سنتر فيوتشر

Subject: كيمياء اعدادي

Chapter: ثرمو ٢

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لحساب الشغل المبذول لغاز مثالي (Work) for ideal gas

$V = Const$ الحجم ثابت

$dV = Zero$

$W = Zero$

Ex] rigid tank Contain air at 500 kPa & 150°C, as result of heat transefer the temperature and pressure drop to 65°C and 400 kPa. Calculate work done during this process ??

∵ Rigid tank

∴ Volume of tank is Constant

$dV = Zero$

$W = \int_{V_1}^{V_2} p\,dV = Zero$

$P = Const$ الضغط ثابت

$W = P \Delta V$

Ex] piston Contain 0.1 mole of water Vapour at 20 psia & 320°k, heat is now added to the system and temp reach 400°k, if the pressure was Const determine work done by the system

$W = P \Delta V = P(V_2 - V_1)$

$W = P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right)$

$W = nR(T_2 - T_1)$

$W = 0.1\,\text{mole} \times \frac{2\ \text{Calory}}{\text{mole}\ °k}(400 - 320°k)$

$W = 16$ Calory

$P \,\&\, V \neq Const$ الضغط والحجم متغيرين

$W = nRT \ln \frac{V_2}{V_1}$

$W = nRT \ln \frac{P_1}{P_2}$

Ex] Cylinder Contain 0.4 m³ of air at 100 kPa and 80°C, the air is Compressed to 0.1 m³ as the temperature remain Constant: Determine work done during this process

$P_1 V_1 = P_2 V_2 = nRT$

$P_1 V_1 = Const$

$P_1 = \frac{C}{V_1}$

$W = \int_{V_1}^{V_2} p \cdot dV$

$= \int_{V_1}^{V_2} \frac{C}{V} \cdot dV$

$= C \int_{V_1}^{V_2} \frac{dV}{V} = C \ln [V]_{V_1}^{V_2}$

$= C[\ln V_2 - \ln V_1] = C \ln \frac{V_2}{V_1}$

$= P_1 V_1 \ln \frac{V_2}{V_1} = (100)(0.4) \ln \frac{0.1}{0.4}$

$W = -55.45\ kPa \cdot m^3$

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Work done by real gas

لحساب الشغل المبذول لغاز حقيقي

to Calculate the work done by real gas that obey Vander Vall equation when expand at Const temperature from Volume V_1 to final Volume V_2

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \rightarrow \text{Vander Vall equation}$$

As a & b Constant

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$\therefore W = \int_{V_1}^{V_2} P \cdot dV = \int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right) \cdot dV$$

$$= \int_{V_1}^{V_2} \frac{nRT}{V - nb} \cdot dV - \int_{V_1}^{V_2} \frac{an^2}{V^2} \cdot dV$$

$$= nRT \int_{V_1}^{V_2} \frac{dV}{V - nb} - an^2 \int_{V_1}^{V_2} V^{-2} \cdot dV$$

$$= nRT \ln [V - nb]_{V_1}^{V_2} - an^2 \left[\frac{V^{-2+1}}{-2+1}\right]_{V_1}^{V_2}$$

$$= nRT \ln [V - nb]_{V_1}^{V_2} - an^2 \left[\frac{V^{-1}}{-1}\right]_{V_1}^{V_2}$$

$$= nRT \ln [V - nb]_{V_1}^{V_2} + an^2 \left(\frac{1}{V}\right)_{V_1}^{V_2}$$

$$= nRT \left[\ln (V_2 - nb) - \ln (V_1 - nb)\right] + an^2 \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\boxed{W = nRT \ln \frac{V_2 - nb}{V_1 - nb} + an^2 \left(\frac{1}{V_2} - \frac{1}{V_1}\right)} \quad \text{For real gas}$$

Example | find work done by 1 mole of chlorine when expands at Const temperature 50°C from Volume 1 L to final Volume 50 L

① if the chlorine act as ideal gas

② if the chlorine act as real gas $a = 6.493$, $b = 0.05$

Solution |

① if the chlorine act as ideal gas

$$W = nRT \ln \frac{V_2}{V_1}$$

$$W = (1)\left(0.082 \frac{l.atm}{mole\,°k}\right)(50+273)°k \ln \frac{50}{1}$$

$$W = 103.6 \ l.atm$$

② if the chlorine act as real gas

$$W = nRT \ln \left(\frac{V_2 - nb}{V_1 - nb}\right) + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$= (1\ mole)\left(0.082 \frac{l.atm}{mole\,°k}\right)(50+273°k) \ln \left(\frac{50 - 1(0.05)}{1 - 1(0.05)}\right)$$

$$+ 6.493\left(\frac{1}{50} - \frac{1}{1}\right)$$

$$W = 98.747 \ l.atm$$

لاحظ / الشغل المبذول في حالة الغاز الحقيقي أقل من حالة الغاز المثالي

Work in Case of real gas ⟹ Work decrease

Energy

① macroscopic
All forms of energy outside the system
تدرس كل الطاقات خارج النظام

② microscopic
related to structure of molecules forming system

⊛ Internal energy (U) الطاقة الداخلية
all sum of microscopic energy
هى الطاقة المرتبطة بـ structure وانتقال é من مستوى لآخر وهكذا

⊛ kinetic energy (k.E) طاقة الحركة
The energy that the system has due to its motion
هى الطاقة التى يمتلكها النظام نتيجة حركته

$$\boxed{k.E = \frac{1}{2} m v^2}$$

m → الكتلة mass
v → velocity السرعة

⊛ Potential energy (P.E) طاقة الوضع
The energy result of it's elevation in gravitional field
هى الطاقة الناتجة عن ارتفاع الجسم فى مجال الجاذبية الأرضية

$$\boxed{P.E = m.g.Z}$$

m → الكتلة mass
g → عجلة الجاذبية
Z → elevation الارتفاع

Total energy = internal energy + kinetic energy + Potential energy

$$E = U + k.E + P.E$$

$$\Delta E = \Delta U + \Delta k.E + \Delta P.E$$

(*) First Law of thermodynamics has three forms

1- Energy can't be created or destroyed but it can transefer from one form to another

→ law of Conservation of energy قانون بقاء الطاقة

الطاقة لا تفنى ولا تستحدث من العدم ولكن يمكن تحويلها من صورة لأخرى

2- Total amount of energy of system & surrounding are Constant

مجموع طاقتي النظام والمحيط ثابتة

3- During the interaction between system & surrounding

(energy gained by the system) = (energy lost by the surrounding)

الطاقة المكتسبة للنظام والعكس صحيح = الطاقة المفقودة من الوسط

$$\boxed{\Delta E = Q \pm W}$$

As ΔE → net change in total energy التغير في الطاقة الكلية

Q → heat gained or heat lost مقدار الطاقة المكتسبة او المفقودة

W → work done on the system الشغل المبذول على النظام

or work done by the system الشغل المبذول بواسطة النظام

But $\Delta E = \Delta U + \Delta K.E + \Delta P.E$

neglect change in kinetic energy & Potential energy

$\therefore \Delta E = \Delta U$

$$\boxed{\Delta U = Q \pm W}$$

First law of thermodynamics

$$\Delta E = Q \pm W$$

$\Delta E = Q + W$ هشتغل بالصورة دي في المسائل

$\Delta E = Q - W$ هشتغل بالصورة دي في الإثباتات

ملحوظة

$Q \rightarrow +ve$ "gained heat اكتساب حرارة"

$Q \rightarrow -ve$ "loss heat فقد حرارة"

$W \rightarrow +ve$ "work done <u>on</u> system"

$W \rightarrow -ve$ "work done <u>by</u> system"

$\xrightarrow{+ve}$ system $\xleftarrow{-ve}$

خزان صلب

Ex A rigid tank contains hot fluid that is cooled while being stirred by a paddle wheel. The initial internal energy of the fluid is 800 kJ during the cooling process, the fluid losses 500 kJ of heat, and the paddle wheel does 100 kJ of work on fluid. Determine the final internal energy of the fluid ?? Neglect the energy stored in the paddle wheel

$u_1 = 800 \text{ kJ}$

$Q = -500 \text{ kJ}$

$W = +100 \text{ kJ}$

$u_2 = ??$

$$\Delta E = Q + W$$

$$\Delta E = -500 + 100 = -400 \text{ kJ}$$

$$\Delta E = \Delta U + \underbrace{\cancel{\Delta KE}}_{0} + \underbrace{\cancel{\Delta PE}}_{0}$$

neglect energy stored in paddle wheel

$$\Delta E = \Delta U = u_2 - u_1$$

$$-400 = u_2 - 800$$

$$u_2 = -400 + 800$$

$$u_2 = +400 \text{ kJ}$$

Net heat transefer at Constant Volume q_v

$$\Delta E = q - w$$

$$\Delta u = q - w$$

But $w = \int_{v_1}^{v_2} p \cdot dv$

But $\Delta E = \Delta u + \cancel{\Delta KE}^{\,0} + \cancel{\Delta PE}^{\,0}$

$\therefore \Delta E = \Delta u$

at Const Volume
$dv = \text{Zero}$
$w = \text{Zero}$

$$u_2 - u_1 \leftarrow \boxed{\therefore \Delta u = q_v}$$

Net change in internal energy = heat transefer at Const volume

كمية الحرارة المنتقلة عند حجم ثابت = محصلة التغيير في الطاقة الداخلية

ملحوظة: q_v depend on initial and Final state of internal energy

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Net heat transefer at Constant pressure q_p

$$\Delta E = q - w$$

$$q = \Delta E + w$$

$w = p \Delta v$ at Const pressure
$\Delta E = \Delta u$

عند ثبوت الضغط $\boxed{q_p = \Delta u + p \Delta v}$

$$q_p = (u_2 - u_1) + p(v_2 - v_1)$$

$$q_p = u_2 - u_1 + pv_2 - pv_1$$

$$q_p = u_2 + pv_2 - (u_1 + pv_1)$$

$H = u + pv$ → heat Content (or) enthalpy

$$q_p = H_2 - H_1$$

$$\boxed{q_p = \Delta H}$$

net change in enthalpy = net change in heat transefer at Const pressure

كمية الحرارة المنتقلة عند ضغط ثابت = محصلة التغيير في المحتوى الحراري

ملحوظة: q_p depend on initial and Final state of heat Content

Enthalpy :- (H) المحتوى الحرارى

is thermodynamic quantity equivalent to heat content of system

هى كمية ثرموديناميكية مكافئة للمحتوى الحرارى للنظام

→ change in enthalpy associated to particular chemical process

التغير في المحتوى الحرارى مرتبط جزئياً بالعملية الكيميائية

(*) Relation between q_p & q_v :-

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

$$q_p = \Delta U + W \implies \boxed{q_p = q_v + W}$$

$$q_p > q_v$$

q_p is larger than q_v by Work

ملحوظة هامة جداً

- at Const Volume the increase in heat transefer
  → go to increase in internal energy $\boxed{q_v = \Delta U}$
- at Const pressure the increase in heat transefer
  → go to Work
  → go to increase in internal energy. $\boxed{q_p = \Delta U + W}$