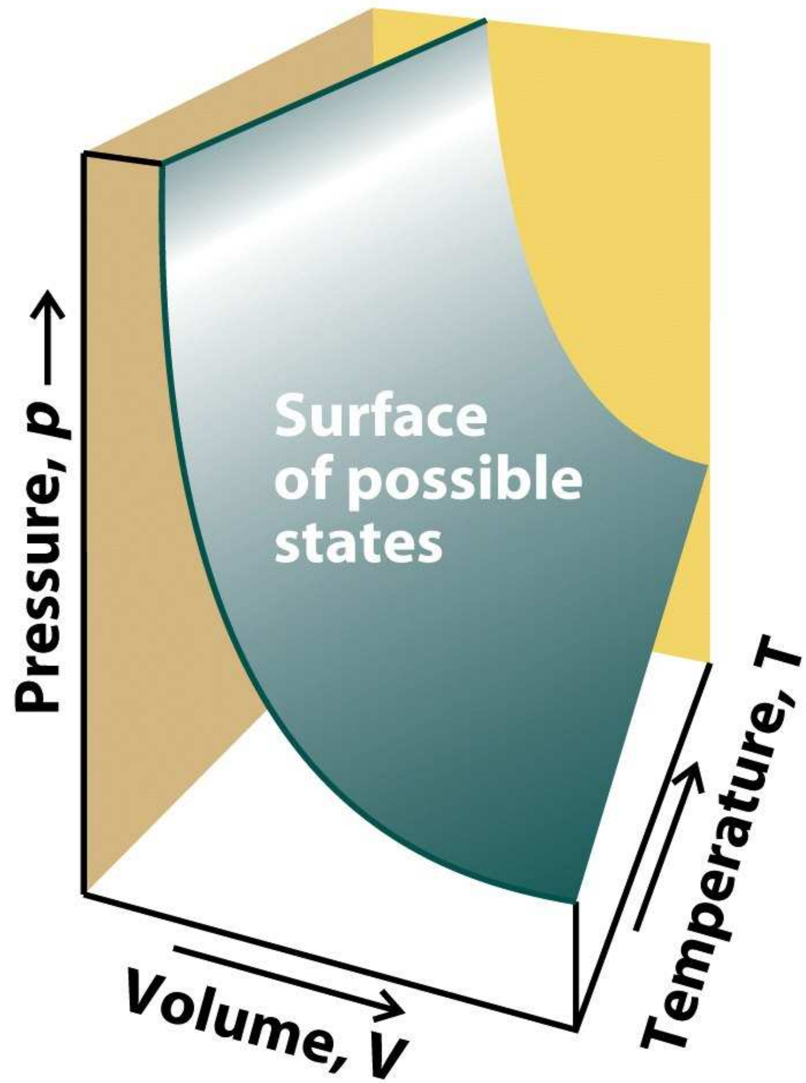
Work, internal energy, heat, state functions, equation of state, heat capacity, enthalpy, and all that

$$dU = \underbrace{\text{đ}q + \text{đ}w}_{\text{path functions}}$$

state function

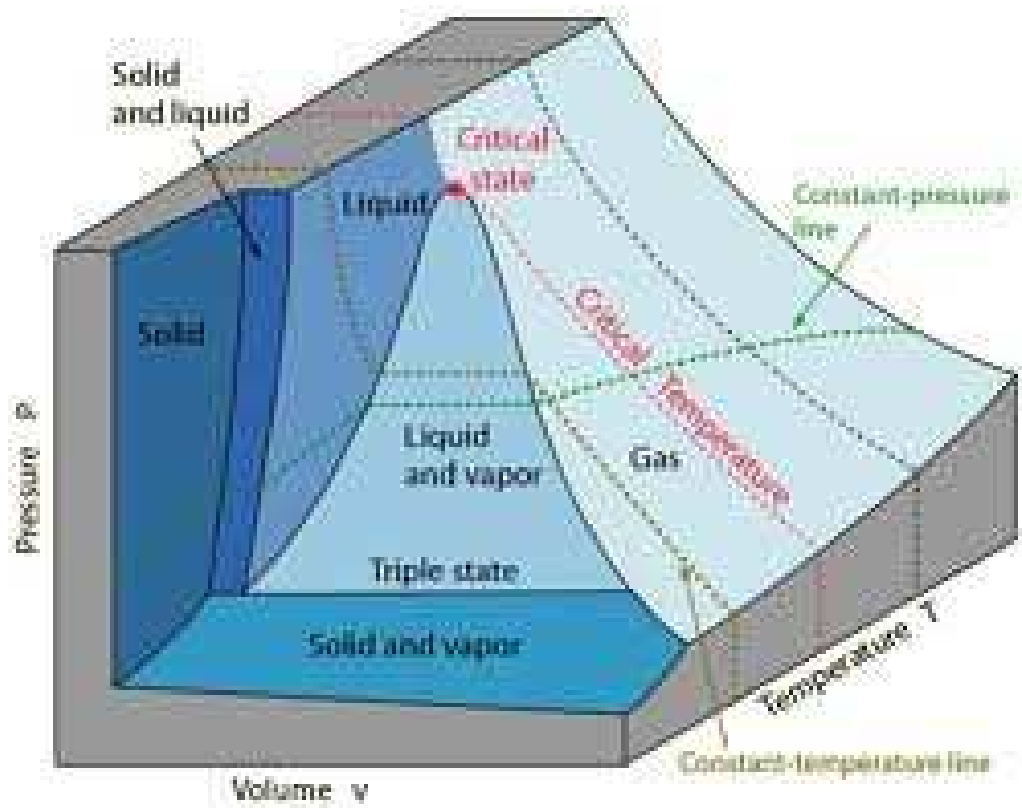
p, V, T diagram of an ideal gas



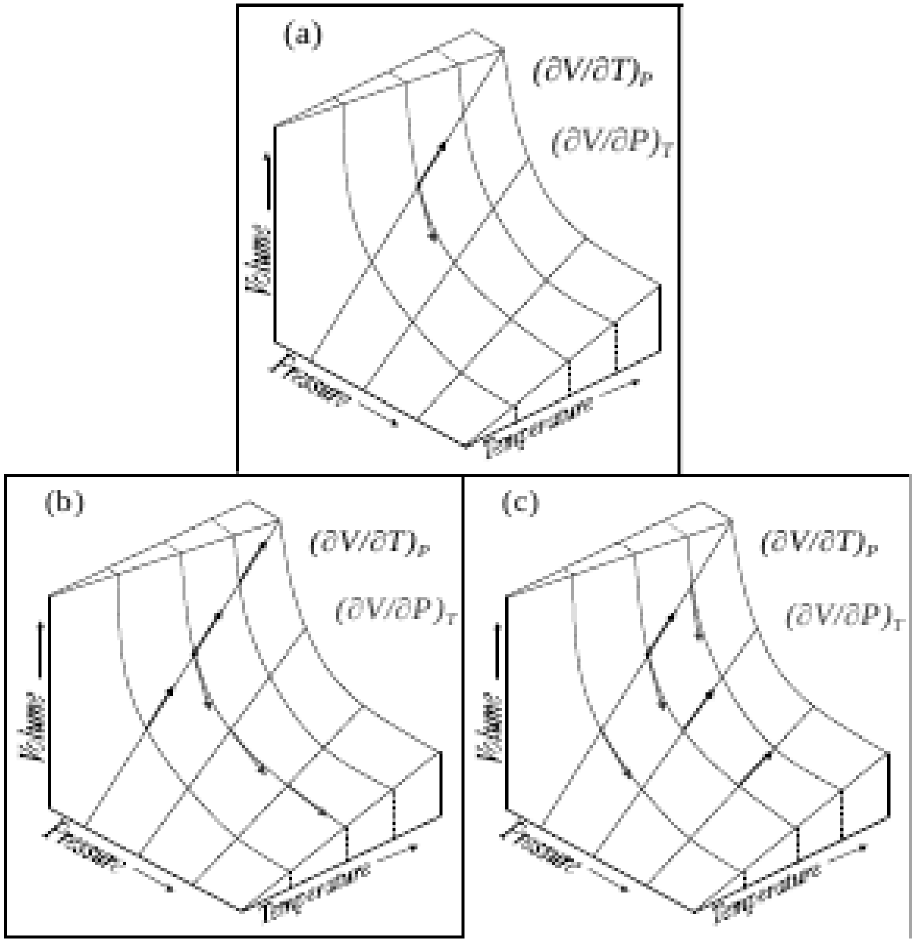
$f(p, V, T) = 0$

Figure 1-8
Atkins Physical Chemistry, Eighth Edition

P, V, T surface of a "real" system



P, V, T surface for an ideal gas with the partial derivatives shown



dU is an exact differential

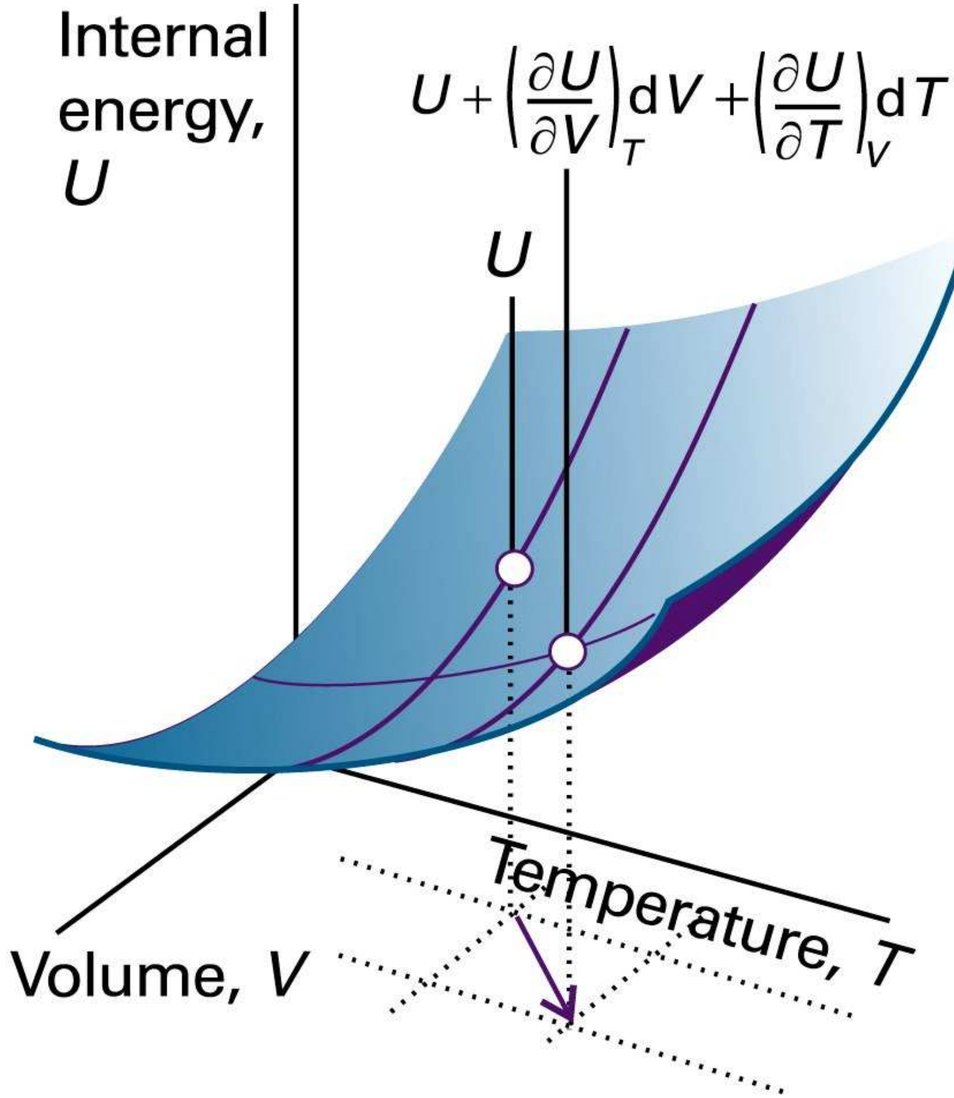


Figure 2-23
Atkins Physical Chemistry, Eighth Edition

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

$$y = f(x)$$

$$dy = f'(x)\,dx$$

$$dw = -P_{ext}\, dV \rightarrow \text{extensive property}$$

$$dU = dq + dw$$

Intensive property → independent of the size of the system

examples are (P, T, ρ)

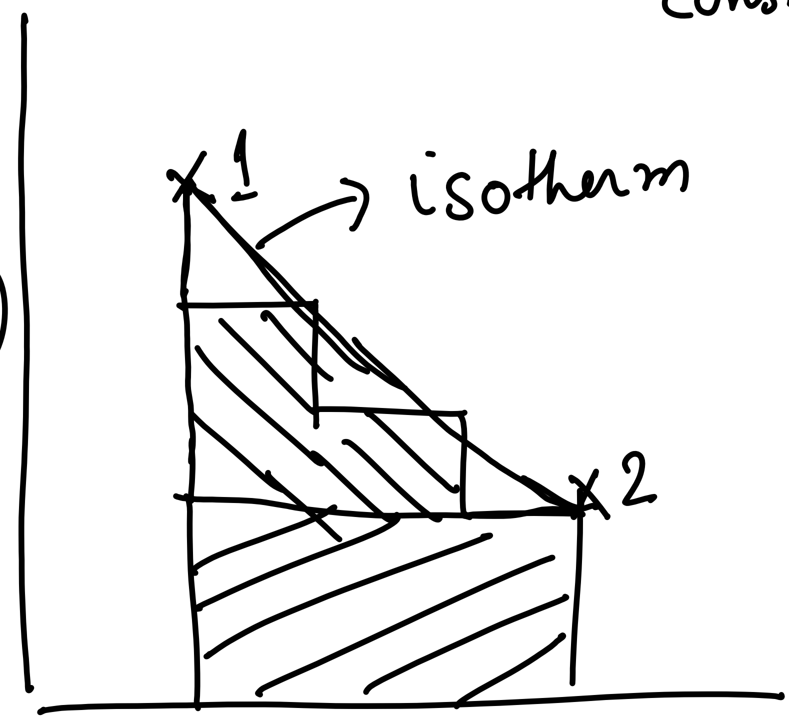
examples of extensive variables

V, mass

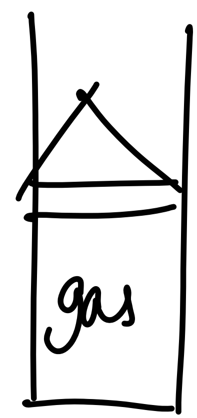
$f\,dL$
$\gamma\,dA$
other types of $=$

Reversibility

System – equation of state $(f(P,V,T)=0)$



constant T



Process

$đq$, $đw$

$$đw = -P_{ext}\, dV$$

$P_{ext} \approx P_{sys} \rightarrow \underline{\underline{EOS}}$

Isothermal Reversible process for an ideal gas

$$đw = -P_{ext}\, dV \quad \text{reversible}$$

$f(P, V, T) = 0$

$$= -P_{sys}\, dV = -\frac{RT}{V} dV$$

$$\underbrace{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}_{\text{isothermal compressibility}} = \beta \qquad \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha$$

$$V(P, T)$$

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

$$= -\beta V\, dP + \alpha V\, dT$$

$$U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \boxed{\left(\frac{\partial U}{\partial V}\right)_T} dV$$

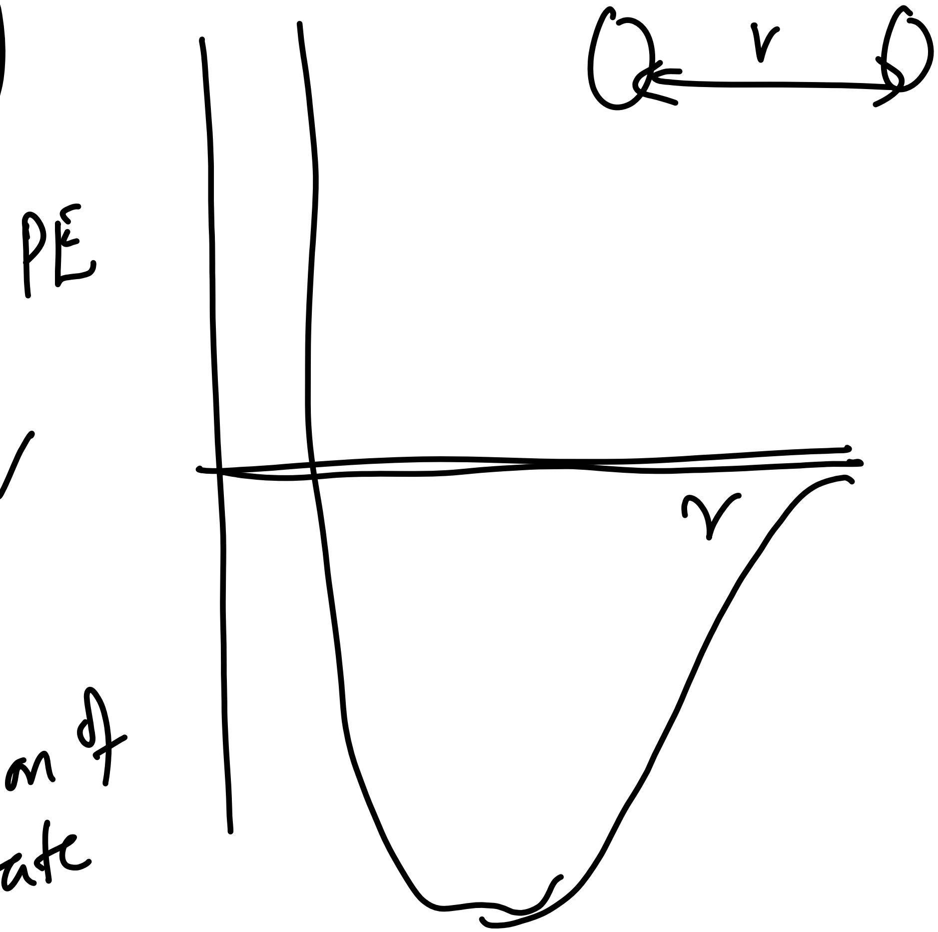
$$C_{P/V} = \left(\frac{đq}{dT}\right)_{P/V}$$

$$dU = đq + dW$$

$$= đq \quad (\text{const volume} \\ \text{P-V work})$$

$$\to g(T,V)$$

$$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{\text{Equation of state}} dV$$



enthalpy

$$dU = \text{đ}q + \underbrace{\text{đ}W}_{-P_{sys}\,dV}$$

constant

$$\text{đ}q = \underbrace{dU + P\,dV}$$

$$= dH$$