

HW #3 Solutions

1.41 a) ~~NEGLECTING ANY MINOR CHANGES DUE~~
~~TO EXPANSION / CONTRACTION OF THE~~
WATER / METAL, THE ENERGY TRANSFER
IS ENTIRELY DUE TO HEAT.

SINCE IT TAKES 4.2 J TO RAISE
WATER 1°C, IT TAKES ABOUT 4 kJ
TO RAISE 250 g OF WATER 4°C

b) SINCE WE PRESUME THERE IS NO ENERGY
TRANSFER W/ THE SURROUNDINGS, CONSERVATION
OF ENERGY TELLS US THAT THE METAL
LOST 4 kJ OF ENERGY.

$$\begin{aligned} c) \quad C &= \frac{\Delta E}{\Delta T} = \frac{4 \text{ kJ}}{100^\circ\text{C} - 24^\circ\text{C}} = \frac{4 \text{ kJ}}{76^\circ\text{C}} \\ &= \frac{1}{19} \text{ kJ}/^\circ\text{C} \approx 53 \text{ J}/^\circ\text{C} \end{aligned}$$

$$d) \quad c = C/M = \frac{53 \text{ J}/^\circ\text{C}}{100 \text{ g}} = 0.53 \text{ J}/^\circ\text{Cg}$$

$$1.45) a) \omega = x \cdot y = x^2 / z$$

(likewise)

$$\omega = x \cdot y = z y \cdot y = y^2 z$$

$$b) \frac{\partial \omega}{\partial x} \Big|_y = \frac{\partial x y}{\partial x} \Big|_y = y$$

$$\frac{\partial \omega}{\partial x} \Big|_z = \frac{\partial x^2 / z}{\partial x} \Big|_z = 2x / z$$

$$= 2y \neq y$$

~~1.50~~ 1.49) @ constant pressure, the

enthalpy change is the heat exchanged

w/ the surroundings, so that

$$\Delta U = Q + W = \Delta H + W = \Delta H - P\Delta V$$

~~But~~ since the reaction changed

1.5 moles of gas into 1.0 mole,
then $P\Delta V = P \left(\frac{1.5 - 1.0}{1.5} \right) V_0$

$$= \frac{3}{3} P V_0 = \frac{1}{3} RT = \frac{1}{2} RT$$

so the reaction extracts

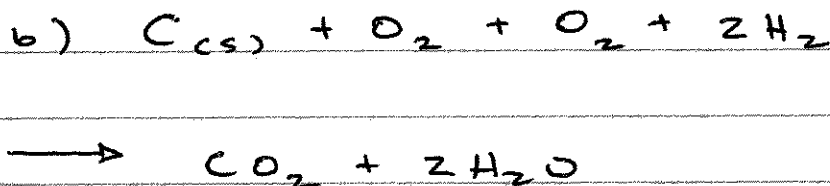
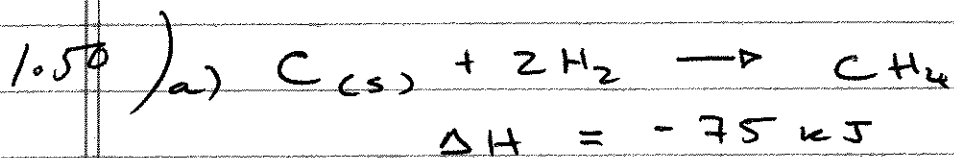
$$\frac{1}{2} RT = 1.2 \text{ kJ of work}$$

from the surroundings, and therefore

of the 286 kJ of heat generated,

almost all (> 99%) comes from the

internal energy of the gas.

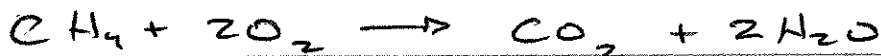


$$\Delta H = 2 \cdot \left[\overset{242}{-286} \text{ kJ} \right] - 394 \text{ kJ}$$

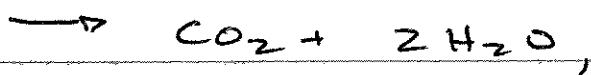
$$= -878 \text{ kJ}$$

c

c) THE ENTHALPY CHANGE IS THE SAME NO MATTER HOW THE REACTION PROCEEDS, i.e. Directly via



OR



SINCE THE ENTHALPY DEPENDS ONLY ON THE INITIAL AND FINAL STATES (THEIR ENERGY, PRESSURE, AND VOLUME) \rightarrow HESS!

WE FIND THEN: 878 803

$$\Delta H = 75 \text{ kJ} - 878 \text{ kJ} = -803 \text{ kJ}$$

d) since pressure is fixed
803

$Q = \Delta H$ so 891 kJ is given off
by the system into its surroundings.

e) The total mole number is the same
for the initial + final states (3),
so the volume is the same
(the temperature is presumably constant).
Therefore:

$$\Delta U = Q \quad \text{[no PV work!]}$$

if the water liquid, then there
is a modification to ΔH for



from $2 \cdot (-242) \text{ kJ}$ to
 $2 \cdot (-286) \text{ kJ}$.

Also, the kinetic mole numbers of gas
is smaller, so we must include a
contribution RT of work extracted
from the surroundings so that

$$\Delta U = \Delta H - RT$$

f) FOR ADIABATIC PROCESS $Q = 0$ AND

FOR PROCESS @ CONSTANT PRESSURE WE

HAVE $\Delta H = Q = 0$.

SO ENTHALPY CHANGE DEPENDS ON THE

EXPERIMENTAL CONDITIONS IT WAS

MEASURED UNDER!

POINTS: NOW WE HAVE IN ADDITION

$$\text{TO } Q = 0 \quad W = \int P dV = 0$$

(VOLUME CONSTANT)

$$\text{SO } \Delta U = 0$$

THE CHEMICAL ENERGY GOES INTO

"HEATING" THE GAS, THOUGH THERE

IS NO "HEAT TRANSFER" OCCURRING ($Q = 0$)

~~THIS~~ IS THE PROPERTY OF THE GAS THAT

RECEIVES THIS HEATING IS ITS ENTROPY,

BUT MORE ON THAT LATER...

$$f) a) \langle n \rangle_N = \sum_{n=0}^N n P_n$$

$$= \sum_{n=1}^N n P_n = \sum_{n=1}^N \left[\frac{1}{2^N} \cdot \frac{N!}{(N-n)! n!} \cdot n \right]$$

$$= \frac{N!}{2^N} \sum_{n=1}^N \frac{1}{(N-n)! (n-1)!}$$

$$= \frac{N!}{2^N} \sum_{n=1}^N \frac{1}{((N-1) - (n-1))! (n-1)!}$$

$$= \frac{N!}{2^N} \sum_{n=0}^{N-1} \frac{1}{((N-1) - n)! n!}$$

$$= \frac{N!}{2^N} \sum_{n=0}^{N-1} \frac{1}{2^{N-1}} \cdot \frac{(N-1)!}{((N-1) - n)! n!}$$

$$= \frac{N!}{2^N} (1) = \frac{N}{2}$$

$$b) \langle n^2 \rangle_N$$

$$= \sum_{n=0}^N n^2 P_n = \sum_{n=1}^N n^2 P_n$$

$$= \sum_{n=1}^N \frac{1}{2^N} \cdot \frac{N!}{(N-n)! n!} \cdot n^2$$

= ... same trick as a) ...

$$= \frac{1}{2} \sum_{n=0}^{N-1} \frac{1}{2^{N-1}} \cdot \frac{(N-1)!}{((N-1)-n)! n!} \cdot (n+1)$$

WHERE DOES THE +1 COME FROM?

$$= \frac{1}{2} \left(\langle n \rangle_{N-1} + 1 \right) = \frac{1}{2} \left(\frac{N-1}{2} + 1 \right)$$

$$= \frac{1}{2} \frac{N+1}{2}$$

$$\sigma_N^2 = \sqrt{\langle n^2 \rangle_N - \langle n \rangle_N^2}$$

$$= \sqrt{\frac{1}{2} \frac{N+1}{2} - \left(\frac{1}{2} \frac{N}{2} \right)^2} = \sqrt{\frac{1}{2}}$$

c) ~~$1/N = 10^{24}$~~

~~$\sigma_N = \frac{1}{2}$~~

c) WE WANT TO KNOW PROBABILITY

THAT $|n - N/2| \geq .01 N$

BUT $.01 N$ IS $.01 \cdot N$ STANDARD
 $\sqrt{N}/2$

DEVIATIONS

$$= \frac{1}{2} \cdot 10^{-2} \cdot \sqrt{10^{24}}^{\frac{1}{2}} = \frac{1}{2} \cdot 10^{10}$$

SO THE PROBABILITY IS NO GREATER THAN

$$1 / \left[\frac{1}{2} \cdot 10^{10} \right]^2 = \frac{4}{10^{20}}$$

i.e. NOT BETTING ODDS.