

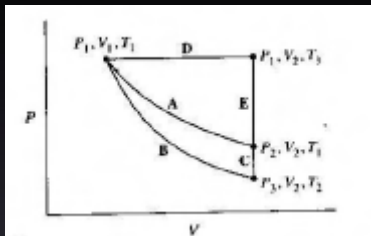
# Class 3

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# Evaluating heat requires knowledge of the path



Determine the heat transfer during an isothermal reversible change from  $(P_1, V_1, T_1)$  to  $(P_2, V_2, T_2)$

For ideal gas, the internal energy is only a function of temperature

$$dU = 0$$

$$dq_{\text{rev}} = -dw_{\text{rev}} = P_{\text{ext}} dV = \frac{RT}{V} dV$$

Last equality because the  $P_{\text{ext}} = P$  for a reversible process and  $P = \frac{RT}{V}$  for an ideal gas

# Constant pressure and constant volume heating

Change from  $(P_1, V_1, T_1)$  to  $(P_2, V_2, T_2)$  broken up into two steps:  
 $(P_1, V_1, T_1)$  to  $(P_1, V_2, T_3)$  followed by  $(P_1, V_2, T_3)$  to  $(P_2, V_2, T_2)$   
First step is a constant pressure reversible heating (path D)

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

$$dU = C_V dT$$

$$dw_{\text{rev}} = P_{\text{ext}} dV = P_1 dV$$

Explain to yourself why each of the equations hold.

Second step is constant volume heating (path E)

$$dU = C_V dT$$

$$dw_{\text{rev}} = P_{\text{ext}} dV = 0$$

Find the heat transfer if this change is by path B + C

$\left(\frac{\partial U}{\partial T}\right)_V$  is not equal to  $\left(\frac{\partial U}{\partial T}\right)_P$

If  $U$  is considered to be a function of  $(T, V)$ , then

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

We will adopt a shortcut: Divide by  $dT$  and apply constant  $P$

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

See Problem 19-27 of McQuarrie and Simon for the mathematically rigorous approach which should give you some practice with partial derivatives

## Enthalpy change at a diff. $T$ from $C_P$

Considering that  $H$  is a function of  $(T, P)$ , we have

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

If only temperature varies, the second term is zero

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

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT$$

We have used here the relation

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

Self-test: Obtain a relation between  $C_P$  and  $C_V$ .

# Some useful partial derivative identities

Reciprocal identity

$$\left(\frac{\partial H}{\partial T}\right)_P = \frac{1}{\left(\frac{\partial T}{\partial H}\right)_P}$$

Cyclic identity

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

Written here for  $H, T, P$ , but true in general

A differential  $dz$

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

is exact if

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

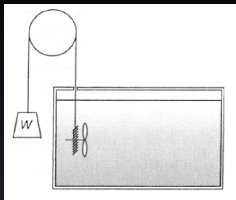
If  $dz$  is an exact differential, then  $\oint dz = 0$  and  $z$  is a state function.

# The need for a measure for irreversibility

Consider two identical bodies that only differ in temperature. The first law, energy conservation, does not suggest that the temperatures of the two bodies will equalize if they are in thermal contact.

- Reversible processes are the limit toward which actual processes may be made to approach indefinitely
- Implies that processes differ from one another in their degree of irreversibility.
- Important to establish a quantitative measure of this degree of irreversibility, or this degree of degradation.

# Entropy should have the form $q/T$



- 1 The weight is allowed to fall, performing work,  $w$ , and the heat produced,  $q$ , enters the heat reservoir at temperature  $T_2$ .
- 2 The heat reservoir at the temperature  $T_2$  is placed in thermal contact with a heat reservoir at a lower temperature  $T_1$ , and the same heat  $q$  is allowed to flow from the reservoir at  $T_2$  to the reservoir at  $T_1$ .
- 3 The weight is allowed to fall, performing work,  $w$ , and the heat produced,  $q$  enters the reservoir at temperature  $T_1$ .

Degradation in 3 is greater than in 1 and 2 (Why?)  $q$  and  $T$  important in defining a quantitative scale of irreversibility.

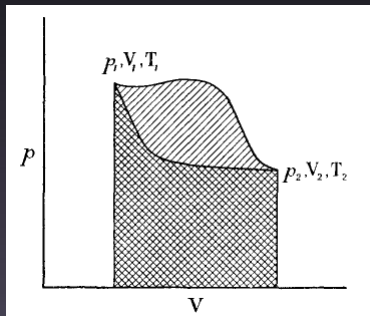


# $dq_{\text{rev}}$ is not an exact differential

Consider an ideal gas undergoing a reversible state change

$$dq_{\text{rev}} = C_V dT + \frac{RT}{V} dV$$

is not an exact differential.



Show this for yourself using the Euler criterion of exactness.

## $dq_{\text{rev}}/T$ is an exact differential

Consider an ideal gas undergoing a reversible state change

$$dq_{\text{rev}}/T = \frac{C_V}{T} dT + \frac{R}{V} dV$$

is an exact differential.

Define a thermodynamic property

$$dS = \frac{dq_{\text{rev}}}{T}$$