# *ChemE 2200 – Chemical Thermodynamics Lecture 4*

*Today:*

Calculating Enthalpy for Pure Substances.
Calculating Enthalpy Changes for Chemical Reactions.
Entropy, $S$, State Function for Spontaneous Change.
Calculating Entropy Changes for Isothermal, Isobaric,
Isochoric, and Adiabatic Changes.

*Defining Question:*

Why is $\delta q$ not a state function but $\delta q_{\mathrm{rev}}/T$ is a state function?

*Reading for Today's Lecture:*

McQuarrie & Simon, Chapter 19.9-19.12, 20.1-20.3

*Reading for Thermodynamics Lecture 5:*

McQuarrie & Simon, Chapter 20.4-20.6

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pair ChemE-affiliated Peer Advisors
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# Recap

Relation between Internal Energy, $U$, and Enthalpy, $H$, both state functions:

$$H = U + PV$$

For changes at constant volume, use Internal Energy, $U$.

$$\Delta U = q \quad \text{for} \quad \Delta V = 0$$

For changes at constant pressure, use Enthalpy, $H$.

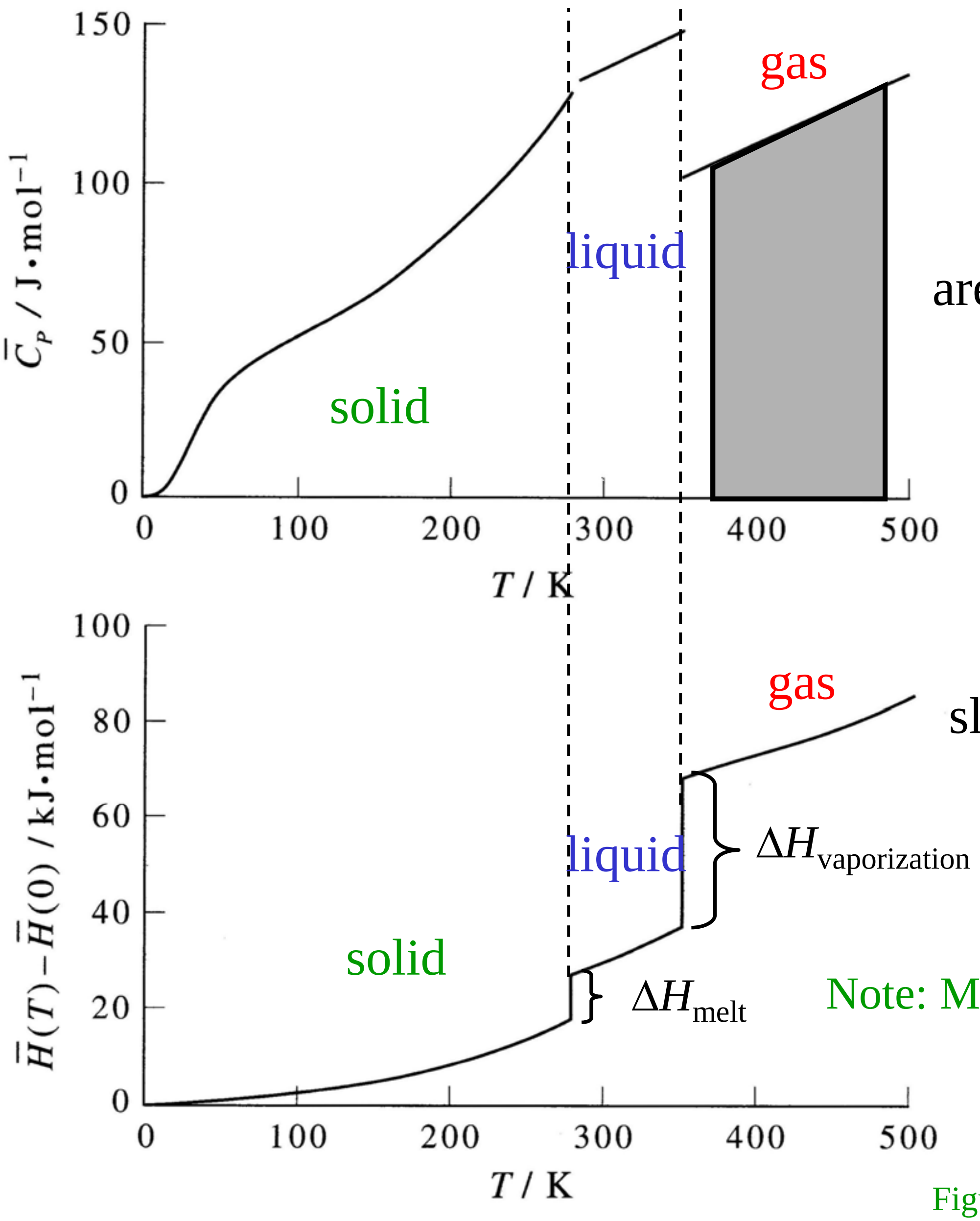
$$\Delta H = q \quad \text{for} \quad \Delta P = 0$$

# Calculating the Enthalpy for a Pure Substance: Benzene

$$\left(\frac{\partial \overline{H}}{\partial T}\right)_P = \overline{C}_{\mathrm{P}} \quad \Rightarrow \quad \Delta H = \int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} \overline{C}_{\mathrm{P}}\, dT$$ for no phase change at constant $P$

heat capacity, $C_{\mathrm{P}}$

enthalpy, $\Delta H$



$$\text{area} = \Delta H = \int_{T_1}^{T_2} \overline{C}_{\mathrm{P}}\, dT$$

$$\text{slope} = \left(\frac{\partial \overline{H}}{\partial T}\right)_P = \overline{C}_{\mathrm{P}}$$

Note: McQuarrie & Simon use $\Delta_{\mathrm{melt}}H$

Figures 19.6 & 19.7 from McQuarrie & Simon

# Calculating the Enthalpy for Pure Substances

Calculate Δ*H* for $H_2O$ from 50°C to 150°C at 1 atm.

Break into steps delineated by phase.

$$\boxed{\begin{array}{c}\text{water}\\ 50^\circ\text{C} \rightarrow 100^\circ\text{C}\end{array}} + \boxed{\begin{array}{c}\text{water} \rightarrow \text{steam}\\ 100^\circ\text{C}\end{array}} + \boxed{\begin{array}{c}\text{steam}\\ 100^\circ\text{C} \rightarrow 150^\circ\text{C}\end{array}}$$

$$\Delta\overline{H} = \int_{50^\circ\text{C}}^{100^\circ\text{C}} \overline{C}_{\text{P,liquid}}\,dT + \Delta\overline{H}_{\text{vap}} + \int_{100^\circ\text{C}}^{150^\circ\text{C}} \overline{C}_{\text{P,vapor}}\,dT$$

# Calculating the Enthalpy Change of Chemical Reaction

std state: 25°C, 1 bar

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O_{(liq)}$$

$$\Delta\bar{H}^{0}_{\text{rxn}} = \bar{H}_{\text{products}} - \bar{H}_{\text{reactants}}$$

*H* of an element in std state is defined to be 0.

$$= (-286\ \text{kJ/mol}) - (0 + \tfrac{1}{2}0) \quad = -286\ \text{kJ/mol}$$

exothermic reaction

Instead of the above calculation, find “Heat of Reaction” in a data table.

Or – in this case – find “Heat of Formation” in a data table.

Data Tables of “Heat of Combustion” are for complete oxidation of a compound.

$$CH_2{=}CH_2 + 2O_2 \rightarrow 2CO_2 + 2H_2O \qquad \Delta\bar{H}^{0}_{\text{combustion}} = -1411\ \text{kJ/mol}$$

Note: *Heat of Combustion* is the change in enthalpy for pure separated reactants in their standard state to pure separated products in their standard state.

# Calculating the Enthalpy Change of Chemical Reaction

What if you cannot find $\Delta H_{\text{rxn}}$ in a data table?

example: $HC{\equiv}CH + H_2 \rightarrow CH_2{=}CH_2 \qquad \Delta H_{\text{rxn}} = \ ?$

Use Hess's Law (1840) *The enthalpy change in a chemical reaction is independent of the path from the initial state to the final state.*

Use reactions for which $\Delta H_{\text{rxn}}$ is known. Add chemical equations like adding algebraic equations.

$$\begin{array}{rlrl}
\text{reaction with reactant:} & HC{\equiv}CH + \cancel{2.5}O_2 \rightarrow \cancel{2CO_2} + \cancel{H_2O} & \Delta\bar{H}^0_{\text{combustion}} & = -1300.\ \text{kJ/mol} \\
\text{reaction with product:} & \cancel{2CO_2} + \cancel{2}H_2O \rightarrow CH_2{=}CH_2 + \overset{1/2}{\cancel{3}}O_2 & -\Delta\bar{H}^0_{\text{combustion}} & = +1411\ \text{kJ/mol} \\
\hline
\text{sum:} & HC{\equiv}CH + \cancel{H_2O} \rightarrow CH_2{=}CH_2 + \cancel{\tfrac{1}{2}O_2} & \Delta\bar{H}^0_{\text{rxn}} & = +111\ \text{kJ/mol} \\
 & H_2 + \cancel{\tfrac{1}{2}O_2} \rightarrow \cancel{H_2O}_{(\text{liq})} & \Delta\bar{H}^0_{\text{combustion}} & = -286\ \text{kJ/mol} \\
\hline
\text{sum:} & HC{\equiv}CH + H_2 \rightarrow CH_2{=}CH_2 & \multicolumn{2}{r}{\boxed{\Delta\bar{H}^0_{\text{rxn}} = -175\ \text{kJ/mol}}}
\end{array}$$

Note: The enthalpy of a chemical reaction is the change in enthalpy for pure *separated* reactants in their standard state to pure *separated* products in their standard state.

# Calculating the Enthalpy Change of Chemical Reaction

example: $HC{\equiv}CH + H_2 \rightarrow CH_2{=}CH_2 \qquad \Delta H_{rxn} = ?$

Use Hess's Law with Heats of Formation

$$\text{HC}{\equiv}\text{CH:} \qquad -1\times(2C(s) + H_2 \rightarrow HC{\equiv}CH) \qquad \Delta\overline{H}^0_{formation} = +227 \text{ kJ/mol}$$

$$\text{CH}_2{=}\text{CH}_2\text{:} \qquad \underline{2C(s) + 2H_2 \rightarrow CH_2{=}CH_2} \qquad \Delta\overline{H}^0_{formation} = +52 \text{ kJ/mol}$$

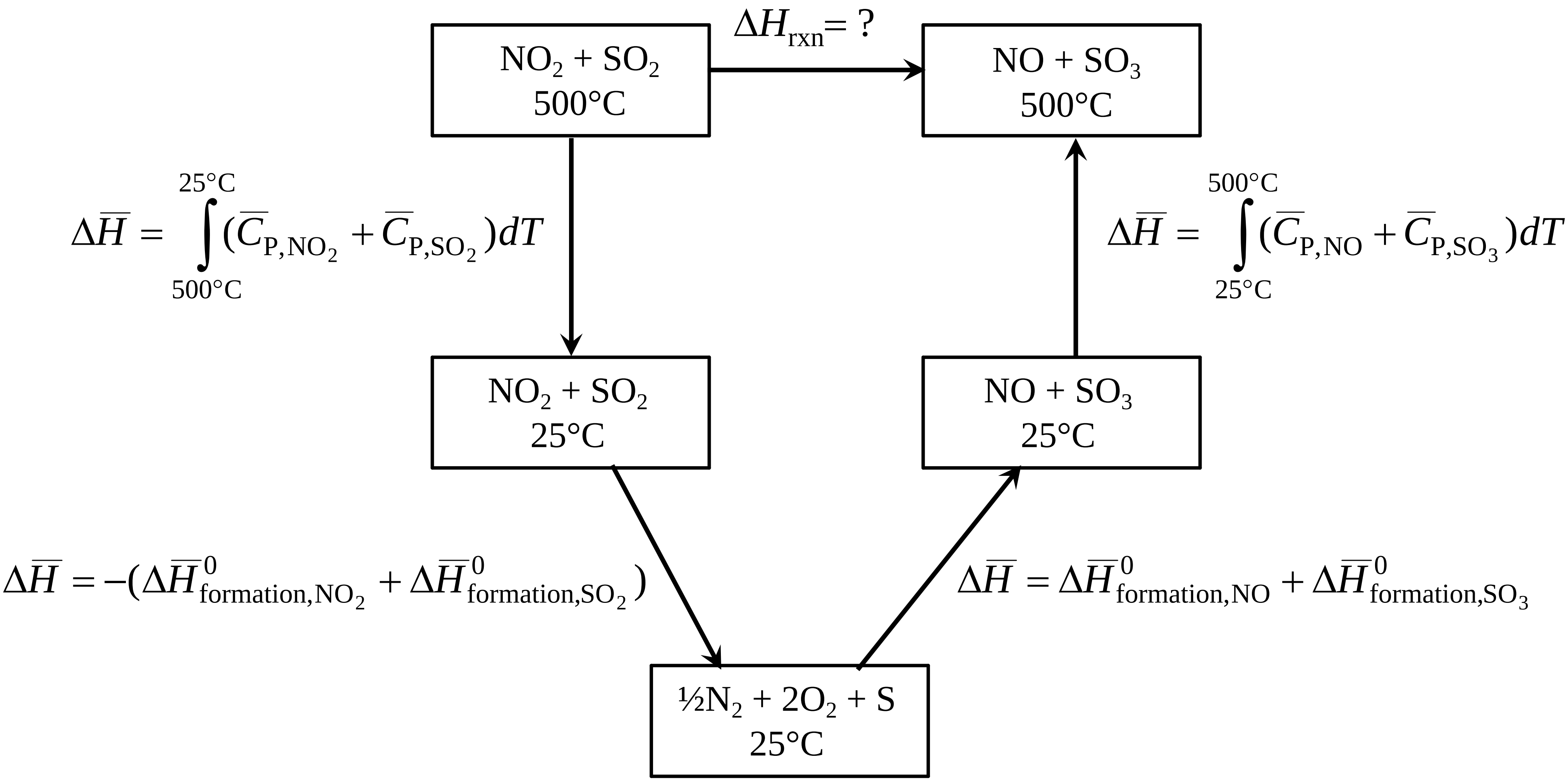
$$\text{sum:} \quad HC{\equiv}CH + H_2 \rightarrow CH_2{=}CH_2 \qquad \boxed{\Delta\overline{H}^0_{rxn} = 52 - 227 = -175 \text{ kJ/mol}}$$

same result.

see *Heats of Formation*, Table 19.2, p. 795 of McQuarrie & Simon.

# Calculating the Enthalpy Change of Chemical Reaction

## Reactions at temperatures other than 25°C



$\Delta H_{rxn} = ?$

$NO_2 + SO_2$
500°C

$NO + SO_3$
500°C

$$\Delta \overline{H} = \int_{500°C}^{25°C} (\overline{C}_{P,NO_2} + \overline{C}_{P,SO_2})\,dT$$

$$\Delta \overline{H} = \int_{25°C}^{500°C} (\overline{C}_{P,NO} + \overline{C}_{P,SO_3})\,dT$$

$NO_2 + SO_2$
25°C

$NO + SO_3$
25°C

$$\Delta \overline{H} = -(\Delta \overline{H}^0_{\text{formation},NO_2} + \Delta \overline{H}^0_{\text{formation},SO_2})$$

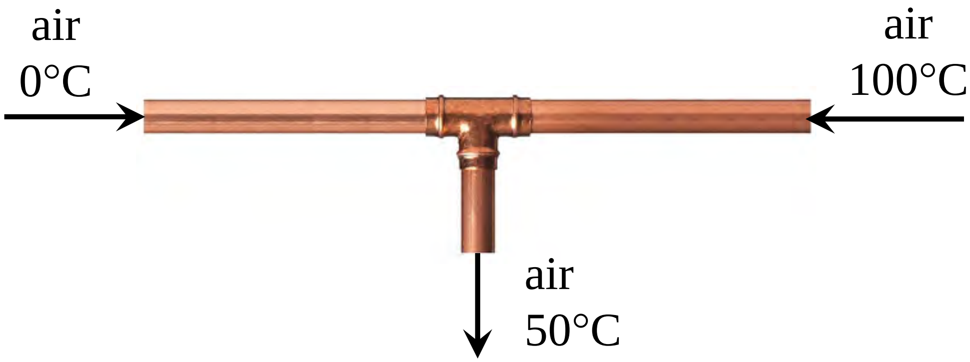
$$\Delta \overline{H} = \Delta \overline{H}^0_{\text{formation},NO} + \Delta \overline{H}^0_{\text{formation},SO_3}$$

$\frac{1}{2}N_2 + 2O_2 + S$
25°C

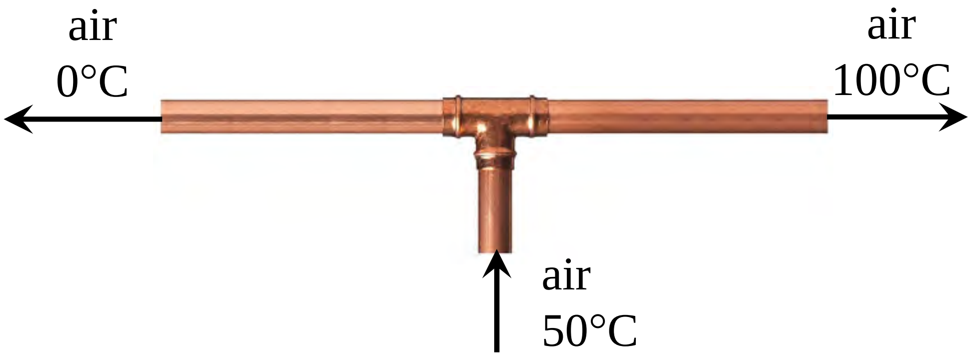
# Spontaneous Processes

McQuarrie & Simon demonstrate spontaneous processes with closed systems: ‘before’ and ‘after.’

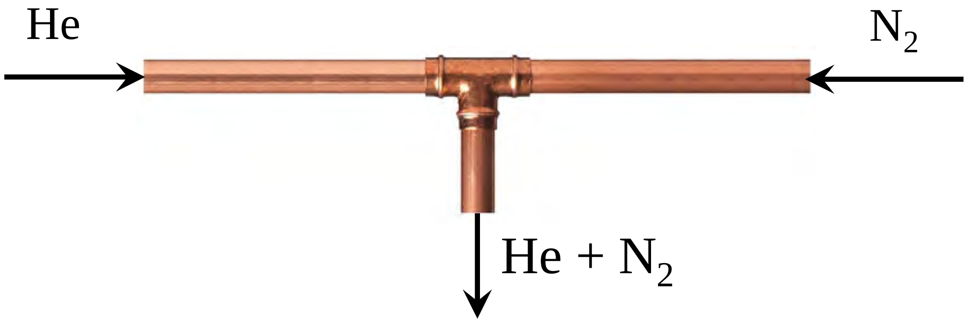
Consider here spontaneous processes with flow systems: ‘in’ and ‘out’



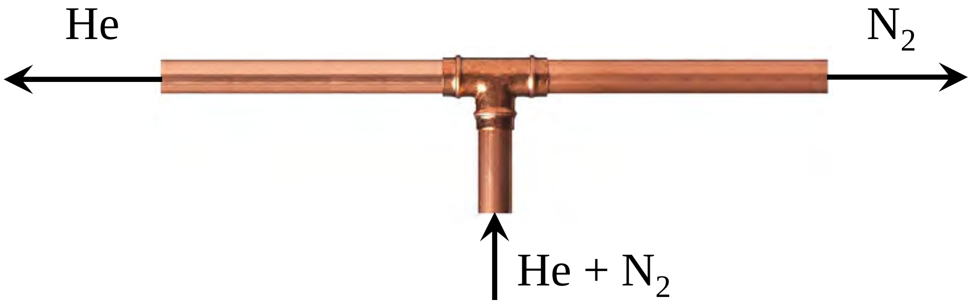
thermal mixing is spontaneous



thermal unmixing is not spontaneous



chemical mixing is spontaneous



chemical separation is not spontaneous

We need a *state function* to indicate which processes are spontaneous.

We expect systems tend to increasing disorder.  How to quantify disorder?

# Aside: State Functions

The *state* of a system is described by $n$, $P$, $V$, $T$, and chemical identity.

A *state function* depends only on the state of the system.

The integral of the *state function* from state 1 to state 2 depends only state 1 and state 2 and not the path from state 1 to state 2.

Consider a quantity $h$ that is a function of two independent variables, $x$ and $y$.

That is, $h = h(x,y)$.

The differential $dh = f(x,y)dx + g(x,y)dy$ is an *exact* differential if

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

Note that $dh = \left(\frac{\partial h}{\partial x}\right)_y dx + \left(\frac{\partial h}{\partial y}\right)_x dy$ is an exact differential

because Euler's theorem requires that $\frac{\partial}{\partial y}\left(\frac{\partial h}{\partial x}\right)_y = \frac{\partial}{\partial x}\left(\frac{\partial h}{\partial y}\right)_x$

*A state function can be expressed as an exact differential.*

# Spontaneous Processes

Classical thermodynamics is based on postulates.

But consider a rationalization of a new state function, which we later show to be *entropy*.

path functions

$$dU = \delta q_{\text{rev}} + \delta w_{\text{rev}}$$

important

$$\delta q_{\text{rev}} = dU - \delta w_{\text{rev}}$$

$P_{\text{external}} = P_{\text{gas}}$ for a reversible process

$$\delta q_{\text{rev}} = C_{\text{V}}dT + P_{\text{gas}}dV$$

Not an exact differential.

For $\delta q_{\text{rev}}$ to be an exact differential, it must be true that $\left(\frac{\partial C_{\text{V}}}{\partial V}\right)_T \overset{?}{=} \left(\frac{\partial P}{\partial T}\right)_V$

Test the relation for an ideal gas: $P = \left(\frac{nR}{V}\right)T \quad \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{nR}{V}\right)T = \frac{nR}{V}$

Euler's Relation

$$\left(\frac{\partial C_{\text{V}}}{\partial V}\right)_T = \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[\left(\frac{\partial U}{\partial V}\right)_T\right]_V = \frac{\partial}{\partial T}(0) = 0$$

Thus $\left(\frac{\partial C_{\text{V}}}{\partial V}\right)_T \neq \left(\frac{\partial P}{\partial T}\right)_V$ $\qquad$ $q$ is not a state function.

# A New State Function

$$\delta q_{\text{rev}} = dU - \delta w_{\text{rev}}$$

The differential can be rendered exact by dividing by *T*. $\frac{1}{T}$ is an integrating factor

$$\frac{\delta q_{\text{rev}}}{T} = \frac{dU}{T} - \frac{\delta w_{\text{rev}}}{T}$$

$$\boxed{\frac{\delta q_{\text{rev}}}{T} = \frac{C_{\text{V}}}{T} dT + \frac{P_{\text{gas}}}{T} dV}$$

$$\left( \frac{\partial (P_{\text{gas}}/T)}{\partial T} \right)_V = \frac{\partial}{\partial T} \left( \frac{nR}{V} \right) = 0 \qquad \left( \frac{\partial (C_{\text{V}}/T)}{\partial V} \right)_T = \frac{1}{T} \left( \frac{\partial C_{\text{V}}}{\partial V} \right)_T = \frac{1}{T}(0) = 0$$

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

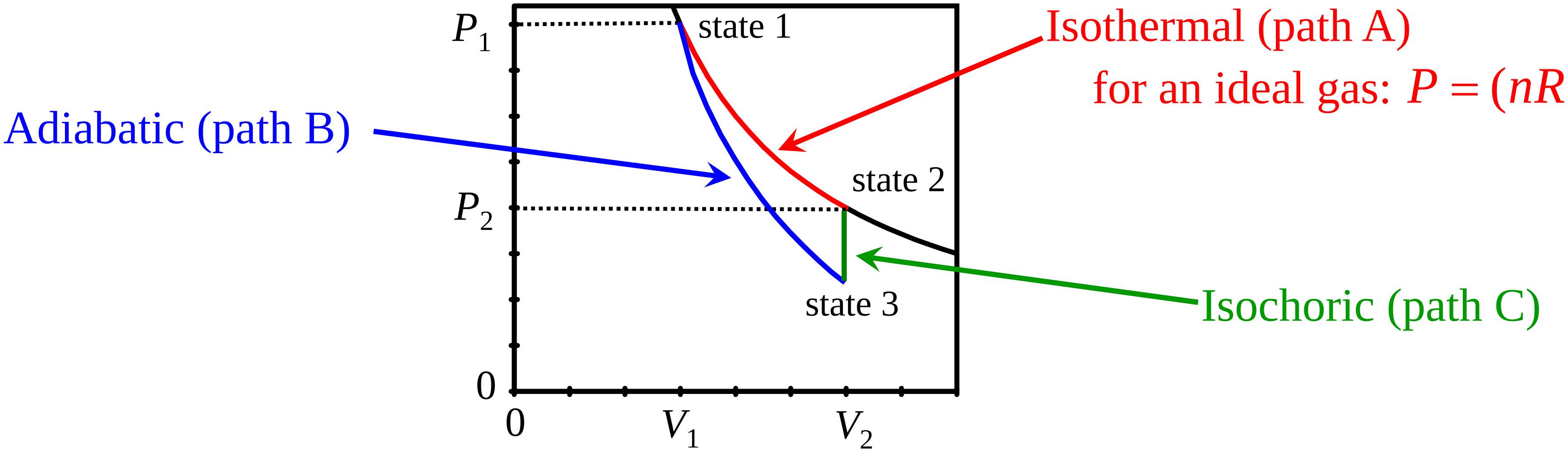
An exact differential!

$$\boxed{\text{Define } \frac{\delta q_{\text{rev}}}{T} \equiv S}$$

Entropy, a state function

# Calculating Entropy Changes – Isothermal Expansion

Recall previous reversible paths:



for an ideal gas: $P = (nRT)\dfrac{1}{V}$

Path A: $\Delta T = 0$ so $\Delta U = 0$ for an ideal gas. $\delta q_{\text{rev}} = -\delta w_{\text{rev}} = P_{\text{gas}} dV = \dfrac{nRT_1}{V} dV$

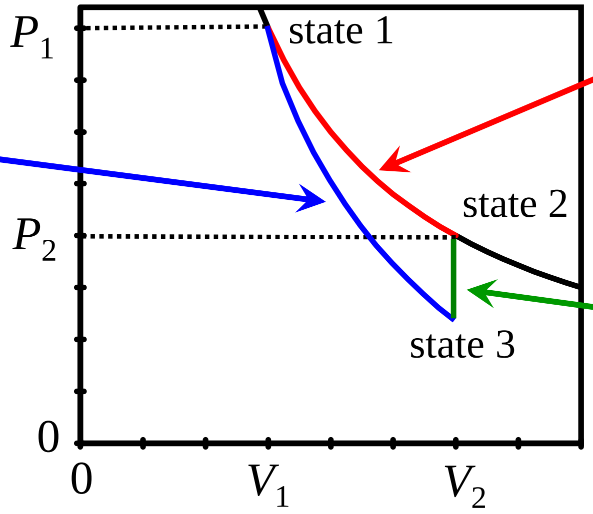
Integrate from state 1 to state 2: $q_{\text{rev}} = -w_{\text{rev}} = nRT_1 \ln \dfrac{V_2}{V_1}$

$$\Delta S_{\text{path A}} = \int_1^2 \frac{\delta q_{\text{rev}}}{T_1} = \int_{V_1}^{V_2} \frac{1}{T_1} \frac{nRT_1}{V} dV = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \frac{V_2}{V_1}$$

$$\boxed{\Delta S = nR \ln \frac{V_2}{V_1} \quad \text{for reversible, isothermal expansion of an ideal gas}}$$

$$V_2 > V_1 \Rightarrow \Delta S_{\text{path A}} > 0$$

# Calculating Entropy Changes – Adiabatic Expansion, Isochoric Heating



Adiabatic (path B)

Isothermal (path A)

for an ideal gas: $P = (nRT)\dfrac{1}{V}$

Isochoric (path C)

Paths B + C: $\boxed{q_{\text{rev, B}} = 0 \ \text{(adiabatic)}}$ $\quad w_{\text{rev, C}} = 0 \ (\Delta V = 0) \quad w_{\text{rev, B}} = -q_{\text{rev, C}} = -\int_{T_3}^{T_1} C_{\text{V}}\, dT$

$$\boxed{\Delta S_{\text{path B}} = 0 \ \text{ for reversible, adiabatic expansion of an ideal gas}}$$

$$\Delta S_{\text{path C}} = \int_3^2 \frac{\delta q_{\text{rev}}}{T} = \int_{T_3}^{T_1} \frac{C_{\text{V}}}{T} dT$$

How to evaluate? Use $\Delta U$ to derive a relation.

$$\Delta U_{\text{path A}} = \Delta U_{\text{path B}} + \Delta U_{\text{path C}} = 0$$

$$\Delta U_{\text{path B}} = -\Delta U_{\text{path C}}$$

$$-P dV = -C_{\text{V}} dT$$

$$\frac{nRT}{V} dV = C_{\text{V}} dT$$

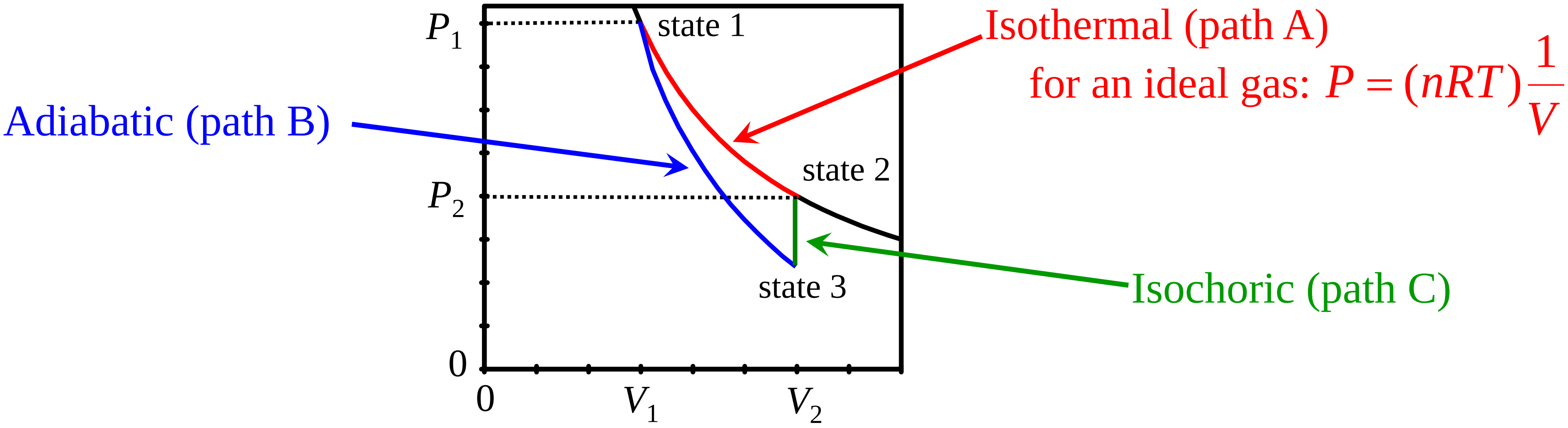
separate ‘n’ integrate

$$\int_{V_1}^{V_2} \frac{nR}{V} dV = \int_{T_3}^{T_1} \frac{C_{\text{V}}}{T} dT$$

$$\therefore \ \Delta S_{\text{path C}} = \int_{V_1}^{V_2} \frac{nR}{V} dV = nR \ln \frac{V_2}{V_1}$$

$$\boxed{\Delta S = nR \ln \frac{V_2}{V_1} \ \text{ for reversible, isochoric heating of an ideal gas}}$$

# Calculating Entropy Changes – Isochoric Heating



Adiabatic (path B)

Isothermal (path A)

for an ideal gas: $P = (nRT)\dfrac{1}{V}$

Isochoric (path C)

$$\boxed{\Delta S \;=\; nR\ln\frac{V_2}{V_1} \quad \text{for reversible, isochoric heating of an ideal gas}}$$

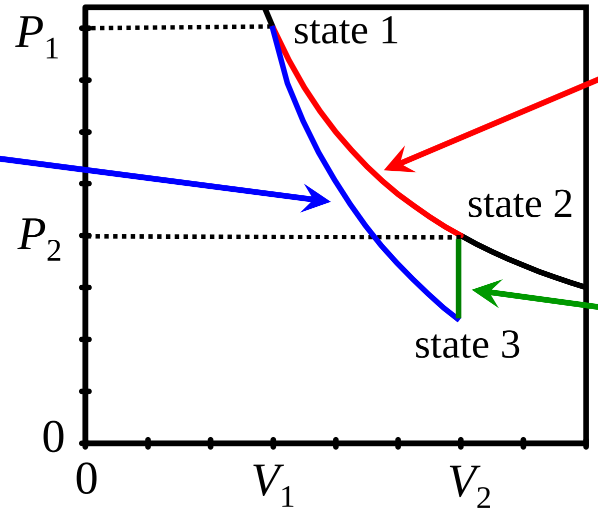
But an isochoric process is at constant volume. In this case, a path at volume $V_2$.

So what is $V_1$ for an isochoric process at $V_2$ ?

$V_1$ is the volume at the intersection
of an isothermal path from state 2
and an adiabatic path from state 3.

If your task is to calculate the entropy change for an isochoric path,
you must find $V_1$ at the intersection of an isothermal path from state 2
and an adiabatic path from state 3.

# Calculating Entropy Changes – Adiabatic Expansion, Isochoric Heating



Adiabatic (path B)

Isothermal (path A)

for an ideal gas: $P = (nRT)\dfrac{1}{V}$

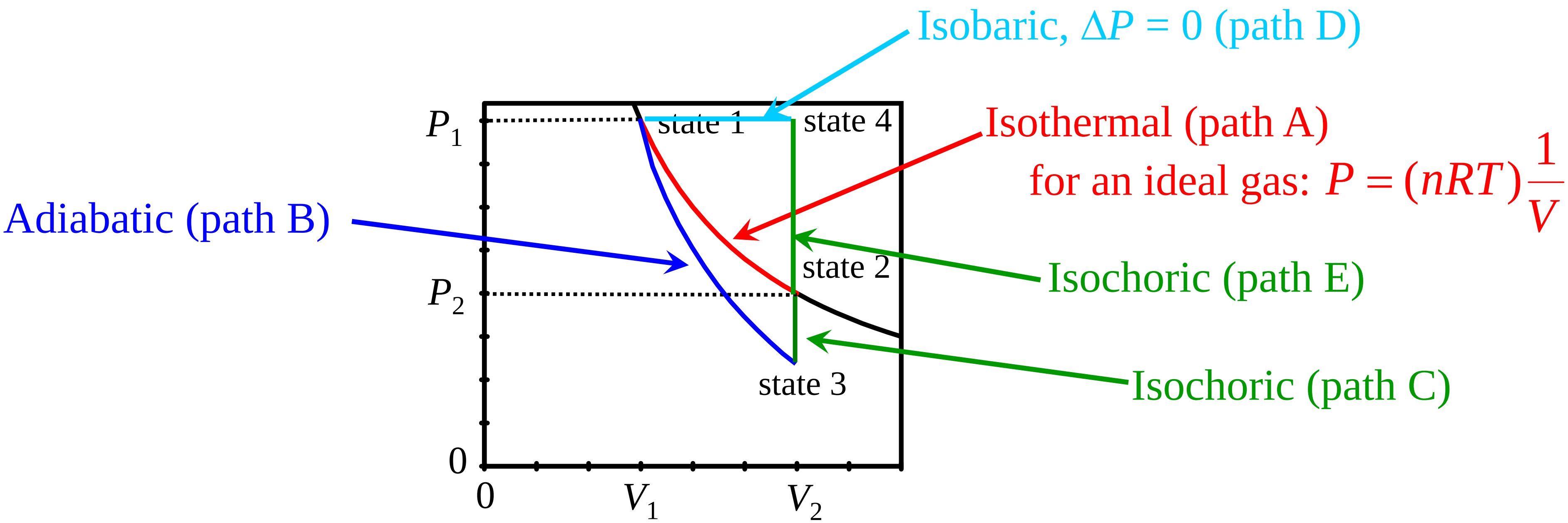
Isochoric (path C)

$$\Delta S_{\text{paths B+C}} = 0 + nR\ln\frac{V_2}{V_1} = nR\ln\frac{V_2}{V_1}$$

$$\Delta S_{\text{path A}} = nR\ln\frac{V_2}{V_1}$$

Change in entropy is independent of path.
Entropy is a state function.

# Calculating Entropy Changes – Isobaric Expansion, Isochoric Cooling



Isobaric, $\Delta P = 0$ (path D)

Isothermal (path A)

for an ideal gas: $P = (nRT)\dfrac{1}{V}$

Adiabatic (path B)

Isochoric (path E)

Isochoric (path C)

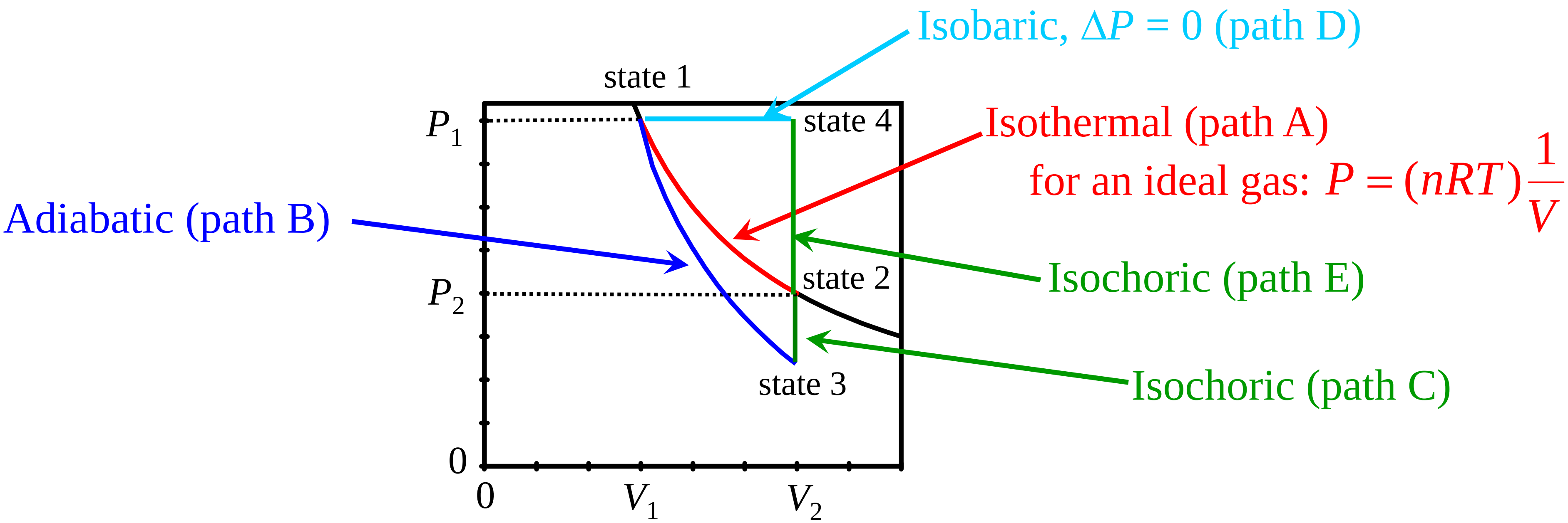
$$\text{Recall } \Delta U_{\text{path D}} = q_{\text{rev, D}} + w_{\text{rev, D}} = \left[\int_{T_1}^{T_4} C_V\,dT + P_1(V_4 - V_1)\right] - P_1(V_4 - V_1) = \int_{T_1}^{T_4} C_V\,dT$$

$$\Delta U_{\text{path E}} = q_{\text{rev, E}} + \cancelto{0}{w_{\text{rev, E}}} = \int_{T_4}^{T_1} C_V\,dT = -\int_{T_1}^{T_4} C_V\,dT \qquad \Delta U_{\text{paths D+E}} = 0$$

$$\Delta S_{\text{path D}} = \int_1^4 \frac{\delta q_{\text{rev, D}}}{T} = \int_{T_1}^{T_4} \frac{C_V}{T}\,dT + \int_{V_1}^{V_2} \frac{P_1}{T}\,dV = \int_{T_1}^{T_4} \frac{C_V}{T}\,dT + \int_{V_1}^{V_2} \cancel{P_1}\frac{nR}{\cancel{P_1}V}\,dV = \int_{T_1}^{T_4} \frac{C_V}{T}\,dT + nR\ln\frac{V_2}{V_1}$$

$$\Delta S_{\text{path E}} = \int_4^2 \frac{\delta q_{\text{rev, E}}}{T} = \int_{T_4}^{T_1} \frac{C_V}{T}\,dT = -\int_{T_1}^{T_4} \frac{C_V}{T}\,dT$$

# Calculating Entropy Changes – Isobaric Expansion, Isochoric Cooling



Isobaric, $\Delta P = 0$ (path D)

Isothermal (path A)

for an ideal gas: $P = (nRT)\frac{1}{V}$

Adiabatic (path B)

Isochoric (path E)

Isochoric (path C)

$$\Delta S_{\text{paths D + E}} = \cancel{\int_{T_1}^{T_4} \frac{C_V}{T}\,dT} + nR\ln\frac{V_2}{V_1} - \cancel{\int_{T_1}^{T_4} \frac{C_V}{T}\,dT} = nR\ln\frac{V_2}{V_1}$$

$$\Delta S_{\text{path A}} = nR\ln\frac{V_2}{V_1}$$

$$\Delta S_{\text{paths B + C}} = nR\ln\frac{V_2}{V_1}$$

Change in entropy is independent of path.
Entropy is a state function.