

Energy Tutorial Two : Thermodynamics

Answers

1. Words: 'energy is conserved' or 'The change in internal energy equals the sum of the work done on the system plus the heat transferred to the system!'

Equation: $\Delta U = W^{on} + Q^{in}$ or $\Delta U = -W^{by} + Q^{in}$
 or $dU = \delta W + \delta Q$ etc.

all system prop.

$$H = U + PV$$

(defn)

2. D \rightarrow (since enthalpy Σ a property of a system: $H = U + PV$)

3. False - eg internal energy includes chemical bond energy, etc, while thermal energy is just 'microscopic kinetic energy'

Example of when internal = thermal is the ideal gas

↳ molecules don't interact



Note:
Thermal energy is a property & is not Q , which is a transfer of energy

4. Closed: no mass transfer between system & environment. Allows energy transfer

Isolated: neither mass nor energy transfer



5.
$$Q = \frac{mc_p \Delta T}{= 2 \text{ kg} \times 0.98 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \times (6 \text{ K})}$$

$\Delta T(\text{K}) = \Delta T(\text{ }^{\circ}\text{C})$
since 273 'cancels'.
(But $T(\text{K}) \neq T(\text{ }^{\circ}\text{C})$!)

$\approx \boxed{11.8 \text{ kJ}}$

6.
$$Q = \frac{mc_p \Delta T}{= 1.6 \times 10^3 \cancel{\text{g}} \times 0.9 \frac{\text{J}}{\cancel{\text{g} \cdot \text{K}}} \times (13 \text{ K})}$$

$= 18720 \text{ J} \approx \boxed{18.7 \text{ kJ}}$

7.
$$Q = mc_p \Delta T \quad \text{or} \quad Q = C_p \Delta T ; \quad C_p = mc_p$$

$\Rightarrow C_p = \frac{Q}{\Delta T} = \frac{8.8 \times 10^3 \text{ J}}{50 \text{ }^{\circ}\text{C}} \approx \boxed{176 \text{ J}/{}^{\circ}\text{C}}$

$c_p = C_p/m = \frac{176 \text{ J}/{}^{\circ}\text{C}}{400} \approx \boxed{0.44 \text{ J/g. }^{\circ}\text{C}}$

8.
$$Q = L_f \cdot m = 23 \times \frac{10^5 \text{ J}}{10^3 \text{ g}} \times 50 \text{ g} \approx 1150 \text{ J} = \boxed{1.15 \text{ kJ}}$$

9.
$$Q = L_f \cdot m \Rightarrow L_f = Q/m = \frac{856 \times 10^3 \text{ J}}{2 \times 10^3 \text{ g}} \approx \boxed{428 \text{ J/g}}$$

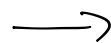
10.
$$W = P \cdot \Delta V \quad \text{at constant pressure.} \quad (W = \int_{V_i}^{V_f} P dV = P \Delta V \quad \text{if P const.})$$

& $1 \text{ Pa} = 1 \text{ N/m}^2$

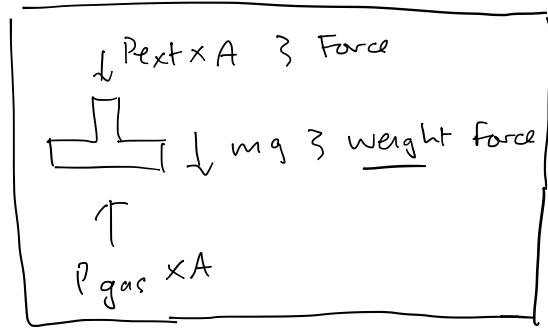
$1 \text{ L} = 1 \times 10^{-3} \text{ m}^3$

$\Rightarrow W = 101,325 \frac{\text{J}}{\text{m}^3} \times (70 - 42) \times 10^{-3} \text{ m}^3$

$\approx \boxed{2837 \text{ J}}$



11. Force balance
(assume equilibrium) :



$$P_{\text{ext}} \times A + mg = P_{\text{gas}} \times A$$

$$\Rightarrow P_{\text{gas}} = P_{\text{ext}} + \frac{mg}{A}$$

$$\left(\begin{array}{l} \text{units?} \\ \text{kg} \cdot \frac{\text{m}}{\text{s}^2} \cdot \frac{1}{\text{m}^2} = \text{kg} \cdot \frac{\text{m}^2}{\text{s}^2} \cdot \frac{1}{\text{m}^3} \\ = \text{J/m}^3 \end{array} \right)$$

$$= 101,325 \text{ J/m}^3 + 10 \text{ kg} \times 9.81 \text{ m/s}^2$$

$$0.7 \text{ m}^2$$

$$\approx 101,465 \text{ J/m}^3$$

Only a 'small' difference ($\sim 0.1\%$)
→ hence we usually neglect it.

12. $\boxed{\Delta U = W^{\text{on}} + Q^{\text{in}}}$ in general

adiabatic: $Q^{\text{in}} = 0$

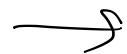
$$\Rightarrow \boxed{\Delta U = W^{\text{on}}} \text{ or } \boxed{\Delta U = -W^{\text{by}}} \leftarrow *$$

for adiabatic.

13. Mine: Entropy production is always non-negative (≥ 0)
(in any system)

Other: Entropy is always non-decreasing ($\Delta S \geq 0$ for isolated)
(total) in an isolated system.
carried, eg along with heat

(Note: $\Delta S = \underbrace{\text{entropy production}}_{\substack{\text{can be} \\ \text{-ve if} \\ \text{transport out} \\ \text{enough entropy!}}} + \underbrace{\text{entropy transport}}_{\substack{\geq 0 \text{ always!} \\ \text{can be +ve or -ve}}} \quad \bar{J}_S = Q/T$)



14. constant pressure. (+ work is PV work only)

(Why? Not examined, but:

$$\rightarrow \text{def: } H = U - (-PV) = U + PV \quad (1)$$

$$\rightarrow \begin{matrix} \text{1st law} \\ \text{with} \\ \text{PV work only} \end{matrix} \quad dU = \underbrace{-pdV}_{\text{work}} + SQ \quad (2)$$

$$(1): dH = dU + pdV + VdP \quad \underbrace{pdV}_{d(PV)} \text{ & chain rule}$$

$$(2): dU + pdV = SQ$$

$$\Rightarrow dH = SQ + VdP.$$

If $P = \text{constant}$, $dP = 0$

$$\Rightarrow dH = \underline{SQ} .$$

$$15. W_{\text{isothermal}}^{\text{by}} = nRT \ln \frac{V_f}{V_i} \quad \begin{matrix} \text{ratio is} \\ \text{dimensionless} \end{matrix}$$

$$= 1.9 \text{ mol} \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 300 \text{ K} \ln \left(\frac{67}{42} \right)$$

$$\approx 2213 \text{ J}$$

$$\approx \underline{|2.2 \text{ kJ}|}$$



16. $PV = nRT$ & $T = \text{constant} = 300K$

$$\Rightarrow P_i = \frac{nRT}{V_i}; P_f = \frac{nRT}{V_f}$$

$$V_i = 42L \times \frac{10^{-3}m^3}{1L} = 42 \times 10^{-3} m^3$$

$$V_f = 67 \times 10^{-3} m^3$$

$$\Rightarrow P_i \approx 112.8 \text{ kPa}$$

$$P_f \approx 70.7 \text{ kPa}$$

Note: pdV is work i.e. $W = \int pdV$
 PV is not!

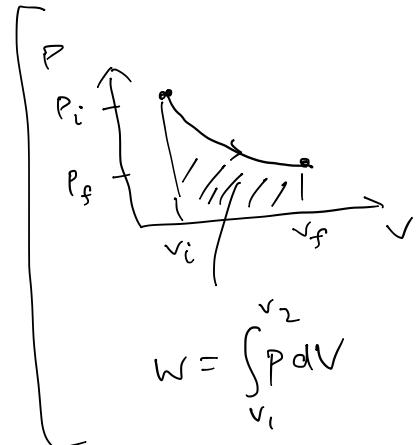
$$\rightarrow PV = nRT$$

relates
current state vars

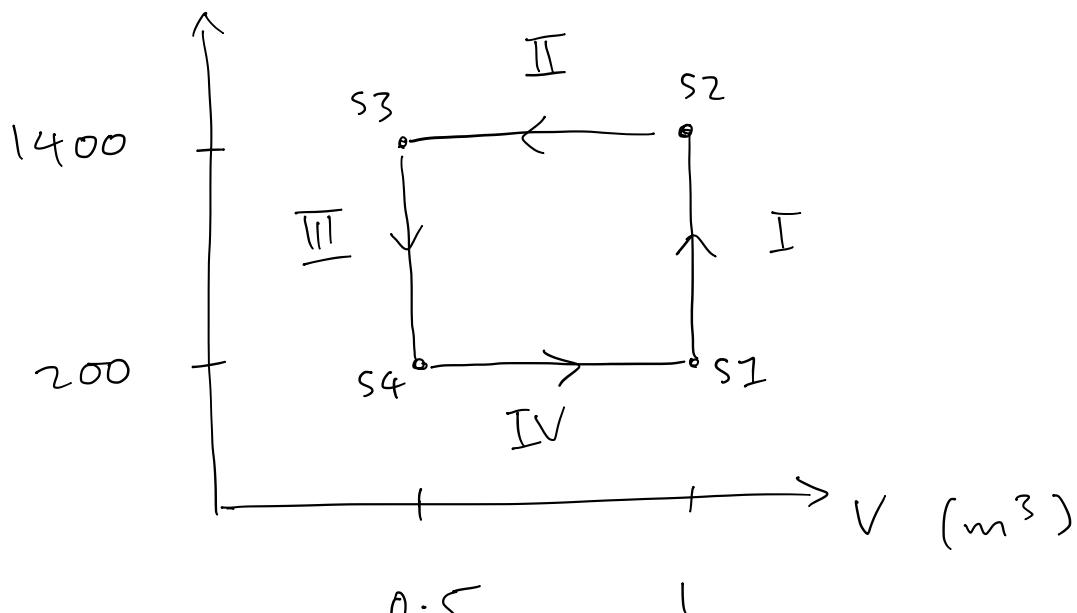
$$P_1 V_1 = nRT_1$$

$$P_2 V_2 = nRT_2$$

etc



17. A. $P(\text{kPa})$



17 cont'd

$$B. \quad W_{\text{by}}^{\text{Net}} = \underbrace{W^I + W^{\text{II}}}_{\text{isovolumetric}} + W^{\text{III}} + W^{\text{IV}} \quad (\text{W by})$$

$$\begin{aligned} W^{\text{II}} &= P_{\text{II}} \cdot (V_f - V_i) \\ &= 1400 \times 10^3 \frac{\text{J}}{\text{m}^3} \times (0.5 - 1) \text{ m}^3 \\ &= -700 \times 10^3 \text{ J} \\ &= -700 \text{ kJ} \end{aligned}$$

$$\begin{aligned} W^{\text{IV}} &= P_{\text{IV}} \cdot (V_f - V_i) \\ &= 200 \times 10^3 \times (1 - 0.5) \text{ J} \\ &= 100 \text{ kJ} \end{aligned}$$

$$W_{\text{by}}^{\text{Net}} = -600 \text{ kJ} \quad (\text{more done on than by})$$

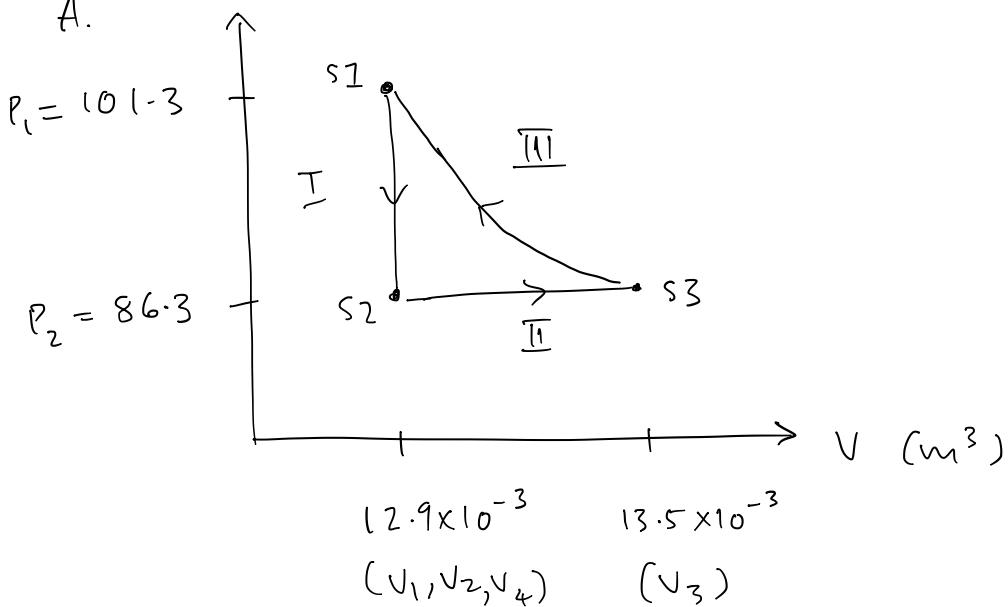
C. Lyde $\Rightarrow \underline{\Delta U = 0}$ (returns to same state).



$$18. \quad P(v_2 P_a)$$

$$13.5 L = 13.5 \times 10^{-3} m^3$$

A.



$$B. \quad W_{by}^{Net} = \cancel{W^I} + W^{II} + W^{III}$$

\downarrow isochoric.

$$\begin{aligned} W_{by}^{II} &= P_{II} \cdot (v_3 - v_2) \\ &= 86.3 \times 10^{-3} \times (13.5 - 12.9) \times 10^{-3} \text{ J} \\ &\approx 51.8 \text{ J} \end{aligned}$$

$$\begin{aligned} W_{by}^{III} &= \frac{P_i V_i - P_f V_f}{\gamma - 1}, \quad \gamma = 1.4 \\ &= \frac{P_3 V_3 - P_4 V_4}{0.4} = \frac{P_3 V_3 - P_1 V_1}{0.4} \\ &= \frac{86.3 \times 10^{-3} \times 13.5 \times 10^{-3} - 101.3 \times 10^{-3} \times 12.9 \times 10^{-3}}{0.4} \\ &\approx -354.3 \text{ J} \end{aligned}$$

$$\Rightarrow \underline{\underline{W_{by}^{Net}}} \approx -302.5 \text{ J} \quad \left(\begin{array}{l} \text{ie more done on} \\ \text{than by} \end{array} \right)$$

(-ve net work by).

19. Note: $Q = 0 \cancel{\leftarrow} \Delta T = 0$
 adiabatic \neq isothermal!

$$T_i = T_3 = 311\text{K}$$

$$T_f = T_4 = T_1 = 350\text{K} \quad (\text{since } P_4 \text{ & } V_4 \text{ same})$$

$$\Delta T = T_f - T_i = 39\text{K} \quad \text{as } P_1, V_1$$

$$\Rightarrow \Delta H = n c_p \Delta T$$

$$= 0.45 \text{ mol} \times \left(\frac{7}{2}\right) \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 39\text{K}$$

$$\approx 511 \text{ J}$$

20.
 A. Isothermal expansion

$$W^{\text{by}} = nRT \ln \left(\frac{V_f}{V_i} \right) \quad \left. \begin{array}{l} n = 1 \text{ mol} \\ R = 8.314 \text{ J/mol} \cdot \text{K} \\ T = 700\text{K}, V_f = 1.054 \times 10^{-2} \text{ m}^3 \\ V_i = 2.11 \times 10^{-3} \text{ m}^3 \end{array} \right\}$$

$$\Rightarrow W^{\text{by}} = \underline{\underline{|9362 \text{ J}|}}$$

B. Constant volume
 $\Rightarrow \underline{\underline{|W^{\text{by}} = 0|}}$ (no PV work for constant vol).



20 cont'd.

c. Constant pressure: $w^{by} = P_x (V_f - V_i)$

- $P = \underline{3.451 \times 10^5 \text{ J/m}^3}$

- $V_i = \underline{1.054 \times 10^{-2} \text{ m}^3}$ (final vol. after A & B - sequential)

- $V_f = \frac{n \times R \times T_f}{P_f} = \frac{1 \times 8.314 \times 350}{3.451 \times 10^5 \text{ J/m}^3} \text{ J} \approx \underline{8.433 \times 10^{-3} \text{ m}^3}$

$$\Rightarrow w^{by} = 3.451 \times 10^5 \times (8.433 \times 10^{-3} - 1.054 \times 10^{-2}) \text{ J}$$

$$\Rightarrow w^{by} \approx \boxed{-727.1 \text{ J}} \quad (V_f < V_i)$$

d. Adiabatic

$$w^{by} = \frac{P_i V_i - P_f V_f}{\gamma - 1}$$

$$P_i = 3.451 \times 10^5 \text{ J/m}^3 \quad] \quad V_i = \frac{n R T_i}{P_i} \approx 8.42 \times 10^{-3} \text{ m}^3$$

$$T_i = 350 \text{ K}$$

$$P_f = 2.758 \times 10^6 \text{ J/m}^3 \quad] \quad V_f = \frac{n R T_f}{P_f} \approx 1.91 \times 10^{-3} \text{ m}^3$$

$$T_f = 634 \text{ K}$$

$$\Rightarrow w^{by} = \frac{3.451 \times 10^5 \times 8.42 \times 10^{-3} - 2.758 \times 10^6 \times 1.91 \times 10^{-3}}{1.4 - 1}$$

$$\approx \boxed{-5905 \text{ J}} \quad (\text{note: } V_f < V_i \\ \Rightarrow \text{ve } w^{by}).$$

20 Cont'd

e). Heated at constant pressure.

$$W^{\text{by}} = P \cdot (V_f - V_i) \quad (\text{isobaric})$$

V_f, V_i ? Use $PV = nRT$ & $T_i = 634, T_f = 700\text{K}$

$$\Rightarrow V_f = \frac{nRT_f}{P} \rightarrow \left. \begin{array}{l} \\ \end{array} \right\} \text{Calc & plug into} \\ \& V_i = \frac{nRT_i}{P} \rightarrow \left. \begin{array}{l} \\ \end{array} \right\} P \cdot (V_f - V_i)$$



$$\begin{aligned} W^{\text{by}} &= P \cdot (V_f - V_i) = P \left(\frac{nRT_f}{P} - \frac{nRT_i}{P} \right) \\ &= nR(T_f - T_i) \\ &= 1 \times 8.314 \times (700 - 634) \\ &\approx \boxed{549 \text{ J}} \end{aligned}$$



21.

$$\text{A. } \gamma_{\max} = \frac{T_{\text{Hot}} - T_{\text{cold}}}{T_{\text{Hot}}}$$

$$= \frac{950 - 450}{950}$$

$$\approx \underline{53\%}$$

B. either $T_{\text{Hot}} \uparrow$ or $T_{\text{cold}} \downarrow \} \text{ expect.}$

Check:

$$\gamma_{\max}^{\text{Hot} \uparrow} = \frac{1025 - 450}{1025} \approx \underline{56\%}$$

$$\gamma_{\max}^{\text{cold} \downarrow} = \frac{950 - 375}{950} \approx \underline{61\%}$$

$$\Rightarrow \gamma_{\max}^{\text{new}} \approx \underline{61\%}$$

(by changing $T_{\text{cold}} \downarrow$)

22.

A. Thermal efficiency in general:

$$\frac{W_{\text{by}}^{\text{NET}}}{Q^{\text{in}}} = \frac{(580.8 - 357) \text{ J}}{383.5 \text{ J}}$$

$$\approx 0.58 \quad (\underline{58\%})$$

B. Real engine deviates from ideal cycle,
friction, heat loss to surroundings etc.

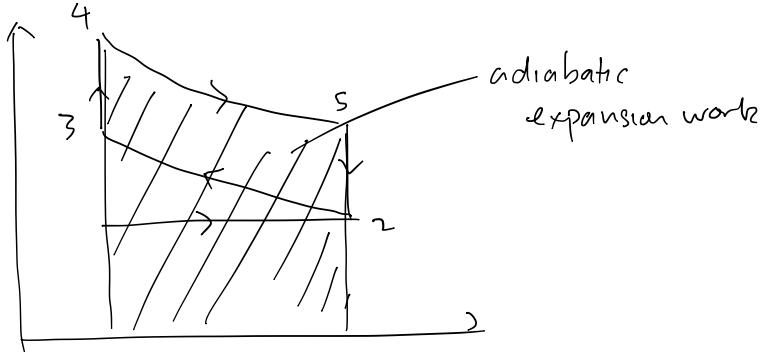
23.

A. On graph:

$1 \rightarrow 2$ intake

$3 \rightarrow 4$ combustion

B.



→ Not equal to net work

$\Rightarrow w^{\text{net}}$ accounts for $2 \rightarrow 3$,

i.e. Work of compression

(-ve work done by).

c) . $V_2 = \text{cylinder vol} = 0.8 \text{ L} = \boxed{8 \times 10^{-4} \text{ m}^3}$

$$V_3 = V_2/8 = \boxed{1 \times 10^{-4} \text{ m}^3}$$

$$V_4 = V_3 = \boxed{1 \times 10^{-4} \text{ m}^3}$$

$$V_5 = V_2 = \boxed{8 \times 10^{-4} \text{ m}^3}$$

$$n = \frac{P_2 V_2}{R T_2} \text{ (say)} = \frac{1.1 \times 10^5 \text{ Pa} \times 8 \times 10^{-4} \text{ m}^3}{8.314 \frac{\text{J}}{\text{mol.K}} \times 323 \text{ K}} \\ \approx \boxed{0.0328 \text{ mol}}$$

$$T_4 = \frac{P_4 V_4}{n R} = \frac{6.4 \times 10^6 \times 1 \times 10^{-4}}{0.0328 \times 8.314} \approx \boxed{2347 \text{ K}}$$

* $\left[\begin{array}{l} \text{NOTE: Table has error} \rightarrow T_3 \text{ should be } \frac{1486 \text{ K}}{\text{not } 742 \text{ K}} \end{array} \right]$ *

23 Cont'd

$$a) \quad W^{2 \rightarrow 3} = \frac{P_i V_i - P_f V_f}{\gamma - 1} = \frac{P_2 V_2 - P_3 V_3}{0.4}$$

$$= \frac{1.1 \times 10^5 \times 8 \times 10^{-4} - 4.04 \times 10^6 \times 1 \times 10^{-4}}{0.4}$$

$$\approx \underline{-790 \text{ J}} \quad (\text{compression})$$

$$W^{4 \rightarrow 5} = P_i V_i - P_f V_f = \frac{P_4 V_4 - P_5 V_5}{0.4}$$

$$= \frac{6.4 \times 10^6 \times 1 \times 10^{-4} - 1.74 \times 10^5 \times 8 \times 10^{-4}}{0.4}$$

$$\approx \underline{1252 \text{ J}} \quad (\text{expansion})$$

$$W^{\text{Net}} = W^{2 \rightarrow 3} + W^{4 \rightarrow 5}$$

$$= -790 + 1252 \text{ J}$$

$$\approx \underline{462 \text{ J}} \quad (\text{net})$$

$$e). \quad Q^{3 \rightarrow 4} = n C_V (T_4 - T_3)$$

$$= 0.0328 \times 20.78 \times (2347 - 1486) \quad]$$

$$\approx \underline{587 \text{ J}} \quad (+\text{ve in})$$

note again:
T₃ is 1486 K
not -42 K.

$$Q^{5 \rightarrow 2} = n C_V (T_2 - T_5)$$

$$= 0.0328 \times 20.78 \times (323 - 511)$$

$$\approx \underline{-128 \text{ J}} \quad (-\text{ve in H is out})$$

$$f). \quad \eta = \frac{W^{\text{net}}}{Q^{\text{in}}} = \frac{462 \text{ J}}{587 \text{ J}} \approx 0.79 \quad (79\%)$$

24.

A. Net = In - Out

$$\Rightarrow \text{net transport of entropy in.} = \frac{Q^{\text{in}}}{T^{\text{in}}} - \frac{Q^{\text{out}}}{T^{\text{out}}}$$

B. $\Delta S = 0$ for cycle (all state vars back to same value)

C. 2nd Law:

$$\Delta S \geq \text{Transported} \quad (\Delta S = \text{Transported} + \underbrace{\text{Produced}}_{\geq 0})$$

$$\Rightarrow 0 \geq \text{Transported}$$

i.e. $\frac{Q^{\text{in}}}{T^{\text{in}}} - \frac{Q^{\text{out}}}{T^{\text{out}}} \leq 0$ (using A).

$$\Rightarrow \frac{Q^{\text{in}}}{T^{\text{in}}} \leq \frac{Q^{\text{out}}}{T^{\text{out}}}$$

$$\frac{Q^{\text{in}}}{Q^{\text{out}}} \leq \frac{T^{\text{in}}}{T^{\text{out}}}$$

i.e. $\frac{Q^{\text{out}}}{Q^{\text{in}}} \geq \frac{T^{\text{out}}}{T^{\text{in}}}$

i.e. $1 - \frac{Q^{\text{out}}}{Q^{\text{in}}} \leq 1 - \frac{T^{\text{out}}}{T^{\text{in}}}$

i.e. $\eta \leq \eta_{\text{carnot}}$

□

25.

$$A. \Delta G^{\text{overall}} = \Delta G^{\text{products}} - \Delta G^{\text{reactants}}$$

$$B. \Delta G =$$

$$\left[4 \times \left(86.6 \frac{\text{kJ}}{\text{mol}} \right) + 6 \times \left(-228.6 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

-

$$\left[4 \times \left(-16.5 \frac{\text{kJ}}{\text{mol}} \right) + 5 \times 0 \right]$$

$$= -959.2 \text{ kJ/mol}$$

C. $\Delta G < 0 \Rightarrow$ exergonic, spontaneous

26. Heat absorbed by water

$$Q_w = C_w \cdot m \cdot \Delta T$$

$$= 4.184 \frac{\text{J}}{\text{g.deg.}} \times 1200 \text{ g} \times 16^\circ\text{C}$$

$$\approx 80,333 \text{ J} \quad (80.3 \text{ kJ})$$

— corrected

Heat absorbed calorimeter

$$Q_c = C_c \cdot \Delta T = 900 \frac{\text{J}}{\text{°C}} \times 16^\circ\text{C}$$

$$= 14,400 \text{ J} \quad (14.4 \text{ kJ})$$

Total absorbed

$$Q^{\text{tot}} = Q_w + Q_c \approx \underline{\underline{94.7 \text{ kJ}}}$$

→

26 cont'd.

$$\text{'heat of reaction'} = \Delta H = -Q^{\text{absorbed, tot.}} \\ = \underline{-94.7 \text{ kJ}}$$

(ie heat is released)

$$\frac{\Delta H}{\text{mol}} ? \Rightarrow \frac{-94.7 \text{ kJ}}{3 \text{ g}} \times \frac{25 \text{ g}}{\text{mol}} = \underline{-789 \text{ kJ/mol}}$$

- corrected

27. From table 4, pg. 98.

$$\text{Acetylene (g)} : -1300 \text{ kJ/mol} \times \frac{1 \text{ mol}}{26.04 \text{ g}}$$

$$\approx -50 \text{ kJ/g}$$

$$= -50 \text{ kJ} \times \frac{10^3 \text{ MJ}}{10^3 \text{ kJ}} \times \frac{10^3 \text{ g}}{\text{kg}}$$

$$= \underline{-50 \text{ MJ/kg}}$$

(cf Petrol : -46 MJ/kg)

Note: More negative \rightarrow more heat given off/
ie energy available

\Rightarrow Acetylene has 'greater' energy density
than petrol

i.e.

$$|\Delta H_c|_{\text{acetylene}} > |\Delta H|_{\text{petrol}}$$