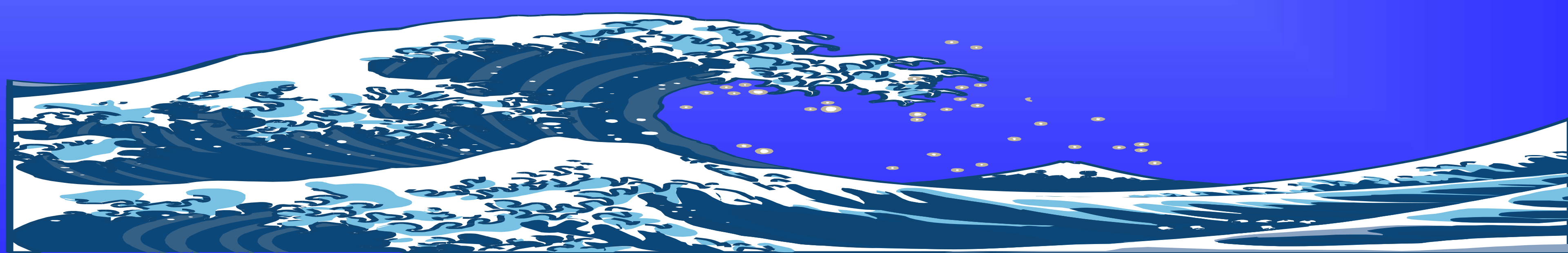
Tożsamości termodynamiczne

treści fakultatywne



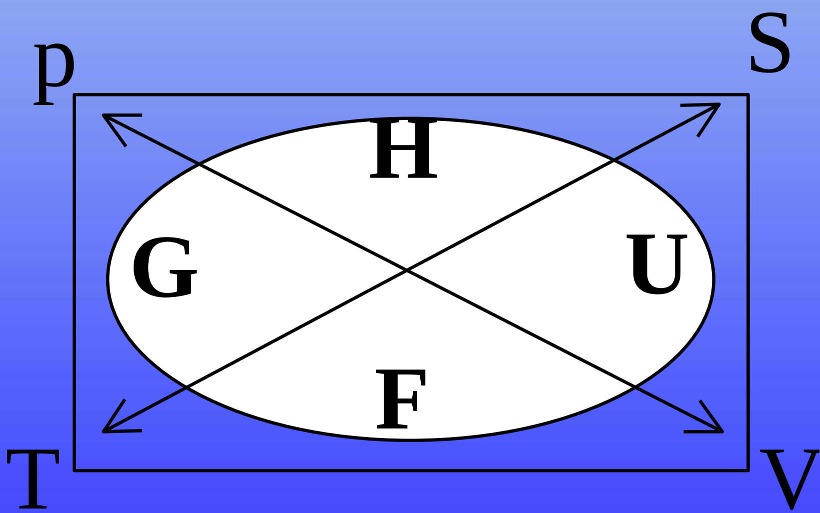
Tożsamości termodynamiczne

Związki pomiędzy funkcjami termodynamicznymi

$$H = U + pV$$

$$G = H - TS$$

$$F = U - TS$$



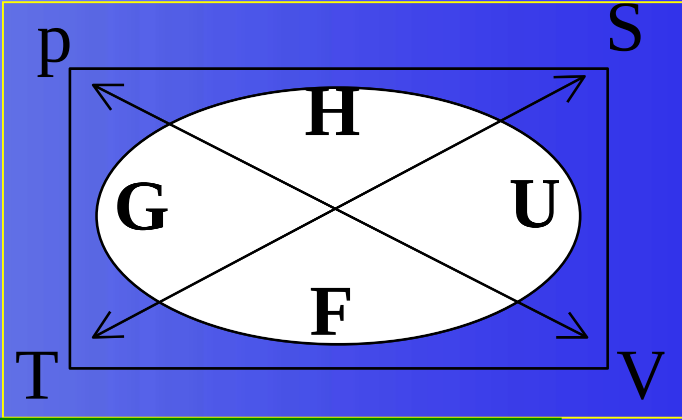
$$dU = TdS - pdVp$$

$$dH = TdS + Vdp$$

$$dF = -SdT - pdV$$

$$dG = -SdT + Vdp$$

Tożsamości termodynamiczne Relacje Maxwell'a:



Potencjały termodynamiczne

U = U(S,V)

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P$$

termodynamiczna definicja temperatury

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V$$

H = H(S,P)

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

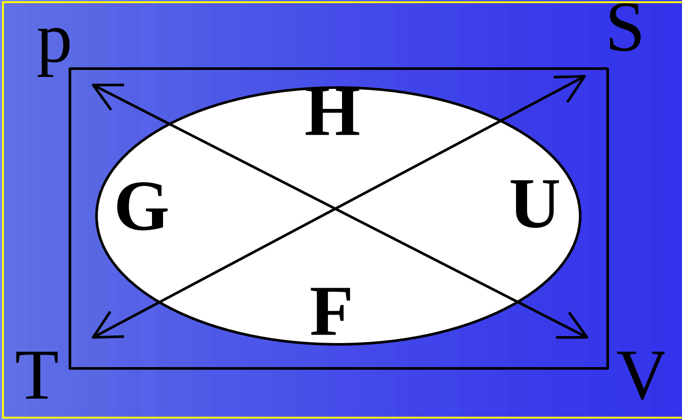
$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Tożsamości termodynamiczne

Relacje Maxwell'a:



Potencjały termodynamiczne

F = F(T,V)

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right)_V$$

G = G(T,P)

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Równania Gibbsa-Helmholtza

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_{V,\xi}$$

czyli

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

$$F = U - TS \qquad U = F + TS$$

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V} \qquad U = F - T\left(\frac{\partial F}{\partial T}\right)_{V,\xi}$$

$$G = H - TS \qquad H = G + TS$$

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

Pierwsze termodynamiczne równanie stanu

Różniczkując równie Gibbsa-Helmolza względem objętości:

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial F}{\partial V}\right)_T - T\left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V$$

ponieważ

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

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V}$$

Pierwsze termodynamiczne równanie stanu.

Drugie termodynamiczne równanie stanu

Różniczkując równie Gibbsa-Helmolza względem ciśnienia:

ponieważ

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

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial G}{\partial p}\right)_T - T\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T\right]_p$$

$$\boxed{\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p}$$

Drugie termodynamiczne równanie stanu.

Przykład stosowania tożsamości termodynamicznych

Zależność pomocnicza ułatwiająca kreślenie, czy wyrażenie różniczkowe jest różniczką zupełną:

$$df = g(x,y)dx + h(x,y)dy$$

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

Przykład:

$$dU = TdS - pdV$$

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

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p$$

$$\left(\frac{\partial}{V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial T}{\partial V}\right)_S$$

$$\left(\frac{\partial}{S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V = \left(\frac{\partial T}{\partial S}\right)_V$$

bo:

$$\left(\frac{\partial}{V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V$$

Przykład stosowania tożsamości termodynamicznych

Relacje Maxwell'a:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

Zadanie: udowodnić powyższe relacje!

Przykład stosowania tożsamości termodynamicznych

I sposób: z różniczek zupełnych

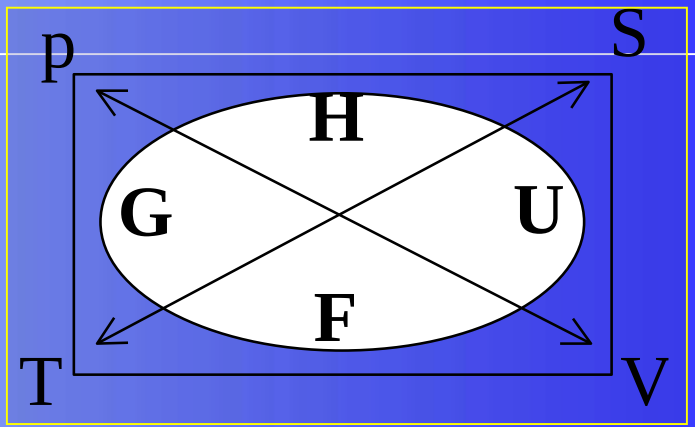
$$dU = TdS - pdVp \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$dH = TdS + Vdp \qquad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$dF = -SdT - pdV \qquad \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$dG = -SdT + Vdp \qquad \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

Tożsamości termodynamiczne



II sposób: z relacji Maxwella

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P; \qquad \left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial U}{\partial P}\right)_S = V$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P; \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

Przykład stosowania tożsamości termodynamicznych
Zależność zmian entalpii od temperatury

V=const

Jakie wielkości należy zmierzyć, aby scharakteryzować H=H(T)

$$H(T,p,\xi) \qquad dH = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial H}{\partial p}\right)_{T,\xi} dp + \left(\frac{\partial H}{\partial \xi}\right)_{T,p} d\xi$$

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp + Q_{r,p} d\xi$$

przy braku reakcji chemicznej

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + C_p dT$$

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V + C_p$$

Jaka jest wartość tej pochodnej?

Korzystając z relacji:

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

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

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

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

$$\left(\frac{\partial p}{\partial T}\right)_V=-\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}=\frac{\alpha}{\kappa_T}$$

$$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,\xi}\qquad \kappa_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,\xi}$$

Tożsamości termodynamiczne

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{\left(\frac{\partial p}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_p}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_p$$

współczynnik Joule'a-Thomsona

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

$$\left(\frac{\partial H}{\partial p}\right)_T = -\mu \cdot C_p$$

$$\boxed{\left(\frac{\partial H}{\partial T}\right)_V = \left(1 - \frac{\alpha \cdot \mu}{\kappa_T}\right) \cdot C_p}$$