# Test for exactness of differentials

If $dG$ is an exact differential,

then $dG$ can be written as

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

$$= A(x,y)\,dx + B(x,y)\,dy$$

$$\longrightarrow \boxed{\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}} \longrightarrow \frac{\partial^2 G}{\partial y \partial x} = \frac{\partial^2 G}{\partial x \partial y}$$

$$dG = \underbrace{2xy^3}_{A}dx + \underbrace{3x^2y^2}_{B}dy$$

$$\frac{\partial A}{\partial y} = 6xy^2 \quad ; \quad \frac{\partial B}{\partial x} = 6xy^2 \checkmark$$ dG is exact

$$dF = \underbrace{2xy^2}_{A}dx + \underbrace{3x^2y^3}_{B}dy$$

$$\frac{\partial A}{\partial y} = 4xy \quad ; \quad \frac{\partial B}{\partial x} = 6xy$$ dF is inexact

$\int dF$ depend on path

Consequence if dG is exact

$$\boxed{\int_P^Q dG = G(Q) - G(P)}$$

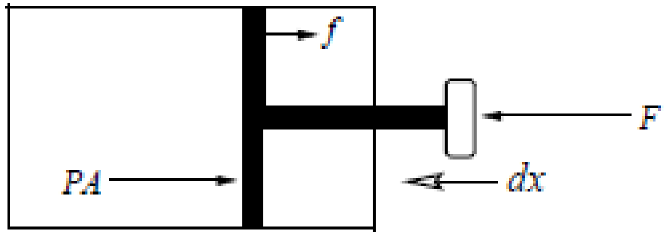
independent of path

# Work

Work done by/on fluids

$$\text{đ}W = +F\,dx = (PA + f)\,dx > 0$$

$$F = PA + f$$

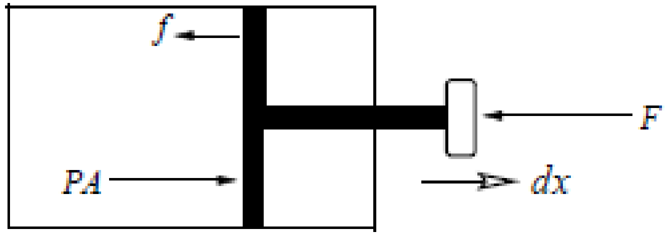



compression

but $A\,dx = -dV$

$$\text{đ}W = -P\,dV + f\,dx$$

$$F = PA - f$$




expansion

$$\text{đ}W = -F\,dx = -(PA - f)\,dx$$

but $A\,dx = dV$

$$\text{đ}W = -P\,dV + f\,dx$$

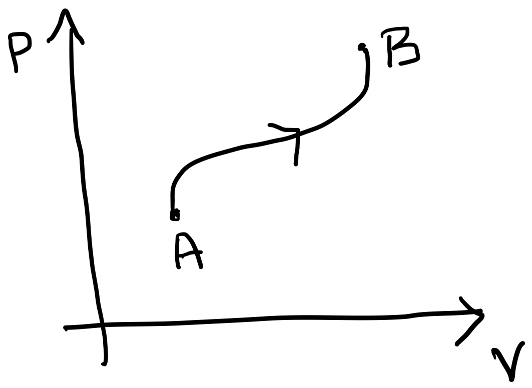
$$\boxed{\text{đ}W \geq -P\,dV} \longrightarrow \text{equality holds for reversible}$$

# Work depends on path

Work done by a fluid during compression or expansion by a finite amount is obtained by integrating đW between initial and final states.

$$W = \int_A^B đW = -\int_A^B PdV$$

In general, work will depend on path choice of $P(V)$.



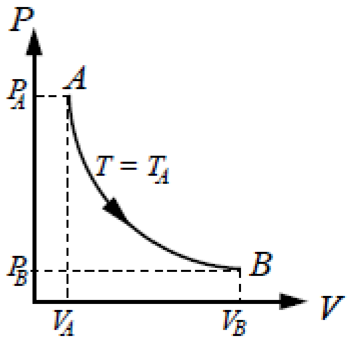

$\nexists$ No $W(P,V)$ such that

$$đW = -PdV \;!!$$

# Illustrative Examples

- Quasistatic Reversible Isothermal expansion of an ideal gas

$PV = nRT$

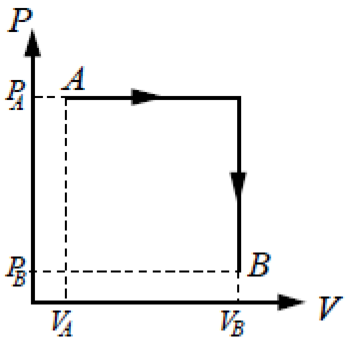



$W = -\int_{V_A}^{V_B} P\,dV = -nRT_A \int_{V_A}^{V_B} \frac{dV}{V}$

$$\boxed{W_{isoth} = -nRT_A \ln \frac{V_B}{V_A}}$$

- Isobaric expansion of the same gas

$P_A = \text{const}$




$W = -\int_{V_A}^{V_B} P\,dV = -P_A (V_B - V_A)$

$$\boxed{W_{isobar} = -nRT_A \left(\frac{V_B}{V_A} - 1\right)}$$

# Work Equation for other systems

Fluids $dW = -PdV$

Soap Films $dW = \gamma dA$

Stretched Wire $dW = Tdl$

Paramagnetic Solid $dW = HdM$

# Work done on a solid

In general $đW = -p\,dV$ may not apply, stress response may not be isotropic

isotropic stress $P$ $\longrightarrow$ isotropic response $dV$, $đW = -p\,dV$

$V(P,T)$ : state fn., isothermal, $P_A \rightarrow P_B$

$$W_{AB} = -\int_A^B P\,dV$$

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

In this case $dT = 0 \longrightarrow$ isothermal

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP$$

compressibility $= \boxed{\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$

$$dV = -\kappa V dP$$

$$W_{AB} = -\int_{P_A}^{P_B} p\, dV = \int_{P_A}^{P_B} \kappa V P dP .$$

almost const for small changes of pr. T

$$\boxed{W_{AB} \approx \frac{\kappa V}{2}\left(P_B^2 - P_A^2\right)}$$

$$dV = \underbrace{\left(\frac{\partial V}{\partial P}\right)_T}_{-\kappa V} dP + \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{\beta V} dT$$

$\beta V \rightarrow$ thermal expansion coeff.

Similarly $P(V, T)$

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$

$$dT = \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial T}{\partial P}\right)_V dP .$$

# Mathematical Interlude

$(x, y, z) \longrightarrow f(x, y, z) = 0$ only 2 independent

$x(y, z)$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad \text{—— (1)}$$

$y(x, z)$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \quad \text{—— (2)}$$

substitute (2) in (1)

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \quad \text{— (3)}$$

$\therefore$ $x, z$ independent

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

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}} \quad \text{— } ③$$

and

$$\left(\frac{\partial x}{\partial z}\right)_y + \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = 0, \quad \text{use } ③$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1} \quad \text{— } ④$$

For a PVT system

$$\underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{-\frac{1}{\kappa V}} \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{\beta V} \left(\frac{\partial T}{\partial P}\right)_V = -1$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{\kappa}{\beta} \quad \text{or} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}$$