$

$$\alpha = \frac{1}{V}\cdot\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{V}\frac{nR}{\left(-\frac{2n^2 a}{V^3}\right)\cdot(V-nb) + \left(p + \frac{n^2 a}{V^2}\right)}$$

Simple integrals

$$\int f(x)\mathrm{d}x = F(x) + C \qquad \int_{x_1}^{x_2} f(x)\mathrm{d}x = F(x_2) - F(x_1)$$

Rules:

$$f(x) = x^n \ (n \neq -1) \quad \rightarrow \quad F(x) = \frac{1}{n+1}x^{n+1}$$

$$f(x) = \frac{1}{x} \quad \rightarrow \quad F(x) = ln(|x|)$$

$$f(x) = e^x \quad \rightarrow \quad F(x) = e^x$$

If the argument is a linear function of x:

$$\int f(ax+b)\mathrm{d}x = \frac{1}{a}F(ax+b) + C$$

Simple integrals

$$\int f(x)\mathrm{d}x = ?$$

a) $f(x) = 2x^3 + 8x + 5$

b) $f(x) = \dfrac{2}{x+5}$

c) $f(x) = e^{(2x-1)} + x^2$

Simple integrals

$$\int f(x)\mathrm{d}x = ?$$

a) $f(x) = 2x^3{+}8x{+}5 \quad \rightarrow \quad \int f(x)\mathrm{d}x = \frac{1}{2}x^4 + 4x^2 + 5x + C$

b) $f(x) = \frac{2}{x+5} \quad \rightarrow \quad \int f(x)\mathrm{d}x = 2ln(x+5) + C$

c) $f(x) = e^{(2x-1)}{+}x^2 \quad \rightarrow \quad \int f(x)\mathrm{d}x = \frac{1}{2}e^{(2x-1)} + \frac{1}{3}x^3 + C$

Simple integrals

Application: Calculate the (reversible) isothermal work required to compress a gas from V_1 to V_2

$$p(V,T) = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$W = -\int_{V_1}^{V_2} p\mathrm{d}V = ?$$

Simple integrals

Application: Calculate the (reversible) isothermal work required to compress a gas from V_1 to V_2

$$p(V,T) = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

$$W = -\int_{V_1}^{V_2} p\mathrm{d}V = -nRT\int_{V_1}^{V_2}\frac{1}{V-nb}\mathrm{d}V + n^2a\int_{V_1}^{V_2}\frac{1}{V^2}\mathrm{d}V$$

$$W = nRTln\Big(\frac{V_1-nb}{V_2-nb}\Big) - \frac{n^2a}{3}\Big(\frac{1}{(V_2)^3} - \frac{1}{(V_1)^3}\Big)$$