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.

c) $C = \dfrac{\Delta E}{\Delta T} = \dfrac{4\text{ kJ}}{100^\circ C - 24^\circ C} = \dfrac{4\text{ kJ}}{76^\circ C}$

$= \dfrac{1}{19}\text{ kJ}/{}^\circ C \simeq 53\text{ J}/{}^\circ C$

d) $c = C/m = \dfrac{53\text{ J}/{}^\circ C}{100\text{ g}} = .53\text{ J}/{}^\circ C\,g$

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

Likewise:

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

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

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

$= 2y \neq y$

~~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

$$P\Delta V = P\left(\frac{1.5 - 1.0}{1.5}\right)V_0$$

$$= \frac{3'}{3} P V_0 = \frac{1}{3}\frac{3}{2} RT = \frac{\cancel{3}}{\cancel{4}} RT \frac{1}{2}$$

SO THE REACTION EXTRACTS

$$\frac{1}{2}\frac{\cancel{3}}{\cancel{4}} RT \approx 1.2 \text{ kJ}$$ OF WORK

FROM THE SURROUNDINGS, AND THEREFORE OF THE 286 KJ OF HEAT GENERATED, ALMOST <u>ALL</u> (> 99%) COMES FROM THE INTERNAL ENERGY OF THE GAS.

1.50) a) $C_{(s)} + 2H_2 \longrightarrow CH_4$

$\Delta H = -75\ kJ$

b) $C_{(s)} + O_2 + O_2 + 2H_2$

$\longrightarrow CO_2 + 2H_2O$

$$\Delta H = 2 \cdot \left(-\overset{242}{\cancel{286}}\ kJ\right) - 394\ kJ$$
$$= -\underset{878}{\cancel{966}}\ kJ$$

c

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

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

OR

$CH_4 + 2O_2 \longrightarrow C_{(s)} + 2H_2 + 2O_2$

$\longrightarrow CO_2 + 2H_2O$,

SINCE THE ENTHALPY DEPENDS ~~of~~ ONLY ON THE INITIAL AND FINAL STATES (THEIR ENERGY, PRESSURE, AND VOLUME) ← FIXED!

WE FIND THEN:

$$\Delta H = 75\ kJ - \overset{878}{\cancel{966}}\ kJ = -\overset{803}{\cancel{891}}\ kJ$$

d) SINCE PRESSURE IS FIXED

$Q = \Delta H$ SO ~~841~~ 803 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:

$\Delta U = Q$ [NO PV. WORK!]

IF THE WATER LIQUIFIED, THEN THERE IS A MODIFICATION TO ΔH FOR

$O_2 + 2H_2 \longrightarrow 2H_2O$

FROM $2 \cdot (-242)$ kJ TO
$2 \cdot (-286)$ kJ.

ALSO, THE FINAL 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!

BONUS: NOW WE HAVE IN ADDITION TO $Q = 0$ $W = -\int P dV = 0$ (VOLUME CONSTANT)

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 REFLECTS THIS HEATING IS ITS ENTROPY, BUT MORE ON THAT LATER...

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

$$= \sum_{\substack{\cancel{n=0} \\ n=1}}^{N} n P_n = \sum_{n=1}^{N} \left[\frac{1}{2^N} \cdot \frac{N!}{(N-n)!\, n!} \cdot n \right]$$

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

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

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

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

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

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) ...

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

WHERE DOES THE +1 COME FROM?

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

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

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

$$= \sqrt{\frac{N}{2} \cdot \frac{N+1}{2} - \frac{N}{2} \cdot \frac{N}{2}} = \frac{\sqrt{N}}{2}$$

~~c) IF $N = 10^{24}$~~

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

c) WE WANT TO KNOW PROBABILITY

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

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

DEVIATIONS

$$= \frac{1}{2} \cdot 10^{-2} \cdot (10^{24})^{1/2} = \frac{1}{2} \cdot 10^{10}$$

SO THE PROBABILITY IS NO GREATER THAN

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

i.e. NOT BETTING ODDS.