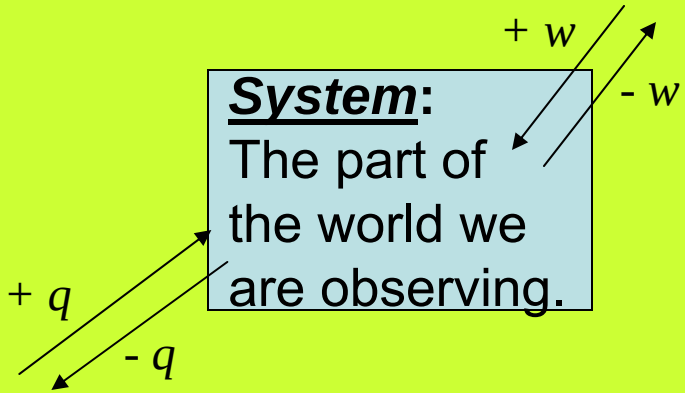
Work and Heat Definitions

Surroundings:
Everything outside system

Work, w: transfer of energy as a result of unbalanced forces



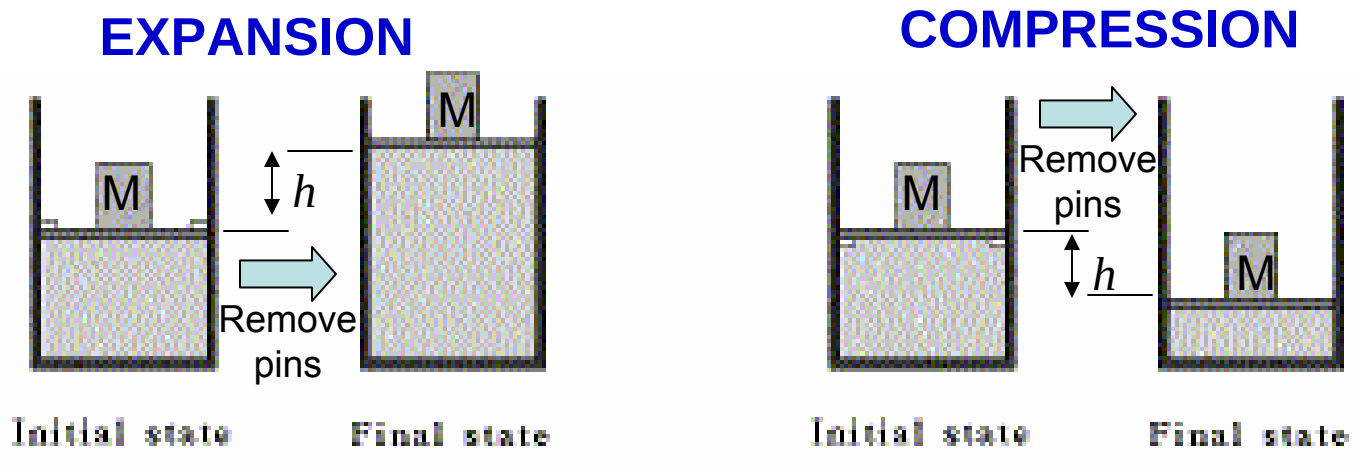
Heat, q: transfer of energy resulting from a temperature difference

Heat Sign convention:
Positive – heat is input to the system
Negative – heat is output from system

Work Sign convention:
Positive – work done on the system
Negative – work done by the system

Expansion and compression

Figure 19.1



Questions

1. What is system? Surroundings?
2. How does initial and final pressure correspond to P_{ext}?
3. What is sign of work for both cases?
4. Exactly how much work has been done?

$$w = -Mgh$$ force*distance

$$w = -\frac{Mg}{A}Ah$$ pressure*volume
(force/area)*(area*height)

$$w = -P_{ext}\Delta V$$

Sign of ΔV? w?

What if P_{ext} is **not** constant?

If P_{ext} is not constant during the expansion (or compression), the work is the integral over the path from V_i to V_f and we need to know how P_{ext} varies with V:

$$w = -\int_{V_i}^{V_f} P_{ext}\, dV$$

General expression. P_{ext} is a function of V.

Work is the area under P_{ext} vs V. . .

Consider an *isothermal compression at constant pressure*, P_{ext}

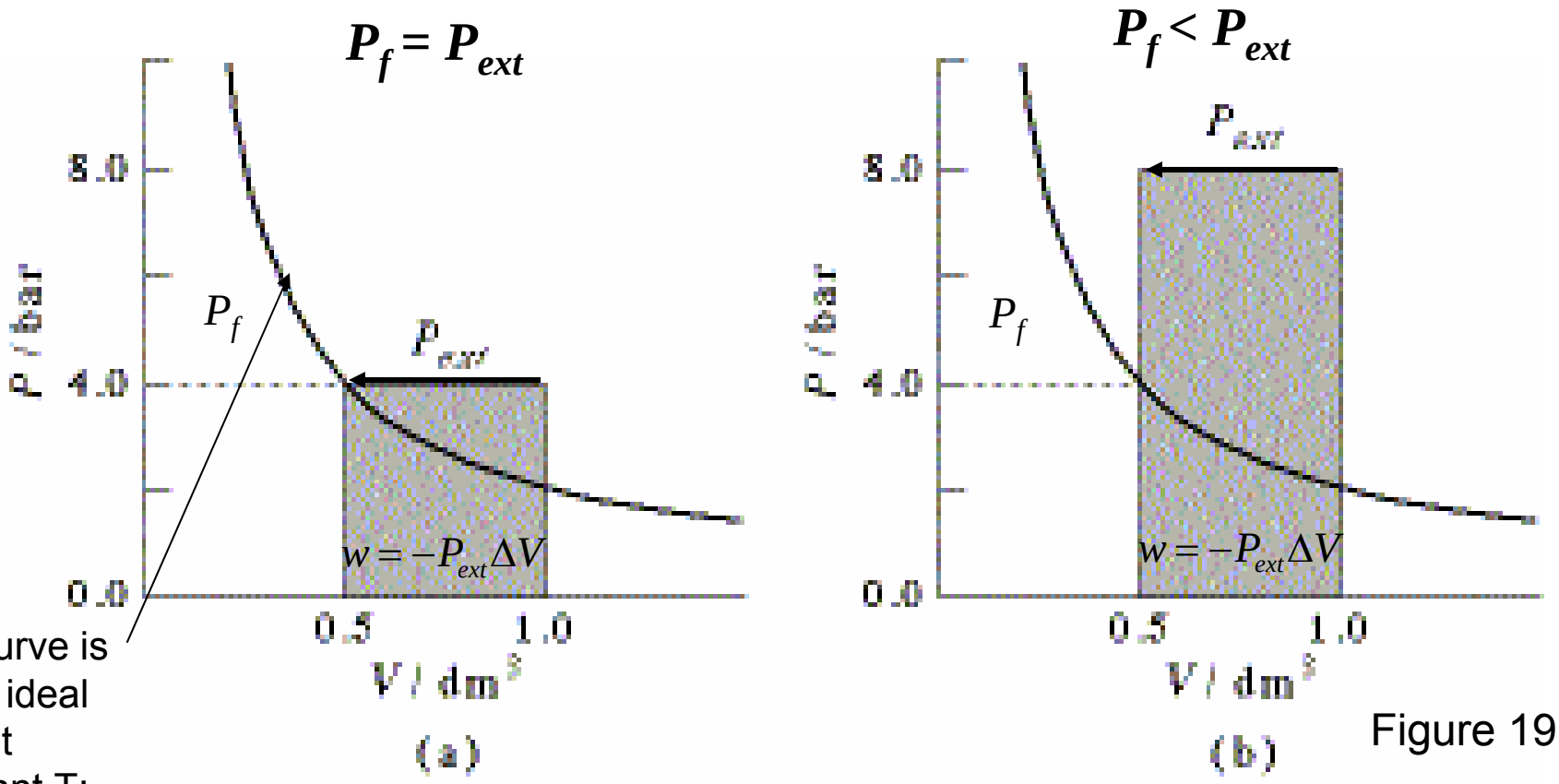


Figure 19.2

The curve is for an ideal gas, at constant T:

$$P = \frac{nRT}{V}$$

The work is equal to the shaded area: note how it depends on P_{ext}.

Reversible isothermal compression

Work depends on the path taken from V_1 to V_2. For compression, ***the absolute minimum work is done along the reversible path***.

Reversible path: At every infinitesimal step P_{ext} is made infinitesimally larger than P. At every step, P_{ext} is equal to the equilibrium gas pressure, $P_{gas} = \frac{nRT}{V}$.

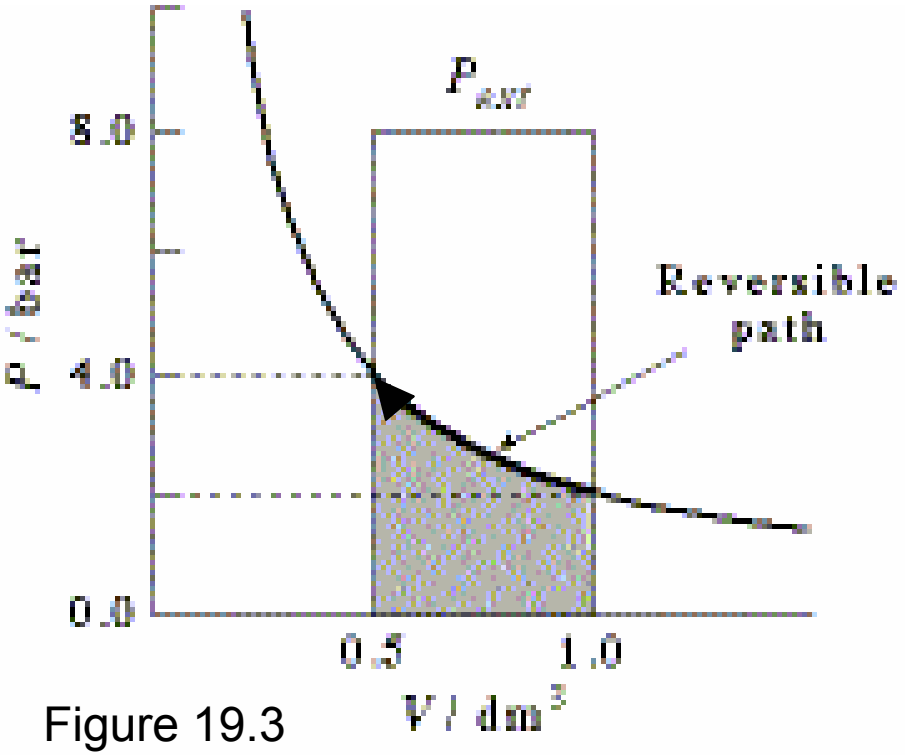


Figure 19.3

$$w_{rev} = -\int_{V_1}^{V_2} P_{gas}\, dV$$

$$w_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V}\, dV$$

$$w_{rev} = -nRT \ln \frac{V_2}{V_1}$$

Is work positive or negative?

Compression: $\ln \frac{V_2}{V_1} < 0$ w = +

Reversible isothermal expression

Work depends on the path taken from V_1 to V_2. For expansion, ***the absolute maximum work is done on surroundings along the <u>reversible</u> path***.

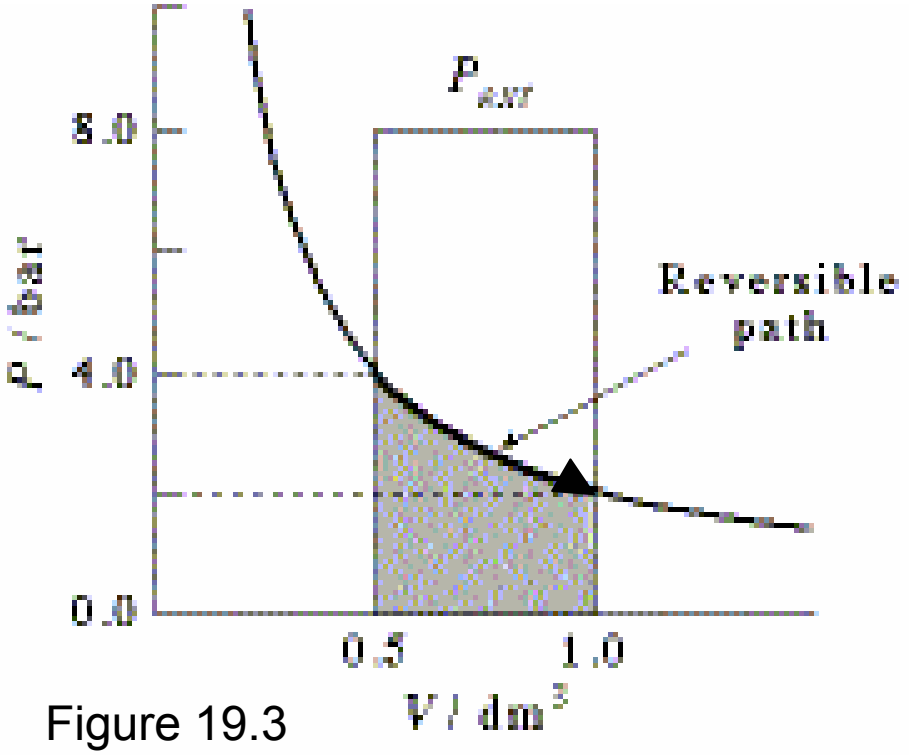


Figure 19.3

$$w_{rev} = -nRT \ln \frac{V_2}{V_1}$$

(Ideal gas)

Is work positive or negative?

Expansion: $\ln \frac{V_2}{V_1} > 0$ w = -

State Functions vs Path Functions

As we've seen, the work depends on the *path* taken between initial and final state. Work and heat are ***path functions***.

State functions don't depend on the path taken but only upon the state of the system. Energy, U or H, are state functions.

Why is this important???

(See Math Chapter H for more detail)

The differentials of *path* functions are inexact and *can't* be integrated normally!
The differentials of *state* functions are exact and *can* be integrated normally!

State functions

$$\int_1^2 dU = U_2 - U_1 = \Delta U$$

Path functions

$$\int_1^2 \delta w = w \qquad \text{(not } \Delta w \text{ or } w_2 - w_1\text{)}$$

$$\int_1^2 \delta q = q \qquad \text{(not } \Delta q \text{ or } q_2 - q_1\text{)}$$

The First Law

The First Law of Thermodynamics:

Energy is Conserved.

$$dU = \delta q + \delta w \qquad \text{Differential Form}$$

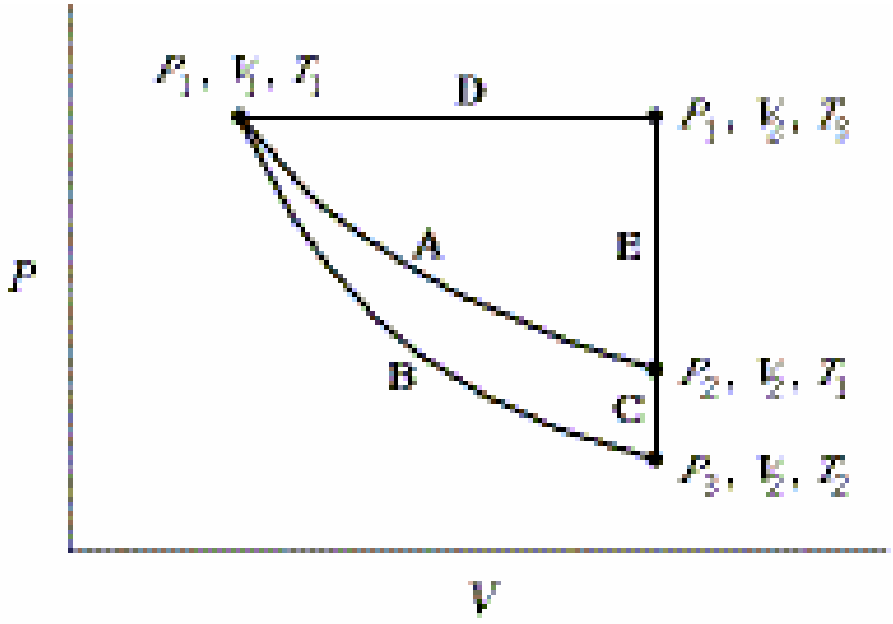
$$\Delta U = q + w \qquad \text{Integral Form}$$

Even though δq and δw are *path* functions (inexact differentials), their sum is a *state* function (exact differential).

Let's explore state vs. path more deeply!

3 reversible paths to the same place…

$$P_1, V_1, T_1 \rightarrow P_2, V_2, T_1$$



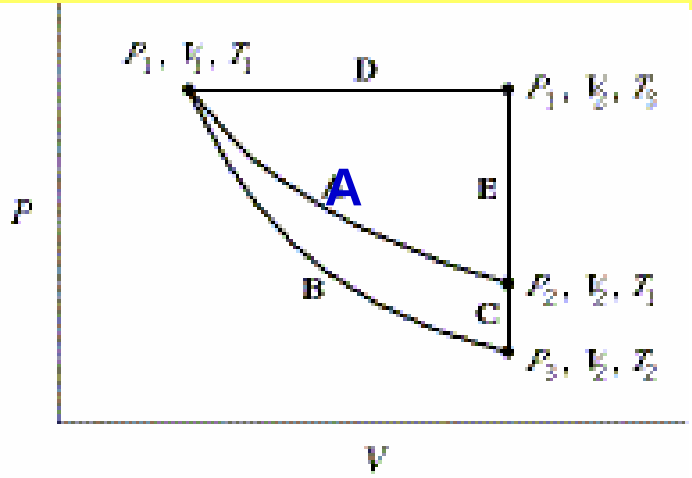
Path A: Reversible isothermal expansion

Path B+C: Reversible adiabatic expansion followed by heating at constant volume

Path D+E: Reversible constant-pressure expansion followed by cooling at constant volume

All three paths are reversible, but will they all involve the same work? ΔU?

Path A: Reversible Isothermal Expansion



$$P_1, V_1, T_1 \rightarrow P_2, V_2, T_1$$

The energy of an ideal gas depends only on the temperature…
Recall U = (3/2)RT

$$\boxed{dU_A = 0} \xrightarrow{dU = \delta q + \delta w} \boxed{\delta w_{rev,A} = -\delta q_{rev,A}}$$

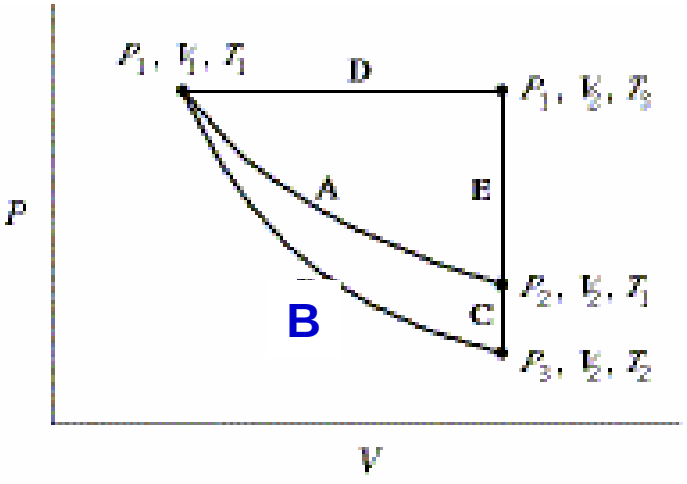
Since the process is reversible…

$$\delta w_{rev,A} = -P_{gas} dV = -\frac{nRT_1}{V} dV$$

$$w_{rev,A} = -nRT_1 \ln \frac{V_2}{V_1} \qquad q_{rev,A} = nRT_1 \ln \frac{V_2}{V_1}$$

Path B: Reversible Adiabatic Expansion

$P_1, V_1, T_1 \rightarrow P_3, V_2, T_2$



Adiabatic: No energy transferred as heat.

So … $q = 0$.

$$dU = \delta w$$

We can get w from dU…

Recall from BZ/PFIG slides: $C_V(T) = \left(\frac{\partial U}{\partial T}\right)_V$

Since ideal gas U depends only on T:

$$C_V(T) = \frac{dU}{dT} \quad \text{or} \quad dU = C_V(T)dT$$

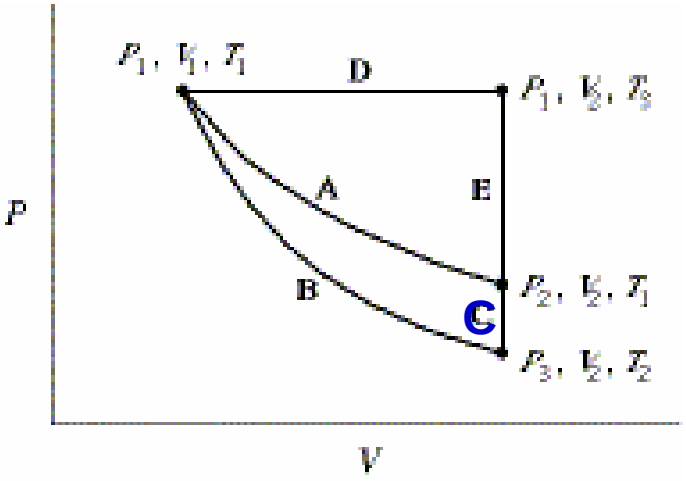
Put it all together…

$$w_{rev,B} = \Delta U_B = \int_{T_1}^{T_2} C_V(T)dT$$

From T_1 to T_2

Path C: Heat at Constant V

$$P_3, V_2, T_2 \rightarrow P_2, V_2, T_1$$



Constant volume = NO PV Work!!

$$\Delta U_C = q_{rev,C} + w_{rev,C} = q_{rev,C}$$

We need to find $q_{rev,C}$ and ΔU_C…

$$q_{rev,C} = \Delta U_C = \int_{T_2}^{T_1} C_V(T)dT$$

From T_2 to T_1

Path B + Path C…

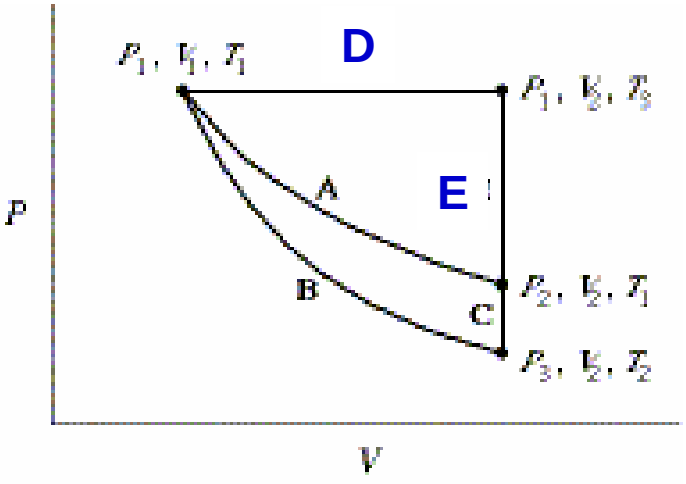
$$\Delta U_B + \Delta U_C = \int_{T_1}^{T_2} C_V(T)dT - \int_{T_1}^{T_2} C_V(T)dT = 0$$

$$w_{rev,B} + w_{rev,C} = \int_{T_1}^{T_2} C_V(T)dT$$

Paths D and E

Path D: Constant pressure expansion

$$P_1, V_1, T_1 \rightarrow P_1, V_2, T_3$$



$$\Delta U_D = \int_{T_1}^{T_3} C_V(T)dT$$

$$w_{rev,D} = -P_1(V_2 - V_1)$$

$$q_{rev,D} = \Delta U_D - w_{rev,D} = \int_{T_1}^{T_3} C_V(T)dT + P_1(V_2 - V_1)$$

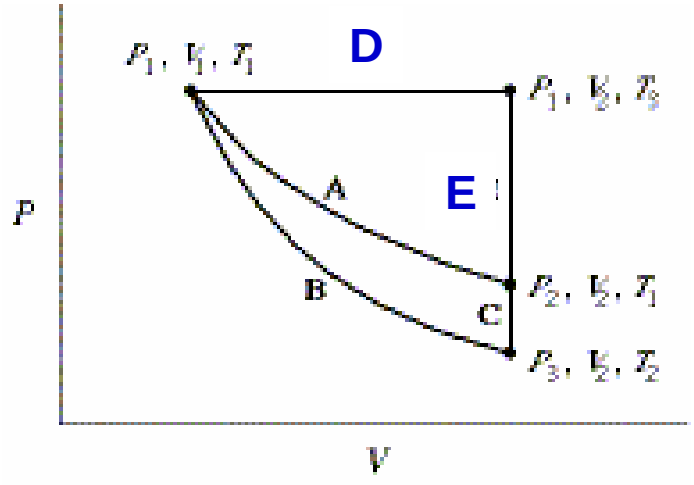
Path E: Cooling at constant V

$$P_1, V_2, T_3 \rightarrow P_2, V_2, T_1$$

$$\Delta U_E = \int_{T_3}^{T_1} C_V(T)dT \qquad w_{rev,E} = 0$$

$$q_{rev,E} = \Delta U_E - w_{rev,E} = \int_{T_3}^{T_1} C_V(T)dT$$

Path D + E



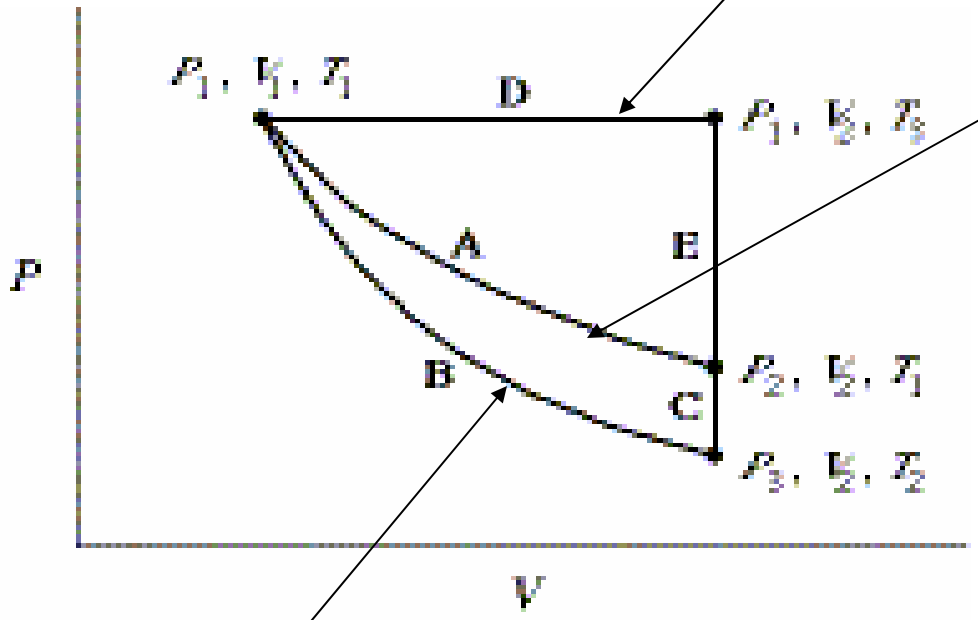
$$q_{rev,D+E} = q_{rev,D} + q_{rev,E} = P_1(V_2 - V_1)$$

$$w_{rev,D+E} = w_{rev,D} + w_{rev,E} = -P_1(V_2 - V_1)$$

$$\Delta U_{D+E} = q + w = 0$$

Summary… q, w, ΔU

$$w_{rev,D+E} = -P_1(V_2 - V_1) \quad q_{rev,D+E} = P_1(V_2 - V_1) \quad \Delta U_{rev,D+E} = 0$$



$$w_{rev,A} = -nRT_1 \ln \frac{V_2}{V_1}$$

$$q_{rev,A} = nRT_1 \ln \frac{V_2}{V_1}$$

$$\Delta U_A = 0$$

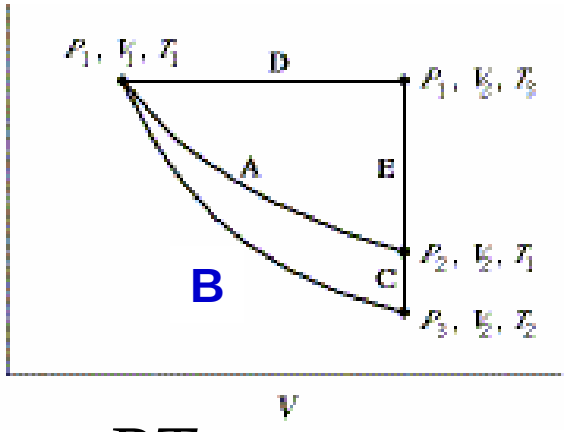
$$w_{rev,B+C} = \int_{T_1}^{T_2} C_V(T)dT \quad q_{rev,B+C} = \int_{T_2}^{T_1} C_V(T)dT \quad \Delta U_{rev,B+C} = 0$$

ΔU, state function, is same for all paths but q_{rev} and w_{rev}, path functions, differ based on path.

Adiabatic Expansion = COOL

Adiabatic so $q = 0$ and $dU = \delta w = dw$

(note that if either δq = 0 or δw = 0 then the remaining differential becomes exact)



For an ideal gas and reversible expansion:

$$dU = C_V(T)dT \qquad dw = -PdV = \frac{-nRT}{V}dV$$

Putting them together…

$$C_V(T)dT = -\frac{nRT}{V}dV \qquad \int_{T_1}^{T_2} \frac{\overline{C}_V}{T}dT = -R\int_{V_1}^{V_2} \frac{1}{V}dV$$

If we know how $\overline{C}_V$ depends on T, we can take both integrals.

For ideal monatomic gas, $\overline{C}_V = 3R/2$

Adiabatic vs. Isothermal Expansion

Adiabatic expansion (ideal monatomic gas):

$$\left(\frac{T_2}{T_1}\right)^{3/2} = \frac{V_1}{V_2} \xrightarrow{PV = nRT} \left(\frac{P_2V_2}{P_1V_1}\right)^{3/2} = \frac{V_1}{V_2}$$

$$\boxed{P_1V_1^{5/3} = P_2V_2^{5/3}}$$

Compare with Boyle's Law for *isothermal* processes:

$$P_1V_1 = P_2V_2$$

Thermochemistry: ΔH and ΔU

Recall: $\Delta H = q_p$, $\Delta U = q_V$, $H = U + PV$

$$\Delta H = \Delta U + P\Delta V + V\Delta P = \Delta U + P\Delta V$$

Melt ice at 0 °C and 1 atm given q_p = 6.01 kJ/mol…

$$\Delta\overline{H} = q_p = 6.01 \text{ kJ/mol}$$

Given the molar volumes, solid: $\overline{V}_s$ = 0.0196 L/mol

liquid: $\overline{V}_l$ = 0.0180 L/mol

Calculate $\Delta\overline{U}$ …

1 L·bar = 100 J
1 L·atm = 101.3 J

Thermochemistry: ΔH and ΔU

Consider vaporization (boiling) of water at 100 °C and 1 atm.

Given: q_p = 40.7 kJ/mol , $\overline{V}_l$ = 0.0180 L/mol , $\overline{V}_g$ = 30.6 L/mol

$$\Delta\overline{H} = q_p = 40.7 \text{ kJ/mol}$$

Calculate $\Delta\overline{U}$…

$$\Delta\overline{U} = \Delta\overline{H} - P\Delta\overline{V}$$

$\Delta\overline{U} = q_V$ the heat to overcome the intermolecular forces holding water together.

Thermochemistry (con't)

We will focus on H since most chemistry is done at constant P…

Consider the absorption and evolution of energy (heat) associated with chemical reactions.

$$\Delta_r H = H_{prod} - H_{react}$$

$q_p = \Delta_r H < 0$

*exo*thermic
(exo = out)

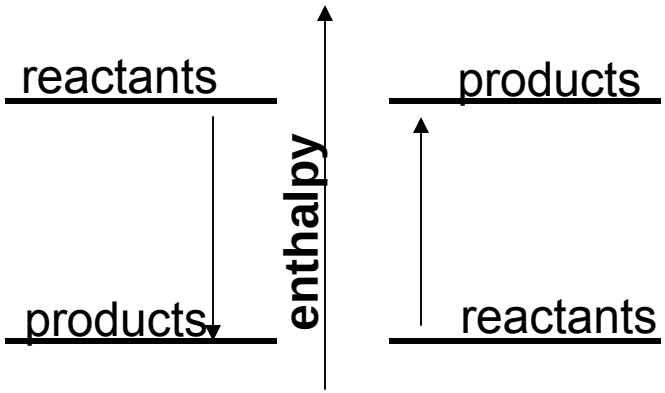


Figure 19.8

$q_p = \Delta_r H > 0$

*endo*thermic
(endo = in)

Release of energy as heat. Heat is one of the products.

Absorb energy as heat. Heat must be supplied to drive the reaction.

Recall demos from last week?!

Subscripts

We, in class and text, adopt the following conventions:

Reaction	Subscript
Vaporization, evaporation	vap
Sublimation	sub
Melting, fusion	fus
Transition between phases	trs
Mixing of fluids	mix
Adsorption	ad
Combustion	c
Formation	f
General reaction	r

Table 19.1

ΔH is additive: Hess's Law

ΔH is a state function, and this means it is an additive property…

If we know (1) and (2),

(1) $C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta_r H(1) = -110.5 \text{ kJ}$

(2) $CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta_r H(2) = -283.0 \text{ kJ}$

We can add them to find (3)…

(3) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

Setup for EX-FL 3 and 4

EX-FL3

Given: $2P_{(s)} + 3Cl_{2(g)} \rightarrow 2PCl_{3(l)} \qquad \Delta_r H = -640 \text{ kJ}$

$2P_{(s)} + 5Cl_{2(g)} \rightarrow 2PCl_{5(s)} \qquad \Delta_r H = -887 \text{ kJ}$

Find:

$PCl_{3(l)} + Cl_{2(g)} \rightarrow PCl_{5(s)} \qquad \Delta_r H =$

EX-FL4

Given: $2Fe_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow Fe_2O_{3(s)} \qquad \Delta_r H = -206 \text{ kJ}$

$3Fe_{(s)} + 2O_{2(g)} \rightarrow Fe_3O_{4(s)} \qquad \Delta_r H = -136 \text{ kJ}$

Find:

$4Fe_2O_{3(s)} + Fe_{(s)} \rightarrow 3Fe_3O_{4(s)} \qquad \Delta_r H =$

The standard reaction enthaply

$\Delta_r H$ is *extensive*: it depends on the number of moles of reactants

To facilitate the tabulation of reaction enthalpies IUPAC has proposed use of the *standard reaction enthaply* (intensive)

$\Delta_r H^\circ$

Defined as: ***one mole of reagent and all reactants and products in their standard states***
(for a gas this is one bar at the temperature of interest)

For example: $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta_r H^\circ = -393.5\ \text{kJ·mol}^{-1}$
(one mole of C is combusted) (Intensive)

Use to get: $2C_{(s)} + 2O_{2(g)} \rightarrow 2CO_{2(g)}$

Standard molar enthalpy of formation

The enthalpy of formation of one mole from the constituent elements is the ***standard molar enthalpy of formation*** (intensive)

$$\Delta_f H^\circ$$

this means all reactants and products in their standard states

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)} \qquad \Delta_f H^\circ = -285.8 \text{ kJ·mol}^{-1} \text{ at } 298.15 \text{ K}$$

Standard states at 1 bar and 298.15 K

One mole of $H_2O_{(l)}$ is 285.8 kJ downhill in enthalpy from the constituent elements

$\Delta_f H^\circ$ for elements – a big zero

To tabulate values for $\Delta_f H^\circ$ the values of $\Delta_f H^\circ$ ***for each pure element in its stable form at one bar and the temperature of interest is set to*** **zero**.

At 25 °C:

$H_{2\,(g)}$	$\Delta_f H^\circ = 0 \ \text{kJ·mol}^{-1}$
$O_{2\,(g)}$	$\Delta_f H^\circ = 0 \ \text{kJ·mol}^{-1}$
$Cl_{2\,(g)}$	$\Delta_f H^\circ = 0 \ \text{kJ·mol}^{-1}$
$Br_{2\,(g)}$	$\Delta_f H^\circ = 30.907 \ \text{kJ·mol}^{-1}$
$I_{2\,(g)}$	$\Delta_f H^\circ = 62.438 \ \text{kJ·mol}^{-1}$
C(diamond)	$\Delta_f H^\circ = 1.897 \ \text{kJ·mol}^{-1}$

Why not zero?

See Table 19.2 for more…

Using $\Delta_f H^\circ$ to get $\Delta_r H$

$$aA + bB \rightarrow yY + zZ$$

$a\Delta_f H^\circ[A]$ $b\Delta_f H^\circ[B]$ $y\Delta_f H^\circ[Y]$ $z\Delta_f H^\circ[Z]$

moles per mole

$$\Delta_r H = \Delta_f H^\circ(products) - \Delta_f H^\circ(reacants)$$

$$\Delta_r H = \left(y\Delta_f H^\circ[Y] + z\Delta_f H^\circ[Z]\right) - \left(a\Delta_f H^\circ[A] + b\Delta_f H^\circ[B]\right)$$

Heat Capacity

Heat capacity is a ***path function***. For example, the amount of energy required to raise the temperature of a substance one degree is ***different if done at constant V or constant P***…

At constant V, the energy added as heat is q_V ($\Delta U = q_V$)

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \approx \frac{\Delta U}{\Delta T} = \frac{q_V}{\Delta T}$$

At constant P, the energy added as heat is q_P ($\Delta H = q_P$)

Which one do you expect to be larger, C_V or C_P? Why?

C_p and Temperature Dependence of ΔH

We can calculate the difference in enthalpy at two different temperatures from the heat capacity at those temperatures:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \xrightarrow{\text{Integrate}} H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_P(T)dT$$

Problem: Phase transitions!!!

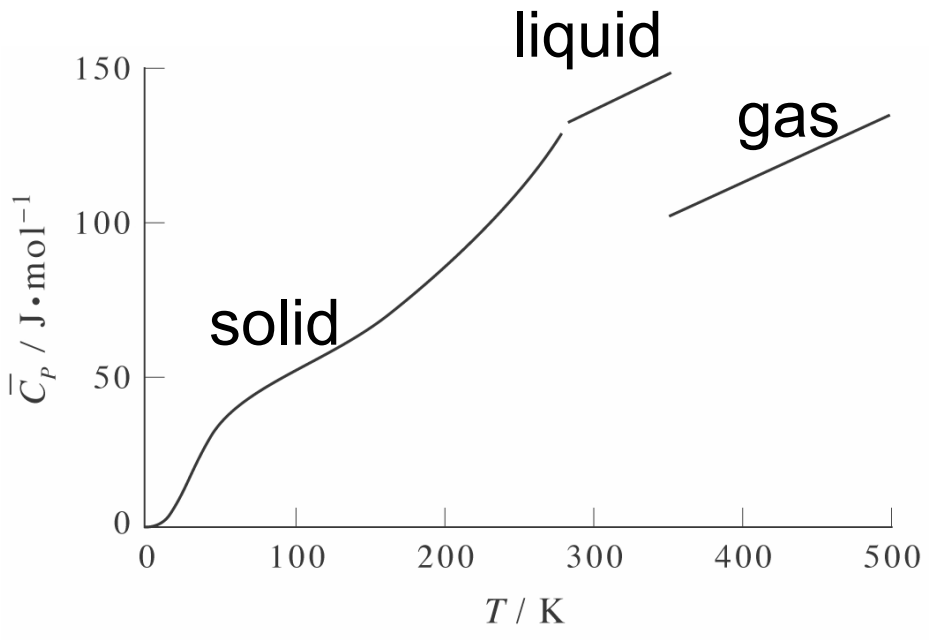
At phase transitions, $C_P \rightarrow \infty$. That is, there is no change in temp as you add heat. Thus, the enthalpy associated with the phase transition must be added in…

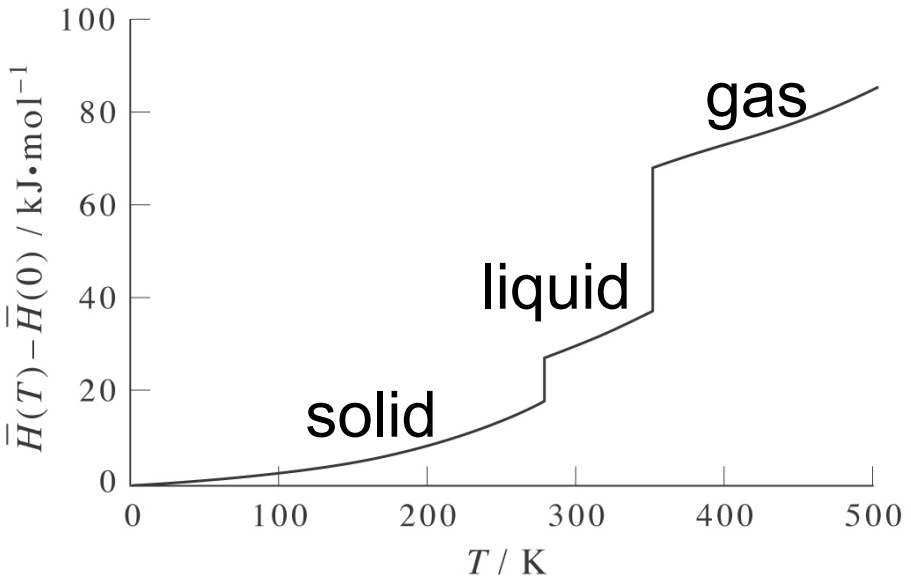
$$H(T) - H(0) = \int_0^{T_{fus}} C_P^s(T)dT + \Delta_{fus}H + \int_{T_{fus}}^{T} C_P^l(T)dT$$

Benzene

Benzene: T_{fus} = 278.7 K, T_{vap} = 353.2 K

Figs 19.5 and 19.6





For $T > T_{vap}$,

$\Delta_r H$ at different T

If you know $\Delta_r H$ at one temp, T_1, and want to know it at another, T_2, we can use the heat capacities:

Reactants $T_2 \xrightarrow[\textbf{Want to know}]{\Delta_r H(T_2)} T_2$ **Products**

$T_1 \xrightarrow[\textbf{Known: Path 1}]{\Delta_r H(T_1)} T_1$

Summary

- Energy is conserved. $dU = \delta q + \delta w$
- U and H are state functions. q, w, C_P and C_V are path functions.
- There are many ways to discuss PV work.
- Understanding the heat consumed or evolved can provide powerful insight into chemical reactions.
- We can use the fact that U and H are state functions to tabulate and calculate thermochemical values.

NEXT: Energy is not enough to predict the direction of a spontaneous process (reaction) – the world prefers disorder…