

Heat capacity: The Temperature-dependence of Enthalpy changes.

Heat capacity (C): the amount of heat required to raise the temperature of the system by 1 deg C - again starting the temperature

From the define of heat capacity

$$C = \frac{\delta q}{dT} \quad (\text{The rate of heat absorbed by the system with increase in temperature})$$

1g mild steel $\Rightarrow 0.460 \text{ J} \Rightarrow 1^\circ\text{C}$
 1g copper $\Rightarrow 0.385 \text{ J}$

The heat capacity at constant pressure C_p

Therefore

$$C_p = \frac{\delta q_p}{dT}$$

specific heat of a substance: The amount of heat required to raise the temperature of 1g of the substance by 1 deg.

but $q_p = \Delta H$ HE(V,P)

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

where the partial differential is used to allow for the fact that the H depends on both pressure and volume, and here the pressure is kept constant.

Similarly, the heat capacity at constant volume

$$C_v = \frac{\delta q_v}{dT} = \left(\frac{\partial U}{\partial T} \right)_v$$

because $q_v = \Delta U$

Heat capacity depend on Temperature, although theories have been produced to explain this dependence the results of experimental determinations are expressed as empirical relationships such as:

$$C_p = a + bT + cT^{-2}$$

a, b, c are constants determined for a substance over a particular range of temperatures.

$$C_p = a + bT + cT^{-2}$$

Substance	C_p (J mol ⁻¹ K ⁻¹)
Methyl	...
...	...
...	...

$$H = F(p, T) = F(T)$$

if we consider the enthalpy change accompanying the change of a system from state A to state B, then

$$\Delta H = H_B - H_A$$

Differentiating with respect to temperature, keeping the pressure constant,

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_p = \left(\frac{\partial H_B}{\partial T} \right)_p - \left(\frac{\partial H_A}{\partial T} \right)_p$$

But $(\partial H / \partial T)_p = C_p$

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_p = C_{p(B)} - C_{p(A)} = \Delta C_p$$

where ΔC_p is the difference between the heat capacity of the system in its final state and the heat capacity of the system in its initial state at constant pressure. This is one of Kirchhoff's equations, and the other can be derived similarly, so that.

$$\left[\frac{\partial(\Delta U)}{\partial T} \right]_v = \Delta C_v$$

المعادلة كيرشوف الثانية
 المتكافئة للمعادلة الأولى
 يمكن اشتقاقها بطريقة مشابهة

وأيضاً يمكن اشتقاق معادلات كيرشوف للحرارة في الحالة المتساوية للضغط لأنهم يعتمدون على تغيرات الحرارة المتكافئة ومن ثم يمكن اشتقاقها أيضاً.

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \cdot dT$$

المعادلة كيرشوف الأولى
 $\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \cdot dT$

where ΔH_2 and ΔH_1 are the enthalpy changes at temperatures T_2 and T_1 respectively.

(*) if C_p is not constant for the system over the range of temperatures concerned, then the empirical expression of the can use

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} (A + BT + CT^{-2}) \cdot dT$$

$$= (AT_2 + \frac{1}{2}BT_2^2 - CT_2^{-1}) - (AT_1 + \frac{1}{2}BT_1^2 - CT_1^{-1})$$

في الحالة التي لا تكون فيها C_p ثابتة يمكن استخدام تعبير تجريبي للحرارة المتكافئة كالتالي $A + BT + CT^{-2}$

في الامام الذي سير فيها احد المكونات للخطوة في تحول طور عند درجة حرارة T_t حيث $T_2 > T_t$

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_t} \Delta C_p (T_1 - T_t) \cdot dt \pm L_t + \int_{T_t}^{T_2} \Delta C_p (T_1 - T_2) \cdot dt$$

$L_t = \text{Transformation}$

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_t} (C_{p1} - C_{p2}) \cdot dt \pm L_t + \int_{T_t}^{T_2} (C_{p1} - C_{p2}) \cdot dt$$

$$\Delta H_{T_2} - \Delta H_{T_1} = (C_{p1} - C_{p2}) \cdot (T_t - T_1) \pm L_t + (C_{p1} - C_{p2}) \cdot (T_2 - T_t)$$

في الامام الذي سير فيها احد المكونات للخطوة في تحول طور عند درجة حرارة T_t حيث $T_2 > T_t$

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في الامام الذي سير فيها احد المكونات للخطوة في تحول طور عند درجة حرارة T_t حيث $T_2 > T_t$

* When no heat energy enters or leaves the system, during a change in the system the change is known as "adiabatic" in this case " $q = \text{Zero}$ "; and the temperature will not remain constant.

* It is found that, assuming that, for 1 mole the difference between C_p and C_v is R , the gas constant.

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

when the system changes adiabatically and reversibly from P_1, V_1 and T_1 to P_2, V_2 and T_2 respectively. γ is the ratio

C_p / C_v for an ideal gas and is greater than unity.

(*) When no heat energy enters or leaves the system during a change in the system, the change is known as adiabatic (التغير الأديباتي)

In this case $q = \text{Zero}$ and the Temperature will not remain constant.

assuming that for 1 mol, Ideal gas adiabatically and reversibly.

$$dW = -\delta W$$

$$dU = C_v dT$$

$$\delta W = P dV$$

$$C_v dT = -P dV$$

$$\text{For 1 mol gas } \Rightarrow P = \frac{RT}{V}$$

$$C_v dT = -\frac{RT}{V} dV$$

$$C_v \frac{dT}{T} = -R \frac{dV}{V}$$

$$C_v \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{V_1}{V_2}\right)$$

$$\left(\frac{T_2}{T_1}\right)^{C_v} = \left(\frac{V_1}{V_2}\right)^R$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{R/C_v}$$

$$\text{but } R = C_p - C_v$$

$$\frac{R}{C_v} = \frac{C_p}{C_v} - 1$$

$$\gamma = \frac{C_p}{C_v} \quad (\text{for ideal gas and its great than unity})$$

$$\therefore \frac{R}{C_v} = \gamma - 1$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

and

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

$$\frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

~~and~~

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \left(\frac{V_1}{V_2}\right)$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma$$

$$P_2 V_2^\gamma = P_1 V_1^\gamma$$