

Quantum Mechanics_Enthalpy

Enthalpy is a defined thermodynamic potential, designated by the letter "H", that consists of the Internal energy of the system (U) plus the product of Pressure (P) and volume (V) of the system:[1]

$$H = U + PV$$

Since enthalpy, H, consists of Internal energy, U, plus the product of Pressure (P) and the volume(V) of the system, which are all functions of the state of the thermodynamic system, enthalpy is a state function.

The unit of measurement for enthalpy in the International System of Units (SI) is the joule, but other historical, conventional units are still in use, such as the British thermal unit and the calorie.

The enthalpy is the preferred expression of system energy changes in many chemical, biological, and physical measurements, because it simplifies certain descriptions of energy transfer. Enthalpy change accounts for energy transferred to the environment at constant pressure through expansion or heating.

The total enthalpy, *H*, of a system cannot be measured directly. The same situation exists in classical mechanics: only a change or difference in energy carries physical meaning. Enthalpy itself is a thermodynamic potential, so in order to measure the enthalpy of a system, we must refer to a defined reference point; therefore what we measure is the change in enthalpy, ΔH . The change ΔH is positive in endothermic reactions, and negative in heat-releasing exothermic processes. ΔH of a system is equal to the sum of non-mechanical work done on it and the heat supplied to it.

For processes under constant pressure, ΔH is equal to the change in the internal energy of the system, plus the work that the system has done on its surroundings.[2] This means that the change in enthalpy under such conditions is the heat absorbed (or released) by the material through a chemical reaction or by external heat transfer. Enthalpies for chemical substances at constant pressure

assume standard state: most commonly 1 bar pressure. Standard state does not, strictly speaking, specify a temperature (see standard state), but expressions for enthalpy generally reference the standard heat of formation at 25 °C.

Enthalpy of ideal gases and incompressible solids and liquids does not depend on pressure, unlike Entropy and Gibbs energy. Real materials at common temperatures and pressures usually closely approximate this behavior, which greatly simplifies enthalpy calculation and use in practical designs and analyses.

Origins

The word *enthalpy* is based on the Greek noun *enthalpos* (ἐνθαλπος), which means *heating*. It comes from the Classical Greek prefix *ἐν-*, *en-*, meaning *to put into*, and the verb *θάλπειν*, *thalpein*, meaning "to heat". The word *enthalpy* is often incorrectly attributed ^[citation needed] to Benoît Paul Émile Clapeyron and Rudolf Clausius through the 1850 publication of their Clausius-Clapeyron relation. This misconception was popularized by the 1927 publication of *The Mollier Steam Tables and Diagrams*. However, neither the concept, the word, nor the symbol for enthalpy existed until well after Clapeyron's death.

The earliest writings to contain the concept of enthalpy did not appear until 1875,^[3] when Josiah Willard Gibbs introduced "a heat function for constant pressure". However, Gibbs did not use the word "enthalpy" in his writings.^[note 1] The actual word first appears in the scientific literature in a 1909 publication by J. P. Dalton. According to that publication, Heike Kamerlingh Onnes (1853–1926) actually coined the word.^[4] Over the years, many different symbols were used to denote enthalpy. It was not until 1922 that Alfred W. Porter proposed the symbol "H" as the accepted standard,^[5] thus finalizing the terminology still in use today.

Formal definition

The enthalpy of a homogeneous system is defined as:^{[6][7]}

$$H = U + pV$$

where

H is the enthalpy of the system

U is the Internal energy of the system

p is the Pressure of the system

V is the Volume of the system.

The enthalpy is an extensive property. This means that, for homogeneous systems, the enthalpy is proportional to the size of the system. It is convenient to introduce the specific enthalpy $h = H/m$ where m is the mass of the system, or the molar enthalpy $H_m = H/n$, where n is the number of moles (h and H_m are intensive properties). For inhomogeneous systems the enthalpy is the sum of the enthalpies of the composing subsystems

$$H = \sum_k H_k$$

where the label k refers to the various subsystems. In case of continuously varying p , T , and/or composition the summation becomes an integral:

$$H = \int \rho h dV,$$

where ρ is the density.

The enthalpy $H(S, p)$ of homogeneous systems can be derived as a characteristic function of the entropy S and the pressure p as follows: we start from the first law of thermodynamics for closed systems for an infinitesimal process

$$dU = \delta Q - \delta W.$$

Here, δQ is a small amount of heat added to the system and δW a small amount of work performed by the system. In a homogeneous system only reversible processes can take place so the second law of thermodynamics gives $\delta Q = T dS$ with T the absolute temperature of the system. Furthermore, if only pV work is done, $\delta W = p dV$. As a result

$$dU = T dS - p dV.$$

Adding $d(pV)$ to both sides of this expression gives

$$dU + d(pV) = T dS - p dV + d(pV)$$

or

$$d(U + pV) = T dS + V dp.$$

So

$$dH(S, p) = T dS + V dp.$$

Other expressions

The expression of dH in terms of entropy and pressure may be unfamiliar to many readers. However, there are expressions in terms of more familiar variables such as temperature and pressure [8][9]

$$dH = C_p dT + V(1 - \alpha T) dp.$$

Here C_p is the heat capacity at constant pressure and α is the coefficient of (cubic) thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p.$$

With this expression one can, in principle, determine the enthalpy if C_p and V are known as functions of p and T .

Notice that for an Ideal gas, $\alpha T = 1$,^[note 2] so that:

$$dH = C_p dT$$

In a more general form, the first law describes the internal energy with additional terms involving the Chemical potential and the number of particles of various types.

The differential statement for dH then becomes:

$$dH = TdS + Vdp + \sum_i \mu_i dN_i$$

where μ_i is the chemical potential per particle for an i -type particle, and N_i is the number of such particles. The last term can also be written as μdn_i (with dn_i the number of moles of component i added to the system and, in this case, μ_i the molar chemical potential) or as μdm_i (with dm_i the mass of component i added to the system and, in this case, μ_i the specific chemical potential).

Enthalpy versus internal energy

The U term can be interpreted as the energy required to create the system, and the pV term as the energy that would be required to "make room" for the system if the pressure of the environment remained constant. When a system, for example, n moles of a gas of Volume V at Pressure p and temperature T , is created or brought to its present state from absolute zero, energy must be supplied equal to its internal energy U plus pV , where pV is the work done in pushing against the ambient (atmospheric) pressure.

In basic physics and statistical mechanics it may be more interesting to study the internal properties of the system and therefore the internal energy is used.^{[10][11]} In basic chemistry, experiments are often conducted at atmospheric pressure and H is therefore more useful for reaction energy calculations. Furthermore the enthalpy is the workhorse of engineering thermodynamics as we will see later.

Relationship to heat

In order to discuss the relation between the enthalpy increase and heat supply we return to the first law for closed systems: $dU = \delta Q - \delta W$. We apply it to the special case

that the pressure at the surface is uniform. In this case the work term can be split in two contributions, the so-called pV work, given by $p dV$ (where here p is the pressure at the surface, dV is the increase of the volume of the system) and other types of work $\delta W'$ such as by a shaft or by electromagnetic interaction. So we write $\delta W = p dV + \delta W'$.

In this case the first law reads

$$dU = \delta Q - p dV - \delta W'$$

or

$$dH = \delta Q + V dp - \delta W'.$$

From this relation we see that the increase in enthalpy of a system is equal to the added Heat

$$dH = \delta Q$$

provided that the system is under constant pressure ($dp = 0$) and that the only work done by the system is expansion work ($\delta W' = 0$)^[12]

Applications

In thermodynamics, one can calculate enthalpy by determining the requirements for creating a system from "nothingness"; the mechanical work required, pV , differs based upon the constancy of conditions present at the creation of the thermodynamic system. Internal energy, U , must be supplied to remove particles from a surrounding in order to allow space for the creation of a system, providing that environmental variables, such as pressure (p) remain constant. This internal energy also includes the energy required for activation and the breaking of bonded compounds into gaseous species.

This process is calculated within enthalpy calculations as $U + pV$, to label the amount of energy or work required to "set aside space for" and "create" the system; describing the work done by both the reaction or formation of systems, and the surroundings. For systems at constant pressure, the change in enthalpy is the heat received by the system.

Therefore, the change in enthalpy can be devised or represented without the need for compressive or expansive mechanics; for a simple system, with a constant number of particles, the difference in enthalpy is the maximum amount of thermal energy derivable from a thermodynamic process in which the pressure is held constant.^[this quote needs a citation]

The term pV is the work required to displace the surrounding atmosphere in order to vacate the space to be occupied by the system.

Heat of reaction

The total enthalpy of a system cannot be measured directly; the *enthalpy change* of a system is measured instead. Enthalpy change is defined by the following equation:

$$\Delta H = H_f - H_i$$

where

ΔH is the "enthalpy change"

H_f is the final enthalpy of the system, expressed in joules. In a chemical reaction, H_f is the enthalpy of the products.

H_i is the initial enthalpy of the system, expressed in joules. In a chemical reaction, H_i is the enthalpy of the reactants.

For an exothermic reaction at constant Pressure, the system's change in enthalpy equals the energy released in the reaction, including the energy retained in the system and lost through expansion against its surroundings. In a similar manner, for an endothermic reaction, the system's change in enthalpy is equal to the energy *absorbed* in the reaction, including the energy *lost by* the system and *gained* from compression from its surroundings. A relatively easy way to determine whether or not a reaction is exothermic or endothermic is to determine the sign of ΔH . If ΔH is positive, the reaction is endothermic, that is heat is absorbed by the system due to the products of the reaction having a greater enthalpy than the reactants. On the other hand if ΔH is negative, the reaction is exothermic, that is the overall decrease in enthalpy is achieved by the generation of heat.

Although enthalpy is commonly used in engineering and science, it is impossible to measure directly, as enthalpy has no datum (reference point). Therefore enthalpy can only accurately be used in a closed system. However, few real-world applications exist in closed isolation, and it is for this reason that two or more closed systems cannot correctly be compared using enthalpy as a basis.

Specific enthalpy

As noted before, the specific enthalpy of a uniform system is defined as $h = H/m$ where m is the mass of the system. The SI unit for specific enthalpy is joule per kilogram. It can be expressed in other specific quantities by $h = u + p\nu$, where u is the specific Internal energy, p is the pressure, and ν is specific volume, which is equal to $1/\rho$, where ρ is the density.

Enthalpy changes

An enthalpy change describes the change in enthalpy observed in the constituents of a thermodynamic system when undergoing a transformation or chemical reaction. It is the difference between the enthalpy after the process has completed, i.e. the enthalpy of the products, and the initial enthalpy of the system, i.e. the reactants. These processes are reversible and the enthalpy for the reverse process is the negative value of the forward change.

A common standard enthalpy change is the enthalpy of formation, which has been determined for a large number of substances. Enthalpy changes are routinely measured and compiled in chemical and physical reference works, such as the CRC Handbook of Chemistry and Physics. The following is a selection of enthalpy changes commonly recognized in thermodynamics.

When used in these recognized terms the qualifier *change* is usually dropped and the property is simply termed *enthalpy of 'process'*. Since these properties are often used as reference values it is very common to quote them for a standardized set of environmental parameters, or standard conditions, including:

- A temperature of 25 °C or 298 K,
- A Pressure of one atmosphere (1 atm or 101.325 kPa),
- A concentration of 1.0 M when the element or compound is present in solution,
- Elements or compounds in their normal physical states, i.e. standard state.

For such standardized values the name of the enthalpy is commonly prefixed with the term *standard*, e.g. *standard enthalpy of formation*.

Chemical properties:

- Enthalpy of reaction, defined as the enthalpy change observed in a constituent of a thermodynamic system when one mole of substance reacts completely.
- enthalpy of formation, defined as the enthalpy change observed in a constituent of a thermodynamic system when one mole of a compound is formed from its elementary antecedents.
- Enthalpy of combustion, defined as the enthalpy change observed in a constituent of a thermodynamic system when one mole of a substance burns completely with oxygen.
- Enthalpy of hydrogenation, defined as the enthalpy change observed in a constituent of a thermodynamic system when one mole of an unsaturated

compound reacts completely with an excess of hydrogen to form a saturated compound.

- Enthalpy of atomization, defined as the enthalpy change required to atomize one mole of compound completely.
- Enthalpy of neutralization, defined as the enthalpy change observed in a constituent of a thermodynamic system when one mole of water is formed when an acid and a base react.
- Standard Enthalpy of solution, defined as the enthalpy change observed in a constituent of a thermodynamic system when one mole of a solute is dissolved completely in an excess of solvent, so that the solution is at infinite dilution.
- Standard enthalpy of Denaturation (biochemistry), defined as the enthalpy change required to denature one mole of compound.
- Enthalpy of hydration, defined as the enthalpy change observed when one mole of gaseous ions are completely dissolved in water forming one mole of aqueous ions.

Physical properties:

- Enthalpy of fusion, defined as the enthalpy change required to completely change the state of one mole of substance between solid and liquid states.
- Enthalpy of vaporization, defined as the enthalpy change required to completely change the state of one mole of substance between liquid and gaseous states.
- Enthalpy of sublimation, defined as the enthalpy change required to completely change the state of one mole of substance between solid and gaseous states.
- Lattice enthalpy, defined as the energy required to separate one mole of an ionic compound into separated gaseous ions to an infinite distance apart (meaning no force of attraction).
- Enthalpy of mixing, defined as the enthalpy change upon mixing of two (non-reacting) chemical substances.

Open systems

In thermodynamic open systems, matter may flow in and out of the system boundaries. The first law of thermodynamics for open systems states: The increase in the internal energy of a system is equal to the amount of energy added to the system by matter flowing in and by heating, minus the amount lost by matter flowing out and in the form of work done by the system. The first law for open systems is given by:

$$dU = \delta Q + dU_{in} - dU_{out} - \delta W$$

where U_{in} is the average internal energy entering the system and U_{out} is the average internal energy leaving the system.

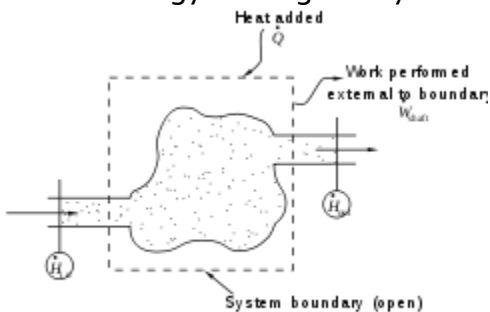


Fig.1 During steady, continuous operation, an energy balance applied to an open system equates shaft work performed by the system to heat added plus net enthalpy added

The region of space enclosed by open system boundaries is usually called a Control volume, and it may or may not correspond to physical walls. If we choose the shape of the control volume such that all flow in or out occurs perpendicular to its surface, then the flow of matter into the system performs work as if it were a piston of fluid pushing mass into the system, and the system performs work on the flow of matter out as if it were driving a piston of fluid. There are then two types of work performed: *flow work* described above, which is performed on the fluid (this is also often called *pV work*), and *shaft work*, which may be performed on some mechanical device.

These two types of work are expressed in the equation:

$$\delta W = d(p_{out}V_{out}) - d(p_{in}V_{in}) + \delta W_{shaft}$$

Substitution into the equation above for the control volume cv yields:

$$dU_{cv} = \delta Q + dU_{in} + d(p_{in}V_{in}) - dU_{out} - d(p_{out}V_{out}) - \delta W_{shaft}$$

The definition of enthalpy, H , permits us to use this thermodynamic potential to account for both internal energy and pV work in fluids for open systems:

$$dU_{cv} = \delta Q + dH_{in} - dH_{out} - \delta W_{shaft}$$

This expression is described by Fig.1. If we allow also the system boundary to move (e.g. due to moving pistons) we get a rather general form of the first law for open systems.[13] In terms of time derivatives it reads

$$\frac{dU}{dt} = \sum_k \dot{Q}_k + \sum_k \dot{H}_k - \sum_k p_k \frac{dV_k}{dt} - P,$$

where Σ represent algebraic sums and the indices k refer to the various places where heat is supplied, matter flows into the system, and boundaries are moving. The \dot{H}_k terms represent enthalpy flows, which can be written as

$$\dot{H}_k = h_k \dot{m}_k = H_m \dot{n}_k$$

with \dot{m}_k the mass flow and \dot{n}_k the molar flow at position k respectively. The term dV_k/dt represents the rate of change of the system volume at position k that results in pV power done by the system. The parameter P represents all other forms of power done by the system such as shaft power, but it can also be e.g. electric power produced by an electrical power plant. Note that the previous expression holds true only if the kinetic energy flow rate is conserved between system inlet and outlet. Otherwise, it has to be included in the enthalpy balance. During steady-state operation of a device (*see turbine, pump, and engine*), the average dU/dt may be set equal to zero. This yields a useful expression for the average power generation for these devices in the absence of chemical reactions

$$P = \Sigma_k \langle \dot{Q}_k \rangle + \Sigma_k \langle \dot{H}_k \rangle - \Sigma_k \left\langle p_k \frac{dV_k}{dt} \right\rangle$$

where the angle brackets denote time averages. The technical importance of the enthalpy is directly related to its presence in the first law for open systems, as formulated above.

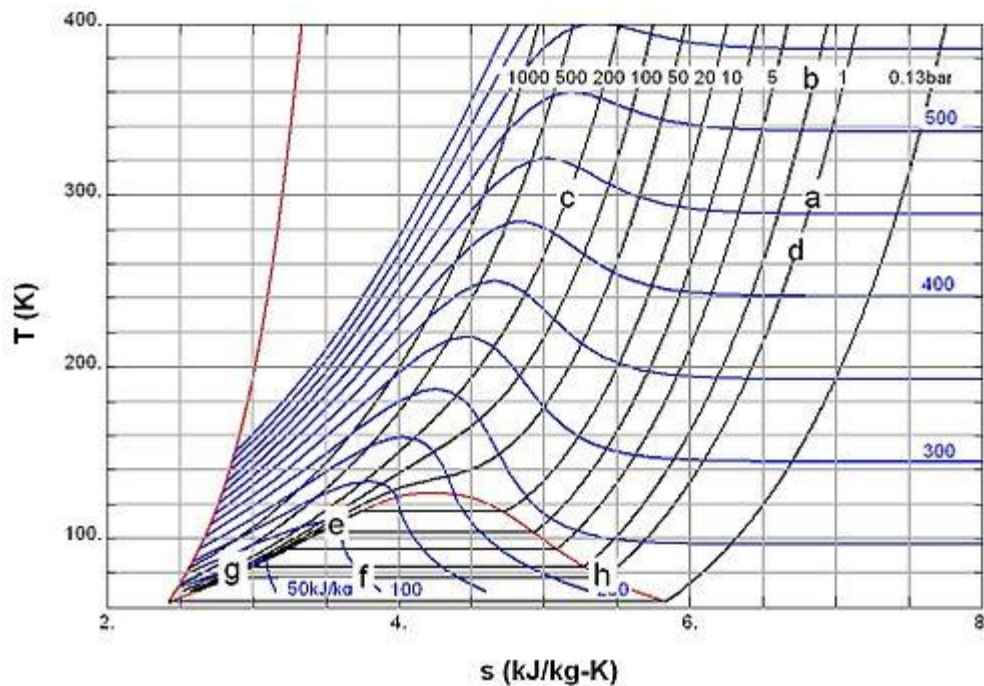


Fig.2 Ts diagram of nitrogen. The red curve at the left is the melting curve. The red dome represents the two-phase region with the low-entropy side the saturated liquid and the high-entropy side the saturated gas. The black curves give the Ts relation along isobars. The pressures are indicated in bar. The blue curves are isenthalps (curves of constant enthalpy). The values are indicated in blue in kJ/kg. The specific points a, b, etc., are treated in the main text.

Diagrams

Nowadays the enthalpy values of important substances can be obtained via commercial software. Practically all relevant material properties can be obtained either in tabular or in graphical form. There are many types of diagrams, such as hT diagrams, which give the specific enthalpy as function of temperature for various pressures and hp diagrams, which give h as function of p for various T . One of the most common diagrams is the temperature-entropy diagram (Ts-diagram). An example is Fig.2, which is the Ts-diagram of nitrogen.[14] It gives the melting curve and saturated liquid and vapor values together with isobars and isenthalps. These diagrams are powerful tools in the hands of the thermal engineer.

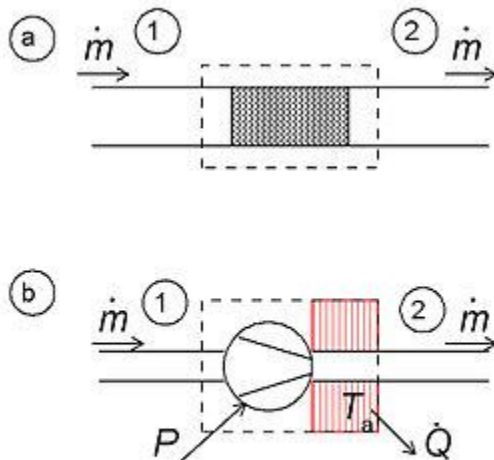


Fig.3 Two open systems in the steady state. Fluid enters the system (dotted rectangle) at point 1 and leaves it at point 2. The mass flow is \dot{m} . a: schematic diagram of the throttling process. b: schematic diagram of a compressor. A power P is applied and a heat flow \dot{Q} is released to the surroundings at ambient temperature T_a .

Some basic applications

The points a through h in Fig.2 play a role in the discussion in this Section.

a $T = 300 \text{ K}$, $p = 1 \text{ bar}$, $s = 6.85 \text{ kJ}/(\text{kgK})$, $h = 461 \text{ kJ}/\text{kg}$;

b $T = 380 \text{ K}$, $p = 2 \text{ bar}$, $s = 6.85 \text{ kJ}/(\text{kgK})$, $h = 530 \text{ kJ}/\text{kg}$;

c $T = 300 \text{ K}$, $p = 200 \text{ bar}$, $s = 5.16 \text{ kJ}/(\text{kgK})$, $h = 430 \text{ kJ}/\text{kg}$;

d $T = 270 \text{ K}$, $p = 1 \text{ bar}$, $s = 6.79 \text{ kJ}/(\text{kgK})$, $h = 430 \text{ kJ}/\text{kg}$;

e $T = 108 \text{ K}$, $p = 13 \text{ bar}$, $s = 3.55 \text{ kJ}/(\text{kgK})$, $h = 100 \text{ kJ}/\text{kg}$ (saturated liquid at 13 bar);

f $T = 77.2 \text{ K}$, $p = 1 \text{ bar}$, $s = 3.75 \text{ kJ}/(\text{kgK})$, $h = 100 \text{ kJ}/\text{kg}$;

g $T = 77.2 \text{ K}$, $p = 1 \text{ bar}$, $s = 2.83 \text{ kJ}/(\text{kgK})$, $h = 28 \text{ kJ}/\text{kg}$ (saturated liquid at 1 bar);

h $T = 77.2 \text{ K}$, $p = 1 \text{ bar}$, $s = 5.41 \text{ kJ}/(\text{kgK})$, $h = 230 \text{ kJ}/\text{kg}$ (saturated gas at 1 bar);

Throttling

Main article: [Joule-Thomson effect](#)

One of the simple applications of the concept of enthalpy is the so-called throttling process, also known as [Joule-Thomson expansion](#). It concerns a steady adiabatic flow of a fluid through a flow resistance (valve, porous plug, or any other type of flow resistance) as shown in Fig.3a. This process is very important since it is at the heart of domestic refrigerators where it is responsible for the temperature drop between ambient temperature and the interior of the fridge. It is also the final stage in many types of liquefiers.

In the first law for open systems (see above), applied to the system in Fig.3a, all terms are zero except the terms for the enthalpy flow. Hence

$$0 = \dot{m}h_1 - \dot{m}h_2.$$

Since the mass flow is constant the specific enthalpies at the two sides of the flow resistance are the same

$$h_1 = h_2$$

that is, the enthalpy per unit mass does not change during the throttling. The consequences of this relation can be demonstrated using Fig.2. Point c in Fig.2 is at 200 bar and room temperature (300 K). A Joule-Thomson expansion from 200 bar to 1 bar follows a curve of constant enthalpy of roughly 425 kJ/kg (not shown in Fig.2) lying between the 400 and 450 kJ/kg isenthalps and ends in point d, which is at a temperature of about 270 K. Hence the expansion from 200 bar to 1 bar cools nitrogen from 300 K to 270 K. In the valve there is a lot of friction and a lot of entropy is produced, but still the final temperature is below the starting value!

Point e is chosen so that it is on the saturated liquid line with $h = 100$ kJ/kg. It corresponds roughly with $p = 13$ bar and $T = 108$ K. Throttling from this point to a pressure of one bar ends in the two-phase region (point f). This means that a mixture of gas and liquid leaves the throttling valve. Since the enthalpy is an extensive parameter the enthalpy in f (h_f) is equal to the enthalpy in g (h_g) multiplied with the liquid fraction in f (x_f) plus the enthalpy in h (h_h) multiplied with the gas fraction in f ($1-x_f$). So

$$h_f = x_f h_g + (1 - x_f) h_h.$$

With numbers: $100 = x_f 28 + (1 - x_f) 230$ so $x_f = 0.64$. This means that the mass fraction of the liquid in the liquid-gas mixture that leaves the throttling valve is 64%.

Compressors

Main article: [Gas compressor](#)

Fig.3b is a schematic drawing of a compressor. A power P is applied e.g. as electrical power. If the compression is adiabatic the gas temperature goes up. In the reversible case it would be at constant entropy, which corresponds with a vertical line in Fig.2. E.g. compressing nitrogen from 1 bar (point a) to 2 bar (point b) would result in a temperature increase from 300 K to 380 K. In order to let the compressed gas exit at ambient temperature T_a heat exchange, e.g. by cooling water, is necessary. In the ideal case the compression is isothermal. The average heat flow to the surroundings is \dot{Q} .

Since the system is in the steady state the first law gives

$$0 = -\dot{Q} + \dot{m}h_1 - \dot{m}h_2 + P.$$

The minimum power, needed for the compression is realized if the compression is reversible. In that case the [second law of thermodynamics](#) for open systems gives

$$0 = -\frac{\dot{Q}}{T_a} + \dot{m}s_1 - \dot{m}s_2.$$

Eliminating \dot{Q} gives for the minimum power

$$\frac{P_{\min}}{\dot{m}} = h_2 - h_1 - T_a(s_2 - s_1).$$

E.g. compressing 1 kg of nitrogen from 1 bar to 200 bar costs at least $(h_c - h_a) - T_a(s_c - s_a)$. With the data, obtained with Fig.2, we find a value of $(430-461) - 300(5.16 - 6.85) = 476$ kJ/kg.

The relation for the power can be further simplified by writing it as

$$\frac{P_{\min}}{\dot{m}} = \int_1^2 (dh - T_a ds).$$

With $dh = Tds + vdp$ this results in the final relation

$$\frac{P_{\min}}{\dot{m}} = \int_1^2 vdp.$$

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14. Figure composed with data obtained with RefProp, NIST Standard Reference Database 23

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