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:

$(x^n)' = nx^{n-1}$ $\qquad (f(x) \cdot g(x))' = f'(x) \cdot g(x) + f(x) \cdot g'(x)$

$(e^x)' = e^x$ $\qquad \left(\frac{f(x)}{g(x)}\right)' = \frac{f'(x) \cdot g(x) - f(x) \cdot g'(x)}{(g(x))^2}$

$(ln(x))' = \frac{1}{x}$ $\qquad (f \circ g)'(x) = f'(g(x)) \cdot g'(x)$

$f'(x) = \, ?$

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

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

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

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

---

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

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

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

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

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

What kind of extremum is it?

Derivatives of functions of a single variable

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

$$f'(x) = 0 = \frac{1}{x} \cdot x^2 + ln(x) \cdot 2x$$

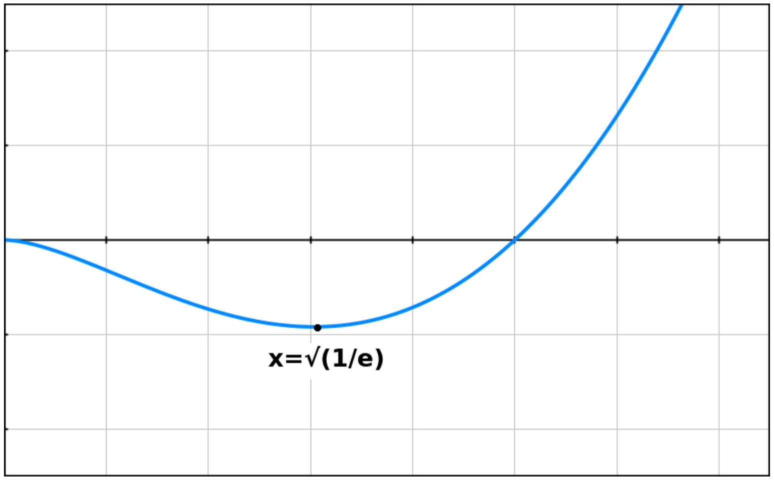
$$ln(x) = -\frac{1}{2}$$

$$x = \frac{1}{\sqrt{e}}$$

What kind of extremum is it?

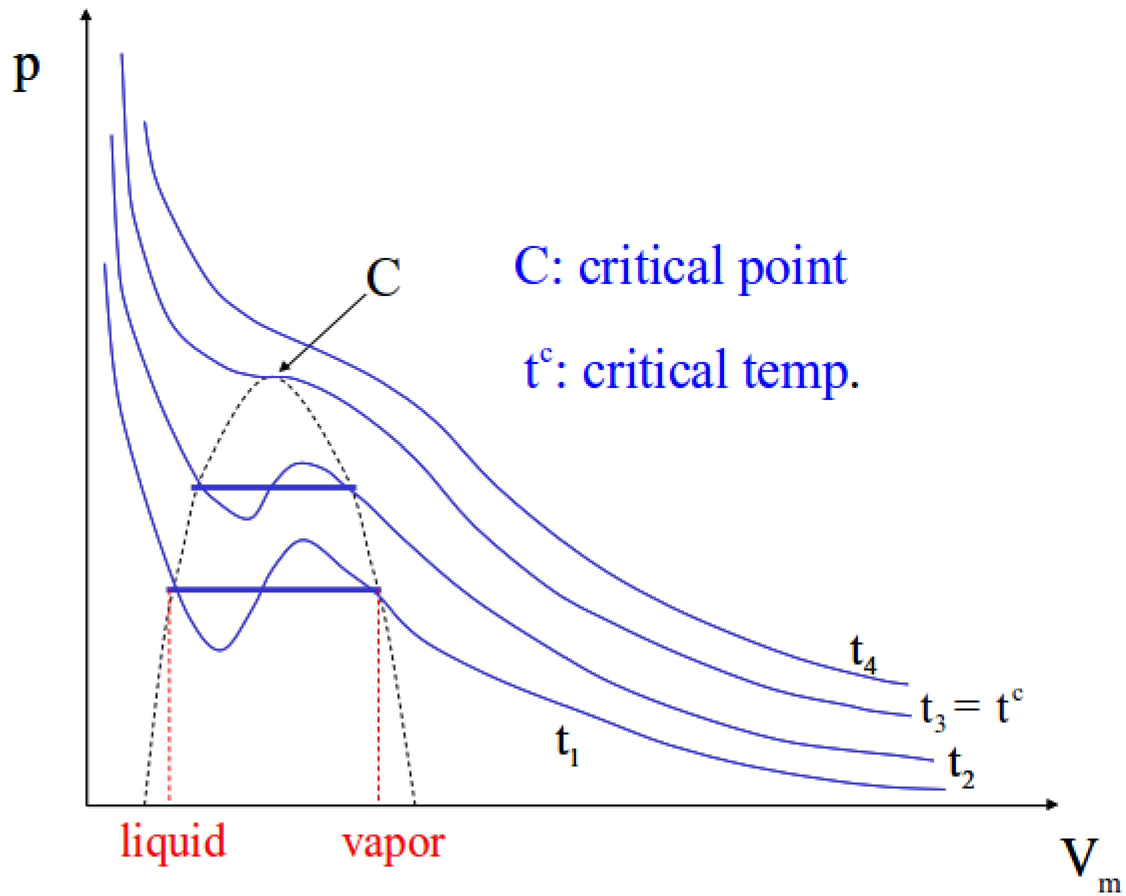
$$f''(x) = 1 + \frac{1}{x} \cdot 2x + ln(x)2$$

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



Derivatives of functions of a single variable

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



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

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

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

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

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

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

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

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

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

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

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

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

$$\ldots \rightarrow \boxed{p(V_m^c) = \frac{a}{27b^2}}$$

Partial derivatives of multivariable functions

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

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

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

---

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

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

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

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

Partial derivatives of multivariable functions

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

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

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

$$\mathrm{d}p = ?$$

Partial derivatives of multivariable functions

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

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

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

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

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

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: $\left(\frac{\partial x}{\partial x}\right)_z = 1 = \left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial x}\right)_z$

Partial derivatives of multivariable functions

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

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

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

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

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \,?$$

Partial derivatives of multivariable functions

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

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

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

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

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

Simple integrals

$\int f(x)\mathrm{d}x = F(x) + C$

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

Rules:

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

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

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

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

Simple integrals

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

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

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

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

Simple integrals

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

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

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

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

Simple integrals

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

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

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

Simple integrals

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

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

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

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