Unutarnja energija i toplinski kapacitet

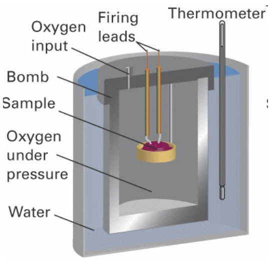
$$dU = dq + dw_{\text{eksp.}} + dw_{\text{dodatni}}$$

Kod adiabatskog kalorimetra volumni rad $dw_{\text{eksp.}}$ i dw_{dodatni} iznose 0.

$$V = \text{konst.}$$

$$\Delta U = q_V$$

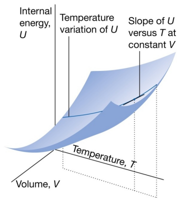
$$q_V = C_V \Delta T$$

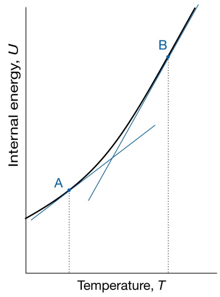


Toplinski kapacitet

Unutarnja energija sustava raste s povećanjem temperature.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$





Toplinski kapacitet

Toplinski kapacitet je ekstenzivna veličina.

Molarni toplinski kapacitet : $C_{V,n} = \frac{C_V}{n}$

Specifični toplinski kapacitet : $C_{V,m} = \frac{C_V}{m}$

Pri konstantnom volumenu : $\Delta U = C_V \Delta T$

$$q_V = C_V \Delta T$$

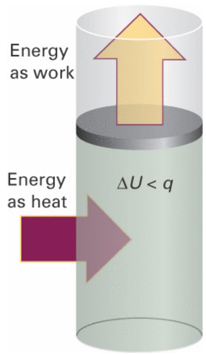
Entalpija H

Funkcija stanja, pri konstantnom tlaku (uobičajeni laboratorijski uvjeti)

$$H = U + pV$$

Promjena entalpije jednaka je dovedenoj toplini pri konstantnom tlaku.

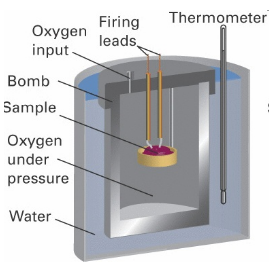
$$\Delta H = q_p$$



Izobarni kalorimetar

Toplinski izolirana posuda otvorena prema vanjskom tlaku.

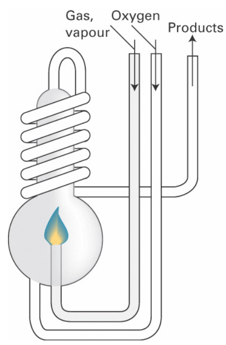
$$\Delta H = q_p$$



Plameni kalorimetar

Za mjerenje entalpije reakcija sagorijevanja.

$$\Delta H = q_p$$



Odnos ΔH i ΔU kod krutina

$CaCO_3$(kalcit) → $CaCO_3$(aragonit) $\Delta U_m = +0.21$ kJ mol^{-1}

ρ(kalcit) = 2.71 g cm^{-3}

ρ(aragonit) = 2.93 g cm^{-3}

$$\Delta H_m - \Delta U_m = -0.28 \text{ J mol}^{-1}$$

Odnos ΔH i ΔU kod plinova

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O\ (l)$ $\Delta n_g = -3$ mol

Za idealni plin:

$$H = U + pV = U + nRT$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H_m - \Delta U_m = \Delta n_g RT = -7400 \text{ J mol}^{-1}$$

Toplinski kapacitet

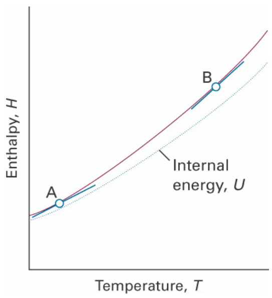
Toplinski kapacitet pri konstantnom tlaku:

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

$$\mathrm{d}H = C_p \mathrm{d}T$$

$$\Delta H = C_p \Delta T$$

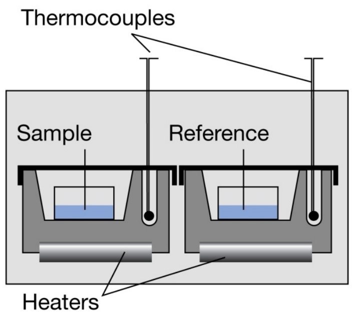
$$\Delta H = q_p$$



Diferencijalna pretražna kalorimetrija DSC

Mjerenje promjene entalpije tijekom kemijske ili fizičke promjene pri konstantnom tlaku.

$$C_{p,ex} = \frac{q_{p,ex}}{\Delta T}$$

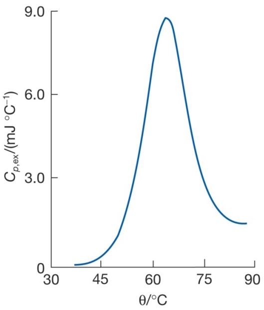


DSC termogram

Protein *Ubiquitin* zadržava nativnu strukturu do temperature od 45°C a dalje dolazi do endotermne konformacijske promjene.

$$C_{p,ex} = \frac{q_{p,ex}}{\Delta T}$$

$$\Delta H = \int_{T_1}^{T_2} C_{p,ex} dT$$



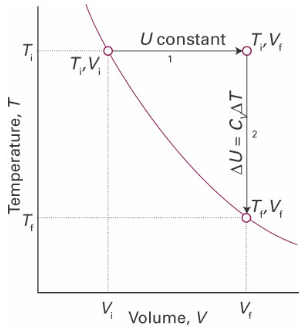
Adiabatska ekspanzija idealnog plina

$$\Delta U = C_V(T_f - T_i) = C_V \Delta T$$

$$w_{adiabatski} = C_V \Delta T$$

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_v}}$$

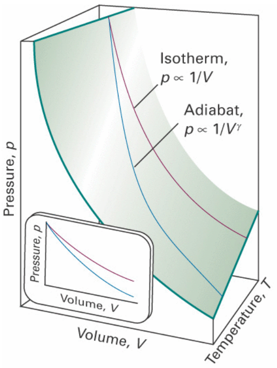
$$P_f V_f^{\frac{C_{p,m}}{C_{V,m}}} = P_i V_i^{\frac{C_{p,m}}{C_{V,m}}}$$



Adiabatska ekspanzija idealnog plina

Izoterma: $P \propto \frac{1}{V}$

Adiabata: $P \propto \frac{1}{V^{\frac{C_{p,m}}{C_{V,m}}}}$



Termokemija

Endotermni procesi: $\Delta H > 0$

Egzotermni procesi: $\Delta H < 0$

Standardno stanje:

Najstabilnije stanje čiste tvari na određenoj temperaturi i pri tlaku od 1 bar.

Termokemija

Vrsta promjene:		
Fazni prijelaz	faza A → faza B	$\Delta_{trs}H$
Taljenje	s → l	$\Delta_{fus}H$
Isparavanje	l → g	$\Delta_{vap}H$
Sublimacija	s → g	$\Delta_{sub}H$
Miješanje	čista tvar → smjesa	$\Delta_{mix}H$
Otapanje	čista tvar → otopina	$\Delta_{sol}H$
Hidratacija	X(g) → X(aq)	$\Delta_{hyd}H$
Atomizacija	spoj(s,l,g) → atomi(g)	$\Delta_{at}H$
Ionizacija	$X(g) \rightarrow X^+(aq)+e^-(g)$	$\Delta_{ion}H$
Dodatak elektrona	$X(g) + e^-(g) \rightarrow X^-(aq)$	$\Delta_{eg}H$
Reakcija	reaktanti → produkti	$\Delta_r H$
Sagorijevanje	$X(s,l,g)+O_2(g) \rightarrow CO_2(g)+H_2O(l,g)$	$\Delta_{trs}H$
Nastajanje	elementi → spoj	$\Delta_f H$
Aktivacija	reaktanti → aktivirani kompleks	$\Delta^{\ddagger}H$

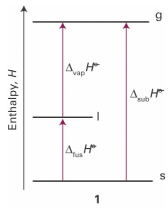
Termokemija

$H_2O(s) \rightarrow H_2O(g)$ $\quad \Delta_{sub}H^{\ominus}$

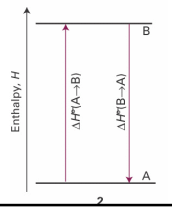
$H_2O(s) \rightarrow H_2O(l)$ $\quad \Delta_{fus}H^{\ominus}$

$H_2O(l) \rightarrow H_2O(g)$ $\quad \Delta_{vap}H^{\ominus}$

$$\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}$$



A → B $\quad \Delta H^{\ominus}(A \rightarrow B) = -\Delta H^{\ominus}(B \rightarrow A)$

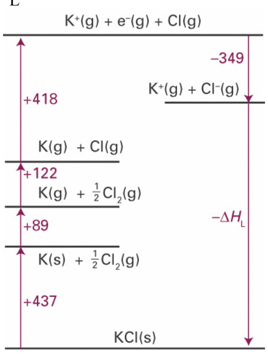


Born-Haberov ciklus

$K^+(g) + Cl^-(g) \rightarrow KCl(s)$ $\quad \Delta_L H^{\ominus}$

	$\Delta H_L/(kJ\ mol^{-1})$
NaF	787
NaBr	751
MgO	3850
MgS	3406

* More values are given in the *Data section*.



Standardna reakcijska entalpija

$$\Delta_r H^{\ominus} = \sum_{produkti} \nu H_m^{\ominus} - \sum_{reaktanti} \nu H_m^{\ominus}$$

Hessov zakon:

Standardna entalpija reakcije jednaka je sumi standardnih entalpija pojedinih reakcijskih stupnjeva na koje se reakcija može podjeliti.

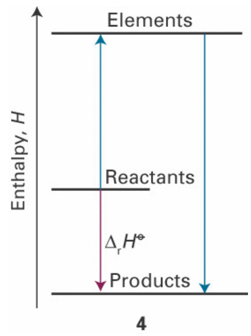
Standardna entalpija nastajanja

Standardna reakcijska entalpija na nekoj temperaturi može se izračunati iz standardnih entalpija stvaranja.

$$\Delta_r H^{\ominus} = \sum_{\text{produkti}} \nu \Delta_f H^{\ominus} - \sum_{\text{reaktanti}} \nu \Delta_f H^{\ominus}$$

	$\Delta_f H^{\ominus}/(\text{kJ mol}^{-1})$
$H_2O(l)$	−285.83
$H_2O(g)$	−241.82
$NH_3(g)$	−46.11
$N_2H_4(l)$	+50.63
$NO_2(g)$	+33.18
$N_2O_4(g)$	+9.16
$NaCl(s)$	−411.15
$KCl(s)$	−436.75

* More values are given in the *Data section*.



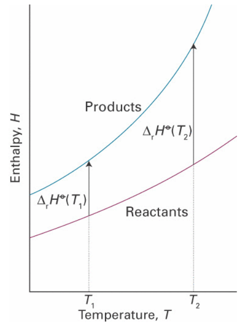
Kirchhoffov zakon

Standardna reakcijska entalpija na nekoj temperaturi može se procijeniti iz standardne reakcijske entalpije na drugoj temperaturi i toplinskih kapaciteta.

$$\Delta H = C_p \Delta T$$

$$\Delta_r H^{\ominus}(T_2) = \Delta_r H^{\ominus}(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\ominus}\, dT$$

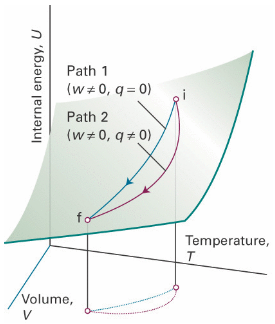
$$\Delta_r C_p^{\ominus} = \sum_{\text{produkti}} \nu C_{p,m}^{\ominus} - \sum_{\text{reaktanti}} \nu C_{p,m}^{\ominus}$$



Egzaktni diferencijali funkc. stanja

S promjenom volumena i temperature sustava mijenja se i unutarnja energija sustava. Adiabatski (1) i neadiabatski (2) put imaju različiti rad i toplinu pri čemu je ΔU ista za oba procesa.

$$\Delta U = \int_i^f dU \qquad q = \int_{i,put}^f dq$$

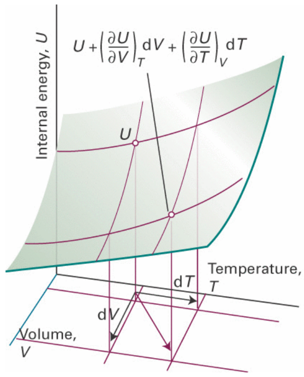


Promjene unutarnje energije

ΔU se može izraziti kao promjena temperature i volumena sustava.

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

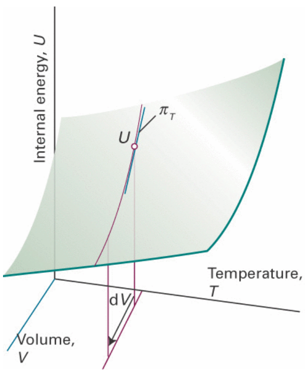
$$\Delta U = \pi_T dV + C_V dT$$



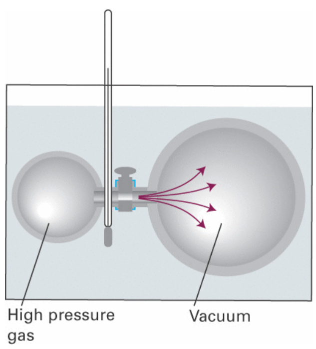
Unutarnji tlak

Nagib funkcije promjene unutarnje energije s promjenom volumena sustava pri konstantnoj temperaturi.

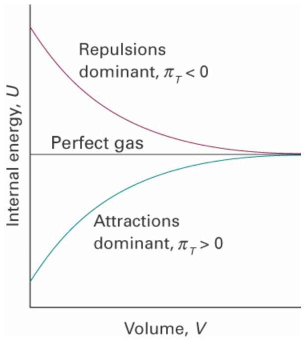
$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$



Jouleov pokus



Jouleov pokus



Promjene unutarnje energije pri konstantnom tlaku

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \qquad \left(\frac{\partial U}{\partial T}\right)_p = \alpha\pi_T V + C_V$$

C_p i C_V idealnog plina

$$C_p - C_V = nR$$