Engineering Thermodynamics

Heat and Work

The first law of thermodynamics states that: Although energy has many forms, the total quantity of energy is constant. When energy disappears in one form, it appears simultaneously in other forms

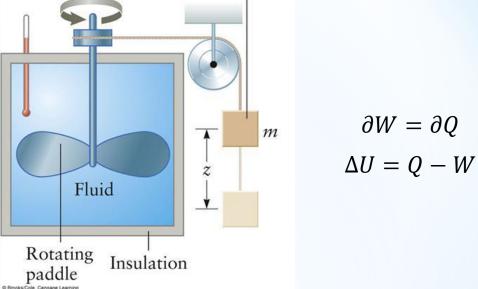
Hence
$$\Delta U + \Delta E_K + \Delta E_P = Q - W$$

Heat and work are forms of energy that are transformed into other forms of energy. If friction is eliminated, work is efficiently transformed to potential, kinetic, electrical and heat energy by a conversion ratio of upto 100%.

Heat on the other hand is readily lost to the surroundings and its conversion into work, mechanical or electrical energy does not exceed 40% efficiency because the flow of heat always takes place from the hotter to the cooler body and never in the reverse direction

The second law describes the direction of energy transfer in spontaneous processes

The relationship between heat and work was established by Joule's experiments on water



Joule tried to convert mechanical energy of rotation of a fan into temperature rise of water. Other methods of work production used by Joule were turbulent motion, electric current, compression and friction. The same relationship between temperature rise and the amount of work applied to water was seen in all experiments:

Temperature rise was found to be 0.241 °C when 1 Joule of work was applied to 1 gram of adiabatically contained water at 14.5 °C The quantitative relationship between work and heat was established as 1 J = 0.241 calories An energy function that is only dependent on the internal condition of the system was necessary

Internal energy U keeps a record of the energetic state of a system, excluding kinetic energy and potential energy

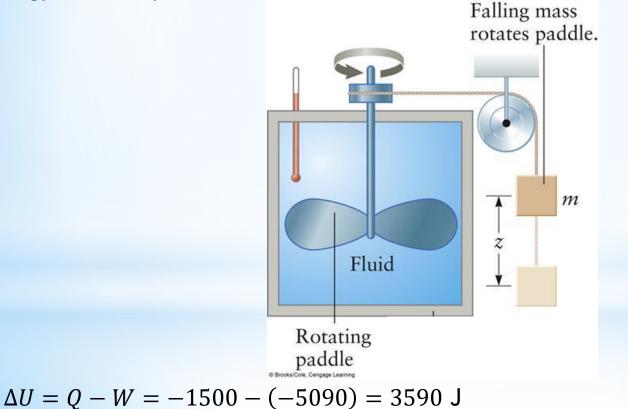
Relativity concept of energies is used since absolute internal energy of a system cannot be measured at any state. Internal energy of system can only be defined or measured relative to a reference state

 $U_2(T_2, P_2)$ $\Delta U = (U_2 - U_1)$ $U_1(T_1, P_1)$

Thermodynamics deals with energy differences rather than absolute values of energies

Internal energy of the system is altered as a result of an energy exchange process. The system may absorb energies of different sorts from its surroundings during the process

Example - The work input to a tank by a paddle wheel is 5090 J. The heat transfer from the tank is 1500 J. Determine the change in the internal energy of the system.

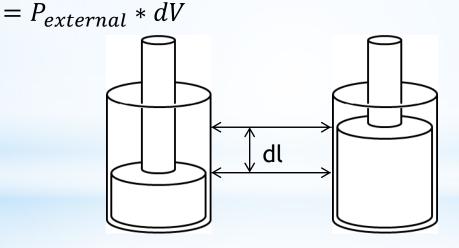


Work is defined as a force F acting through a displacement x in the direction of the force:

$$W = \int_{state 1}^{state 2} Fdx$$

Work performed in a system is grouped into two: $W = W_{expansion} - W_{other}$

 W_{other} which includes electric, friction, turbulent work is often not present $dW_{expansion} = P_{external} * Adl$, since area of a piston is constant



Work done by the system by expansion is considered <u>positive</u> and work done on a system by compression is considered <u>negative</u> Work is not a state function and is dependent on the path During a process, the work done can be found by integrating between V_2 and V_1 only if the relationship between P_{ext} and V is known

$$W = \int_{V1}^{V2} P dV$$

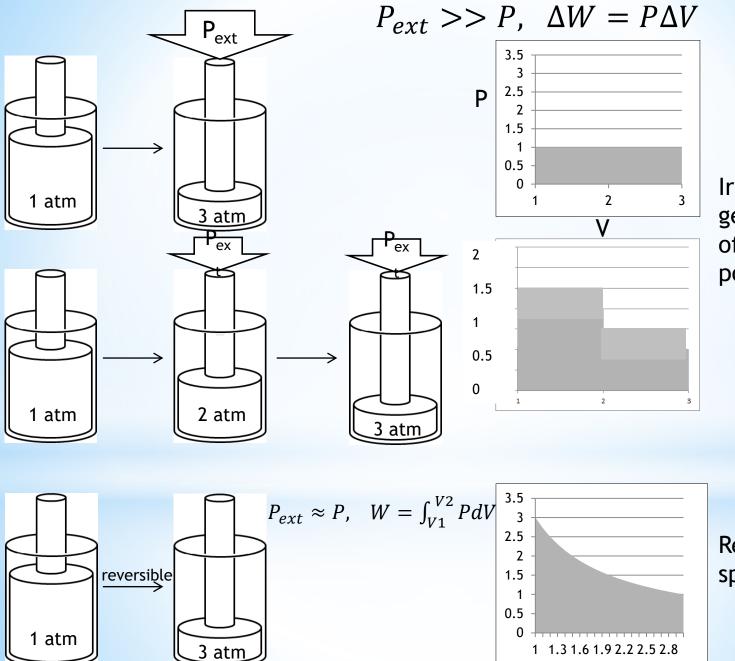
Compression takes place instantaneously and irreversibly if the difference between P and P_{ext} is great

$$P_{ext} >> P$$
, $\Delta W = P \Delta V$

Compression will occur reversibly through a series of equilibrium states if P is only infinitesimally greater than P_{ext}

$$P_{ext} \approx P$$
, $W = \int_{V1}^{V2} P dV$

A reversible process can be defined as one that is performed in such a way that both the system and its local surroundings may be restored to their initial states without producing any permanent changes in the rest of the universe at the conclusion of process Consider 3 isothermal processes with the same initial and final pressures



Irreversible process gets less work out of the system than possible

Reversible process spends more energy

Reversible processes are allowed to occur at infinitely slow rate to maintain a state of equilibrium of the system

Reversible path represents the limiting case of maximum work output The path of a reversible expansion is shown by a curve on P-V coordinates since $P \propto 1/V$

Example - 100 lt of an ideal gas at 300 K and 1 atm pressure expands reversibly to three times its volume by a) an isothermal process, b) an isobaric process. Calculate the work done in each case

a)
$$W = \int_{V1}^{V2} P dV$$
 b) $W = P \int_{V1}^{V2} dV$

Values of <i>R</i>	Units
8.3144621	J • K ⁻¹ • mol ⁻¹
0.082057	L • atm • K ⁻¹ • mol ⁻¹
8.205736×10^{-5}	$m^3 \cdot atm \cdot K^{-1} \cdot mol^{-1}$
8.3144621	L•kPa•K ⁻¹ •mol ⁻¹
8.3144621	m ³ • Pa • K ^{−1} • mol ^{−1}
62.36368	L • mmHg • K ⁻¹ • mol ⁻¹
62.36359	L • torr·K ⁻¹ • mol ⁻¹
83.144621	L • mbar • K ⁻¹ • mol ⁻¹
10.73158	$\mathrm{ft}^3 \cdot \mathrm{psi} \cdot {}^{\mathrm{e}} \mathrm{R}^{-1} \cdot \mathrm{lb} \mathrm{-mol}^{-1}$
0.73024	ft ³ • atm • ⁰R ⁻¹ • lb-mol ⁻¹
The Durchus since	

The *R* value given by the National Institute of Standards and Technology (NIST) is 8.314462 $\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1}$ as of 2010.

Question - Which of the following situations is considered to be a reversible process?

- a) A raw egg is thrown from a second story window to the ground below
- b) The pizza is put into the 200 °C oven and baked for 15 minutes
- c) After the party, Ali damages his car by striking a traffic light
- d) The earthquake destroys an entire neighborhood
- e) None of these are reversible processes

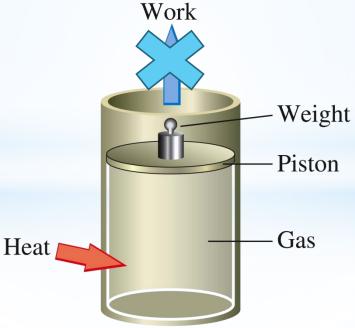
The Constant Volume Process

Internal energy of the ideal gas only changes by heat flow when the piston is not allowed to expand or compress

$$\Delta U = Q - W$$
$$dU = dQ = C_V dT$$

where C_V is the molar constant-volume heat capacity of the gas

 ΔU and C_V of ideal gases are functions of only temperature so ΔU for an ideal gas can always be calculated by $\int C_V dT$, regardless of the process



The Constant Pressure Process

The first law of thermodynamics simplifies accordingly for the special case of constant P:

$$\Delta U = Q - W$$

$$\Delta U = Q - P \Delta V$$

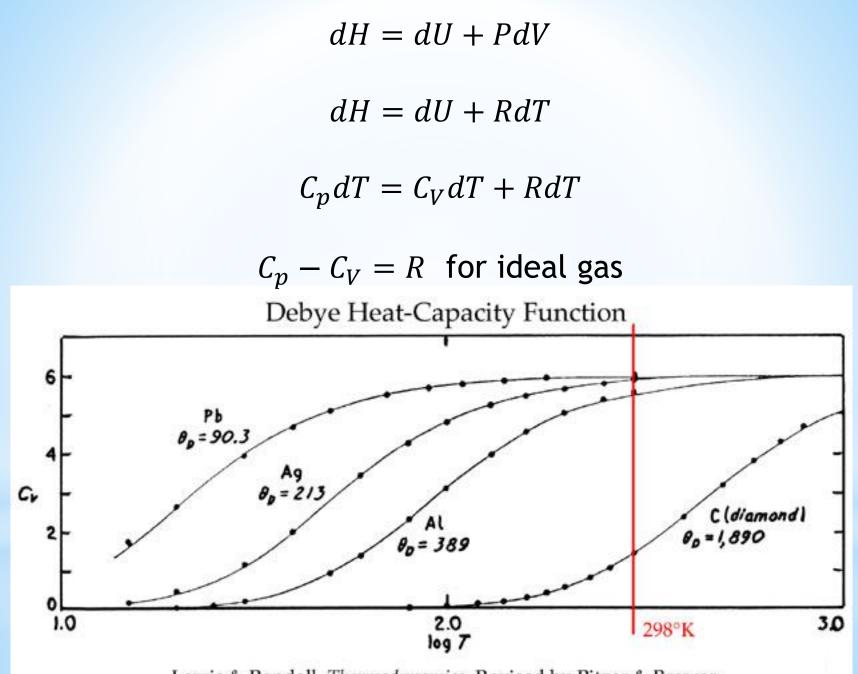
 $Q = \Delta U + P \Delta V$ state function

Enthalpy change $\Delta H = Q$ for a constant P process

$$C = \frac{\delta Q}{dT}$$
$$dH = \delta Q = C_p dT$$
$$H = U + PV = U + RT$$

Both enthalpy and C_p of ideal gases also depend only on temperature

 $dH = C_p dT$ for all process of ideal gas just as $dU = C_V dT$



Lewis & Randall, *Thermodynamics*, Revised by Pitzer & Brewer, 2nd Edition, McGraw-Hill, 1961, p. 56.

The Constant Temperature Process Internal energy of ideal gas stays constant in an isothermal process

$$dU = dQ - dW = 0$$

$$Q = W$$

For a mechanically reversible process work is done by expansion

$$W = \int P dV = \int RT \frac{dV}{V}$$

$$Q = W = RT \ln \frac{V_2}{V_1}$$

Since $P_1/P_2 = V_2/V_1$ for constant temperature,

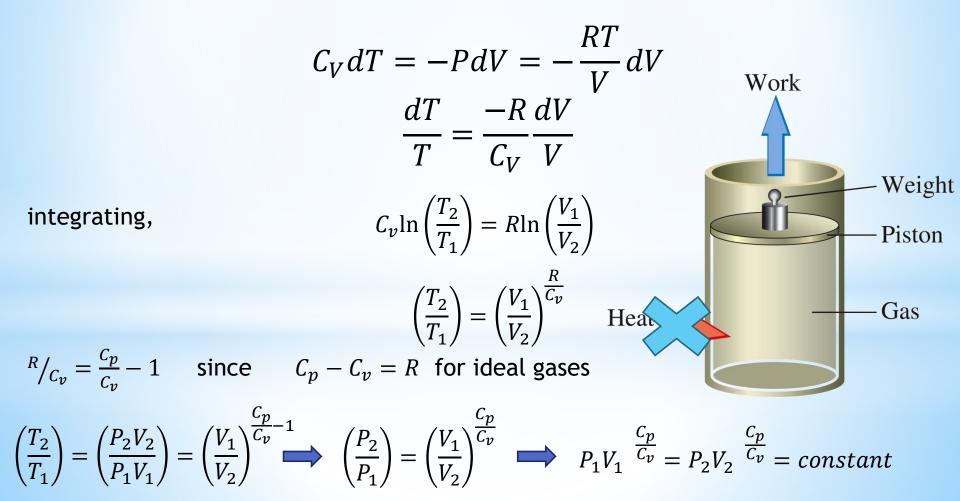
$$Q = W = RT \ln \frac{P_1}{P_2}$$

Work
Weight
Piston
Gas

The Adiabatic Process There is no heat flow into or out of the system in adiabatic processes

$$dU = -dW = PdV$$

Since internal energy change of ideal gas for any process is $dU = C_V dT$,



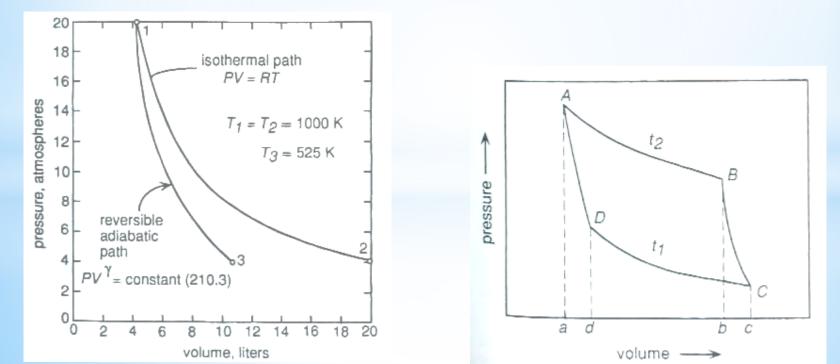
Reversible isothermal expansion of an ideal gas

$$Q = W = \int P \, dV = RT \ln\left(\frac{V_2}{V_1}\right) = RT \ln\left(\frac{P_1}{P_2}\right)$$

so $P_1V_1 = P_2V_2 = constant$

The work done by a reversible isothermal process exceeds that of the reversible adiabatic because the internal energy of the adiabatically contained system decreases while performing work

Isothermal paths are utilized in heat engines to perform higher work



The General Process

When no specific conditions other than mechanical reversibility are present, the following general equations apply to ideal gas:

$$dU = dQ - dW \qquad \Delta U = \Delta Q - \Delta W$$
$$dW = PdV \qquad \Delta W = \int PdV$$
$$dU = C_V dT \qquad \Delta U = \int C_V dT$$
$$dH = C_P dT \qquad \Delta H = \int C_P dT$$

Values for Q cannot be determined directly and is obtained from the first law:

$$dQ = C_V dT + P dV$$

$$Q = \int C_V dT + \int P dV$$

Heat is defined as the form of energy that is transferred through the boundary of a system as a result of temperature difference

Energy cannot be stored in the form of heat energy, it is transferred between bodies of different temperatures and stored as the increase in internal energy of the heated body

Heat is not a state function and is dependent on the path

Computation of heat along different paths give different results

When heat is transferred into the system, Q is considered positive When heat is transferred from the system, Q is considered negative

An *adiabatic path* restricts transfer of energy in and out of the system as heat

$$\delta Q = 0, \qquad dU = -W$$

The work is done by the system in this case at the expense of interal energy

A constant volume path restricts any expansion work

$$dV = 0, \qquad \delta W = P dV = 0$$

so $dU = \delta Q_V,$

A constant pressure path results in the maximum amount of work obtained

$$dU = \delta Q - P dV$$

$$\delta Q_P = d\mathbf{U} + \mathbf{P}dV = d(\mathbf{U} + PV) = dH$$

Enthalpy, a state function, is the representation of heat at constant pressure process

Most processes in practice occur at constant pressure of 1 atm E.g. Smelting, mixing, precipitation

Enthalpies of all phase change and formation processes are tabulated

Positive enthalpy for a process means it requires a heat input and is endothermic Negative enthalpy for a process means it releases heat and is exothermic

Enthalpies of formation of common compounds at STP

Compound	∆H _f (kJ/mol)) Compound	∆H _f (kJ/mol)) Compound	∆H _f (kJ/mol)) Compound	ΔH _f (kJ/mol)
AgBr(s)	-99.5	$H_2O(l)$	-285.8	$C_2H_2(g)$	+226.7	NH₄Cl(s)	-315.4
AgCl(s)	-127.0	$H_2O_2(l)$	-187.6	$C_2H_4(g)$	+52.3	$NH_4NO_3(s)$	-365.1
Agl(s)	-62.4	$H_2S(g)$	-20.1	$C_2H_6(g)$	-84.7	NO(g)	+90.4
$Ag_2O(s)$	-30.6	$H_2SO_4(l)$	-811.3	$C_3H_8(g)$	-103.8	$NO_2(g)$	+33.9
$Ag_2S(s)$	-31.8	HgO(s)	-90.7	n-C ₄ H ₁₀ (g)	-124.7	NiO(s)	-244.3
$Al_2O_3(s)$	-1669.8	HgS(s)	-58.2	n-C ₅ H ₁₂ (l)	-173.1	PbBr ₂ (s)	-277.0
BaCl ₂ (s)	-860.1	KBr(s)	-392.2	C ₂ H ₅ OH(l)	-277.6	PbCl ₂ (s)	-359.2
BaCO ₃ (s)	-1218.8	KCl(s)	-435.9	CoO(s)	-239.3	PbO(s)	-217.9
BaO(s)	-558.1	KClO ₃ (s)	-391.4	$Cr_2O_3(s)$	-1128.4	PbO ₂ (s)	-276.6
BaSO ₄ (s)	-1465.2	KF(s)	-562.6	CuO(s)	-155.2	$Pb_3O_4(s)$	-734.7
CaCl ₂ (s)	-795.0	MgCl ₂ (s)	-641.8	Cu ₂ O(s)	-166.7	PCl ₃ (g)	-306.4
CaCO ₃	-1207.0	$MgCO_3(s)$	-1113	CuS(s)	-48.5	PCl ₅ (g)	-398.9
CaO(s)	-635.5	MgO(s)	-601.8	CuSO ₄ (s)	-769.9	SiO ₂ (s)	-859.4
Ca(OH) ₂ (s)	-986.6	$Mg(OH)_2(s)$	-924.7	$Fe_2O_3(s)$	-822.2	SnCl ₂ (s)	-349.8
CaSO ₄ (s)	-1432.7	MgSO ₄ (s)	-1278.2	$Fe_3O_4(s)$	-1120.9	SnCl ₄ (l)	-545.2
CCl ₄ (l)	-139.5	MnO(s)	-384.9	HBr(g)	-36.2	SnO(s)	-286.2
CH ₄ (g)	-74.8	$MnO_2(s)$	-519.7	HCl(g)	-92.3	SnO ₂ (s)	-580.7
CHCl ₃ (l)	-131.8	NaCl(s)	-411.0	HF(g)	-268.6	$SO_2(g)$	-296.1
CH ₃ OH(l)	-238.6	NaF(s)	-569.0	HI(g)	+25.9	So ₃ (g)	-395.2
CO(g)	-110.5	NaOH(s)	-426.7	HNO ₃ (l)	-173.2	ZnO(s)	-348.0
$CO_2(g)$	-393.5	$NH_3(g)$	-46.2	$H_2O(g)$	-241.8	ZnS(s)	-202.9

The knowledge of the final temperature of the system is not enough to determine the final state of the system since internal energy also depends on pressure

This second variable should either be varied in a specified path or maintained constant during the change

For a constant volume path recall that $dU = \delta Q_V$

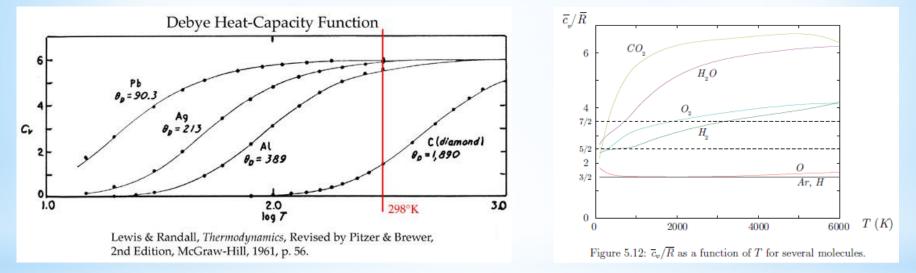
Constant volume heat capacity
$$C_V = \frac{\delta Q}{dT} = \left[\frac{dU}{dT}\right]_V$$
, $dU = C_V dT$
$$\Delta U = \int_{T_1}^{T_2} C_V dT$$

For a constant pressure path recall that $dH = \delta Q_P$

Constant pressure heat capacity $C_P = \frac{\delta Q}{dT} = \left[\frac{dH}{dT}\right]_V$, $dH = C_P dT$ $\Delta H = \int_{T_1}^{T_2} C_P dT$ Heat capacities are extensive properties with the SI unit J/K However it is more convenient to use the heat capacity per unit quantity of the system, thus specific heat or molar heat capacity are used per mole of substance

 $nc_P = C_P$, and $nc_V = C_V$ where c_P and c_V are the molar heat capacities

Heat capacity is a function of temperature



The C_P and C_V values for various gases are independent of temperature over a wide range of temperatures and are considered constant as an approximation to ideal gas law

The values of molar heat capacities for various gases are $C_P = \frac{5}{2}$ and $C_V = \frac{3}{2}$ for monatomic gases (He, Ar, etc.) $C_P = \frac{7}{2}$ and $C_V = \frac{5}{2}$ for diatomic gases (H₂, O₂, CO, etc.) $C_P = 4$ and $C_V = 3$ for polyatomic gases (CO₂, CH₄, SO₂, etc.) Since dH = dU + PdV, C_p is expected to be greater than C_v

If the temperature of an ideal gas is raised by dT at constant volume, all of the internal energy change equals the heat gained during the process However, if the temperature change happens at constant pressure, some energy will be needed to expand the system:

$$\frac{PdV}{dT}$$
 or $P\left(\frac{\delta V}{\delta T}\right)_P$

Hence
$$C_p - C_v = P\left(\frac{\delta V}{\delta T}\right)_P = P\frac{R}{P} = R$$
 for ideal gases

Ideal gas is defined to behave as a gas with infinite intermolecular distance, negligible intermolecular attraction and zero pressure. Hence, internal energy of an ideal gas is a function of temperature and independent of volume and pressure

For real gases,
$$C_p - C_v = \left(\frac{\delta V}{\delta T}\right)_P \left[P + \left(\frac{\delta U}{\delta V}\right)_T\right]$$

The derivation is as follows

Thus,

$$C_{p} = \left(\frac{\delta H}{\delta T}\right)_{p}, C_{v} = \left(\frac{\delta U}{\delta T}\right)_{v}$$

$$H = U + PV$$

$$C_{p} - C_{v} = \left(\frac{\delta U}{\delta T}\right)_{p} + P\left(\frac{\delta V}{\delta T}\right)_{p} - \left(\frac{\delta U}{\delta T}\right)_{v}$$

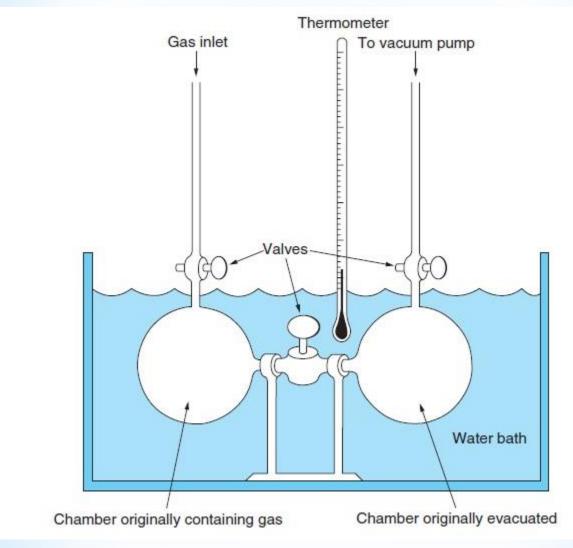
$$dU = \left(\frac{\delta U}{\delta V}\right)_{T} dV + \left(\frac{\delta U}{\delta T}\right)_{v} dT, \text{ since } U = f(V, T)$$

$$\left(\frac{\delta U}{\delta T}\right)_{p} = \left(\frac{\delta U}{\delta V}\right)_{T} \left(\frac{\delta V}{\delta T}\right)_{p} + \left(\frac{\delta U}{\delta T}\right)_{v}$$

$$C_{p} - C_{v} = \left(\frac{\delta U}{\delta V}\right)_{T} \left(\frac{\delta V}{\delta T}\right)_{p} + \left(\frac{\delta U}{\delta T}\right)_{v} + P\left(\frac{\delta V}{\delta T}\right)_{p} - \left(\frac{\delta U}{\delta T}\right)_{v}$$

$$C_{p} - C_{v} = \left(\frac{\delta U}{\delta V}\right)_{T} \left(\frac{\delta V}{\delta T}\right)_{p} + \left(\frac{\delta V}{\delta T}\right)_{p} + P\left(\frac{\delta V}{\delta T}\right)_{p}$$
mpt to evaluate $\left(\frac{\delta U}{\delta V}\right)_{T}$ for cases - loule performed an expension

In an attempt to evaluate $\left(\frac{\delta U}{\delta V}\right)_T$ for gases, Joule performed an experiment which involved filling a copper vessel with a gas at some pressure and connecting this vessel to a similar but evacuated vessel, allowing free expansion of the gas into evacuated vessel



Joule's Experiment Setup

Joule could not detect any change in the temperature of the system...

$$\Delta U = 0, \ \left(\frac{\delta U}{\delta V}\right)_T = 0$$

The system was adiabatic and isothermal so no work was performed

However Joule tried again with more precise instruments and detected a small temperature change which was undetectable by his first experimental setup due to the large heat capacity of the copper vessel which absorbed all the energy itself

 $\left(\frac{\delta U}{\delta V}\right)_T \left(\frac{\delta V}{\delta T}\right)_p$ represents the work done per degree rise in temperature in expanding against the internal cohesive forces acting between the molecules of the gas The term is large for gases and small for liquids and solids so $\left(C_p - C_v\right)_{gas} > \left(C_p - C_v\right)_{condensed}$

For condensed substances $C_p \cong C_v$

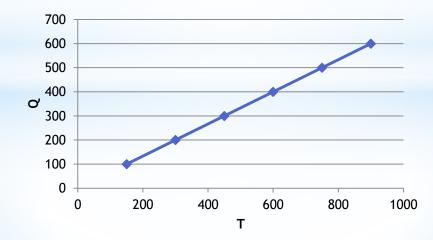
Experimental determination of heat capacities

Calorimeters are used for determination of heat capacities. Amount of heat transferred from a calorimeter to a sample is calculated from the mass and specific heat of the sample

$$Q_P = \Delta H = \int_{T_0}^{T_f} C_P dT, \qquad Q_P = f(T)$$

The process is repeated for several temperatures until a good fit of Q_P versus T is obtained. Specific heat capacity of the sample is determined from temperature dependency of Q_P

Since Q_P is the integral of C_P vs T, the derivative of Q_P vs T gives C_P



Empirical representation of heat capacities

Variation of heat capacity with temperature for a substance is fitted to an expression of the form:

$$C_P = a + bT + \frac{c}{T^2} + dT^3 + \cdots$$

The analytical form of C_P permits the calculation of enthalpy change between specific temperatures

The heat required to change the temperature of the system is calculated as:

$$\Delta H = H_2 - H_1 = n \int_{T_1}^{T_2} C_P dT = n \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2} \right) dT$$

Example - Calculate the heat required when 2 moles of Cu is heated from 100 C to 800 C. C_P =22.65+0.00628T J/mol K

Example - 54 grams of liquid silver at 1027 C and solid silver at 727 C are heated seperately. Calculate the heat required to raise their temperatures by 100 C. Molecular weight = 108 g Melting temperature = 960.8 C TABLO: 5.1 — Bazı maddelere ait $C_p = a + bT + cT^{-2}$ denklemindeki katsayılar, C_p nin boyutları (cal.mol⁻¹ K⁻¹) dir

Madde	а	b×10 ³	C×10-5	Muteber Stcaklık Aralığı, K	Ref.
the state of the s	5,09	2,04	0,36	298Ergime	(1)
Ag (k)	7,30	2,01		Ergime - 1600	(1)
Ag (s)	4,94	2,96		298 Ergime	(1)
A1 (k)	7,00		<u></u>	Ergime - 1273	(1)
Al (s)	5,41	1,50	and the second	298 - Ergin	(1)
Cu (k)	7,50	1,00	1	Ergime - 1600	(1)
Cu (s) Pb (k)	5,63	2,33		298 - Frgime	(1)
Pb (s)		(0,74		Ergime — 1200	(1)
Fe(a)	4,18	5,92		273-1033	(1)
$Fe(\beta)$	9,0			1033 - 1081	(1)
$Fe(\gamma)$	1,84			1181 - 1674	(1)
$Fe(\delta)$	10,5		1	1674 — Ergime	(1)
CuO (k)	9,27	4,8		293 - Ergime	(1)
A1.O. (k)	27,38	3,08	(8,20)	298 - 1800	(1)
AuZn (k)	11,51	3,56	<u> </u>	298 Ergime	(1)
$N_2(g)$	6,65	1,02			·
O ₂ (g)	7,16	1,00	(0,40)	298-3000	(1)
CO (g)	6,59	0,98	(-0,11)	298 2500	(1)
$CO_2(g)$	10,53	2,16	(-2.04)	298 1800	(1)
H ₂ O (g).	6,67	2,56	0,08		
PbS (k)	10,66	3,92	· · · · · · · · · · · · · · · · · · ·	298 - 900	(1)
PbO (sarı)	9,05	6,40	State State State	298 - 1000	(1)
PpSO; (k)	10,96	31,00	. 4,20	298 - 1100	(1)
$SO_2(g)$	10,38	2,54	(-1,42)	298 - 1800	(1)
PbSO ₄ PbO	20,01	37,40	4,20	298 - 1000	(2)
PbSO4 2PbO	29,06	43,80	4,20	298 - 1000	(2)
PbSO, 4PbO	47,16	56,60	4,20	233 - 1000 298 - 1000	(2)

 O Kubaschewski, E. LL. Evans, Metallurgical Thermochemistry, Pergamon Press - 1958.

 H. H. Kellog, S. K. Basu, Transactions — AIME: V. 218, Febr. 1960. Sah. 70. Heat capacity of many substances are unknown. Indirect calculation of the heat capacities of these materials is possible by the "Neumann-Kopp" method:

$$xA(s) + yB(s) = A_xB_y (s)$$
$$C_p (A_xB_y) = x (C_p)A + y(C_p)B$$

Example - Calculate the heat capacity of $PbSO_4PbO$ solid solution using the heat capacity of the solids $PbSO_4$ and PbO

Sensible Heat - The amount of heat that must be added when a substance undergoes a change in temperature from 298 K to an elevated temperature without a change in phase

$$\Delta H = n \int_{298}^{T} C_P dT = \int_{298}^{T} a + bT + \frac{c}{T^2}$$
$$= aT + \frac{b}{2}T^2 - \frac{c}{T} - a * 298 + \frac{b}{2}298^2 - \frac{c}{298}$$

Heat of Transformation - The amount of heat that must be transferred when a substance completely undergoes a phase change without a change in temperature

• Heat of Vaporization: The amount of heat added to vaporize a liquid or amount of heat removed to condense a vapor or gas $Q = mL_v$

where: L - latent heat of vaporization, KJ/kg

m - mass, kg, kg/sec

• Heat of Fusion: It is the amount of heat added to melt a solid or the amount of heat removed to freeze a liquid

$$Q = mL_F$$

where: L - latent heat of fusion, KJ/kg m - mass, kg, kg/sec Example - Calculate the enthalpy change of 1 mole of copper when it is heated from room temperature to 1200 °C $\Delta H_m = 3100 \text{ cal/mol}$ at 1083 °C, $C_P (s) = 5.41 + 0.0015T \text{ cal/mol}$.K, $C_P (l) = 7.50 \text{ cal/mol}$.K

Example - The normal freezing point of mercury is -38.9 °C, and its molar enthalpy of fusion is $\Delta H_{fusion} = 2.29 \text{ kJ/mol}$. What is the enthalpy change of the system when the temperature of 50.0 g of Hg(l) is decreased from 25 °C to -50 °C?

MW_{Hg}=200.6 g, C_P (s)= 8.41+0.0029T+132000/T cal/mol.K, C_P (l)= 7.75-0.0074T-11000 cal/mol.K