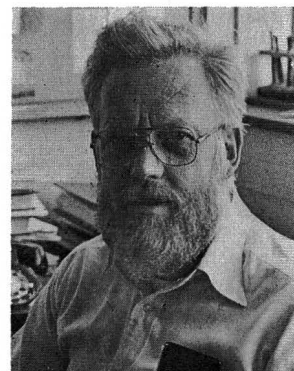


REFERENCE STATES AND RELATIVE VALUES OF INTERNAL ENERGY, ENTHALPY, AND ENTROPY

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MANY PROBLEMS IN chemical engineering thermodynamics require for their solution the application of the balance equations for moles of various chemical species, (total) energy, and entropy. Fairly general forms of these equations, which are applicable to open, moving and deforming, and unsteady state systems, are

$$\frac{dN_j}{dt} = \sum_q w_q x_{q,j} + \sum_i \alpha_{ij} R_i \quad (1)$$

$$\frac{d}{dt} (U_t + K_t + \Phi_t) = Q + W_u + W_{exp} + \sum_q w_q (h_q + k_q + \phi_q) \quad (2)$$

$$\frac{dS_t}{dt} = S + S_G + \sum_q w_q s_q \quad (3)$$

Here, the energy and entropy transfer rates associated with heat transfer, Q and S , are related to the local heat flux vector \mathbf{q} and temperature T on the boundary ∂B of the system B by

$$Q = - \int_{\partial B} (\mathbf{n} \cdot \mathbf{q})$$

$$S = - \int_{\partial B} \frac{1}{T} (\mathbf{n} \cdot \mathbf{q})$$

The second law of thermodynamics requires that the entropy generation rate S_G shall be non-negative, and further, shall be non-negative for every subsystem into which B may be divided. The quantity α_{ij} is the stoichiometric coefficient of the j^{th} chemical species in the i^{th} reaction, R_i is the rate of the i^{th} reaction in the system, and the summation on i in Eq. (1) is over a set of independent reactions [1]. The fact that all valid chemical re-

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action equations must be balanced is expressed by the conditions

$$\sum_j \alpha_{ij} \epsilon_{jk} = 0 \quad (4)$$

and this must be satisfied for all reactions (i) and all elements (k); ϵ_{jk} is the number of atoms of the k^{th} kind of element in one molecule (or meric or repeating unit) of the j^{th} chemical species. The quantity w_q is the molar flow rate of material at the q^{th} port of the system; it is positive if material enters the system at that port but negative if material leaves the system there. The mole fraction of the j^{th} chemical species in this stream is denoted by $x_{q,j}$. Finally, $-W_u$ and $-W_{exp}$ are the rates at which the system performs useful and expansion work on the surroundings, and K_t and Φ_t denote kinetic and potential energy.

Eqs. (1-3) are not valid for systems which exchange matter with their surroundings by diffusion across a permeable boundary, but they are

easily generalized to include that case also. It can be shown that the results to be deduced here apply to these more general systems also, but in the interests of simplicity such systems will not be considered further here.

The quantities U_t and S_t which appear in Eqs. (2) and (3) are the *absolute* values of the internal energy and entropy of the system, respectively, and the quantities h_q and s_q which appear in these equations are the *absolute* values of the enthalpy and entropy of one mole of the q^{th} process stream, respectively. Thermodynamics provides means for calculating *changes* in U_t , S_t , h_q , s_q when the system and the q^{th} process stream experience processes which change their states, but thermodynamics does not identify the states in which these quantities are zero. It is sometimes held that the third law of thermodynamics identifies such a state for the entropy but, within the context of classical thermodynamics at any rate, it is clear that this is not so: the third law, or rather the version of it usually called Nernst's heat theorem, asserts only that the entropy *changes* of certain kinds of systems undergoing certain kinds of isothermal processes approach zero as the temperatures of the processes approach absolute zero [2]. Hence, we do not know how to find the absolute values of U_t , S_t , h_q , and s_q .

However, we need to be able to assign numerical values to internal energy, entropy, etc. if we want to tabulate what effects changes of temperature, pressure, and composition have on them. Hence, reference states for internal energy, entropy, and enthalpy are chosen, and values of internal energy, entropy, and enthalpy relative to the reference states are tabulated. The most familiar example of this is the steam tables, but the utility of enthalpy-composition and related diagrams demonstrated in the well-known Hougen, Watson, and Ragatz book [3] make such diagrams nearly as familiar as the steam tables.

Let U_{trU} be the (absolute) internal energy of the matter of the system being considered when this matter is in the reference state for internal energy, and let S_{trS} be the (absolute) entropy of the matter of the system when this matter is in the reference state for entropy. Then the relative internal energy, U_t' , and relative entropy, S_t' , of the system are defined by

$$U_t' \equiv U_t - U_{trU} \quad (5a)$$

$$S_t' \equiv S_t - S_{trS} \quad (5b)$$

and the calculation of U_t' and S_t' involves only cal-

ulation of *changes* of internal energy and entropy. The reference quantities do not depend on the temperature and pressure of the system, though they do depend on its composition. Similarly, if we let h_{qRH} be the enthalpy of one mole of matter of the q^{th} process stream when this matter is in the reference state for enthalpy, then we can define a relative enthalpy

$$h_q' \equiv h_q - h_{qRH} \quad (5c)$$

as well as a relative entropy

$$s_q' \equiv s_q - s_{qRS} \quad (5d)$$

for the q^{th} process stream. It is necessary to place the subscript q on the reference state quantities h_{qRH} and s_{qRS} because these quantities depend on the composition of the q^{th} stream, and this is not in general the same as the composition of other process streams. However, h_{qRH} and s_{qRS} do not depend on the temperature and pressure of the q^{th} process stream.

If the relative properties U_t' , S_t' , h_q' , s_q' are to be useful then they should obey the same balance equations as do the absolute properties U_t , S_t , h_q , s_q ; that is, the relative properties should obey

$$\begin{aligned} & \frac{d}{dt} (U_t' + K_t + \Phi_t) \\ &= Q + W_u + W_{exp} + \sum_q w_q (h_q' + k_q + \phi_q) \end{aligned} \quad (6)$$

$$\frac{dS_t'}{dt} = S + S_G + \sum_q w_q s_q' \quad (7)$$

where Q , W_u , W_{exp} , S , and S_G are the same quantities that appear in Eqs. (2) and (3). Clearly, if the relative properties satisfy these balance equations they then can be used (correctly) in the calculations of heat and work effects that occur so frequently in applied thermodynamics. I have been unable to find a recent discussion of the choices of reference states which will lead to Eqs. (6) and (7), and so provision of such discussion is the objective of this paper.

REFERENCE STATE 1

The Pure Chemical Compounds at Specified Conditions of T and p

Although it would be possible to choose reference states which are solutions we shall not do so here. Instead, we shall consider only reference states in which only pure substances, unmixed with other substances, are present, and present in states of aggregation that are at least metastable.

If the relative properties . . . are to be useful then they should obey the same balance equations as do the absolute properties . . .

To begin with, we choose the pure substances to be the pure compounds of which the system and the process streams are composed. The reference state for internal energy is assumed to involve in the most general case a different combination of temperature and pressure for each compound, and the temperature and pressure of the reference state for internal energy for a given compound are assumed to be different from the temperature and pressure of the reference state for entropy for that compound. If it is not possible to choose reference states in this very arbitrary way, we want to find that out.

It is easy to show that Eqs. (6) and (7) follow from Eqs. (2) and (3) and the definitions of Eqs. (5) if, and only if, the reference properties satisfy

$$\frac{dU_{trU}}{dt} - \sum_q w_q h_{qrH} = 0 \quad (8)$$

and

$$\frac{dS_{trS}}{dt} - \sum_q w_q s_{qrs} = 0 \quad (9)$$

These equations are general; they must be satisfied for every valid choice of reference states of U_t , H_t , and S_t . It might be supposed at first that the time derivatives in these equations are zero, but such is not in general the case because, as pointed out above, the reference state quantities U_{trU} and S_{trS} depend on the composition of the system and this in general is time varying.

Consider the second of these equations first. Let s_{jrs} be the (absolute) molar entropy of the pure j^{th} compound when it is in the reference state for entropy. Then

$$S_{trS} = \sum_j N_j s_{jrs}$$

and

$$s_{qrs} = \sum_j x_{q,j} s_{jrs}$$

and from these we find that

$$\begin{aligned} \frac{dS_{trS}}{dt} - \sum_q w_q s_{qrs} &= \sum_j s_{jrs} \left(\frac{dN_j}{dt} - \sum_q w_q x_{q,j} \right) \\ &= \sum_j s_{jrs} \sum_i \alpha_{ij} R_i \\ &= \sum_i R_i \sum_j \alpha_{ij} s_{jrs} \end{aligned} \quad (10)$$

where Eq. (1) has been used. If *no chemical reactions occur*, Eq. (10) shows that Eq. (9) is satis-

fied by arbitrary choices of the entropies s_{jrs} , but if reactions occur, Eq. (10) shows that Eq. (9) will be satisfied if and only if we chose these entropies such that

$$\sum_j \alpha_{ij} s_{jrs} = 0 \quad (11)$$

for each and every independent reaction occurring. This shows that if chemical reactions occur, the conditions of temperature and pressure for the entropy reference states of the compounds of which the system is composed cannot be chosen arbitrarily, but must be chosen so that the entropies s_{jrs} satisfy a number of constraints equal to the number of independent reactions which occur.

Consider now Eq. (8). Let u_{jrU} (h_{jrH}) be the (absolute) molar internal energy (enthalpy) of the pure j^{th} compound when it is in the reference state for internal energy (enthalpy). Then

$$U_{trU} = \sum_j N_j u_{jrU}$$

$$h_{qrH} = \sum_j x_{q,j} h_{jrH}$$

and so

$$\begin{aligned} \frac{dU_{trU}}{dt} - \sum_q w_q h_{qrH} &= \sum_j \left(u_{jrU} \frac{dN_j}{dt} - h_{jrH} \sum_q w_q x_{q,j} \right) \\ &= \sum_j (u_{jrU} - h_{jrH}) \frac{dN_j}{dt} \\ &\quad + \sum_i R_i \sum_j \alpha_{ij} h_{jrH} \end{aligned} \quad (12)$$

where again Eq. (1) has been used. This result shows that in the general case Eq. (8) will be satisfied if the reference states for internal energy are chosen so that

$$u_{jrU} = h_{jrH} \quad (13)$$

for all compounds present and

$$\sum_j \alpha_{ij} h_{jrH} = 0 \quad (14)$$

for all independent reactions occurring.

In summary of the case where the reference states involve the pure compounds, we state the following. If no reactions occur, the entropy reference states for the compounds can be chosen with complete arbitrariness, and the same is true of either the internal energy reference states or the enthalpy reference states for the compounds. Once one of these latter sets of states is chosen, however, the other set of states must be chosen so as to satisfy Eq. (13); if Eq. (13) is not satisfied, Eq. (6) will not be true for unsteady state situations in-

volving open systems even though no reactions occur. If chemical reactions occur, Eq. (13) must still be satisfied, and in addition the reference states for entropy and enthalpy must satisfy the constraints imposed by Eqs. (11) and (14). These constraints are inconvenient; Eq. (14) would force us to choose reference state temperatures for the enthalpies of gases to be different for different gases, for example. Hence, we consider a reference state which is not subject to such constraints.

REFERENCE STATE 2

The Pure Elements at Specified Condition of T and p

We assume now that material in a reference state is present as the pure *elements*, unmixed with other elements or compounds, in stable or metastable states of aggregation and (in general) at different conditions of temperatures and pressure for different elements.

Let S_{krS}^E be the (absolute) molar entropy of the k^{th} kind of element in the reference state for entropy. Then

$$S_{trS} = \sum_j \sum_k N_j \epsilon_{jk} S_{krS}^E$$

and

$$S_{qrS} = \sum_j \sum_k x_{q,j} \epsilon_{jk} S_{krS}^E$$

From these, we get

$$\begin{aligned} \frac{dS_{trS}}{dt} - \sum_q w_q S_{qrS} &= \sum_j \sum_k \epsilon_{jk} S_{krS}^E \left(\frac{dN_j}{dt} - \sum_q w_q x_{q,j} \right) \\ &= \sum_i \sum_j R_i S_{krS}^E \sum_j \alpha_{ij} \epsilon_{jk} = 0 \end{aligned}$$

because of Eq. (4). Hence, with this choice of reference state for entropy, Eq. (9) will always be satisfied, even for systems in which chemical reactions occur.

Let u_{krU}^E (h_{krH}^E) be the (absolute) molar internal energy (enthalpy) of the k^{th} kind of element in the reference state for internal energy (enthalpy). Then

$$U_{trU} = \sum_j \sum_k N_j \epsilon_{jk} u_{krU}^E$$

and

$$h_{qrH} = \sum_j \sum_k x_{q,j} \epsilon_{jk} h_{krH}^E$$

From these, we find that Eq. (8) will be satisfied for all cases if we chose reference states for internal energy and enthalpy such that

$$u_{krU}^E = h_{krH}^E \quad (15)$$

and the fact that chemical reactions occur imposes no constraints of the types imposed by Eqs. (11)

and (14). We see, therefore, that the temperature and pressure of the reference state for entropy of a given element can be chosen with complete arbitrariness, as can the temperature and pressure of the reference state for internal energy or enthalpy of a given element.

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RELATION BETWEEN REFERENCE STATES FOR INTERNAL ENERGY AND ENTHALPY

The foregoing analysis shows that if Eqs. (6) and (7) are to be correct in all circumstances, then the temperatures and pressures of any pure substance (compound or element) in the reference states for internal energy and enthalpy must be such that

$$u_{rU} = h_{rH} \quad (16)$$

where we have dropped subscripts and superscripts identifying the particular element or compound considered. If the mole numbers N_j are independent of time, Eq. (6) will be valid even if reference states are not chosen so that Eq. (16) is valid. That means that it is not necessary to choose reference states so that this equation is true if we are dealing with steady state open systems (in which reactions may be occurring) or closed systems in which no reactions are occurring. In all other cases, however, Eq. (16) must be satisfied if Eq. (6) is to hold.

The internal energy and enthalpy in the reference state for internal energy must satisfy the usual relation.

$$h_{rU} = u_{rU} + p_{rU} v_{rU} \quad (17)$$

and combination of this with Eq. (16) shows that

$$h_{rH} - h_{rU} = -p_{rU} v_{rU} \quad (18)$$

This equation tells us how we must choose the reference state for enthalpy if the reference state for internal energy is chosen. In the 1967 ASME steam tables, for example, the reference states for entropy and internal energy are chosen to be liquid water at the triple point (273.16K, 611.2N/m²), and the p-V product for liquid water at this condition is 11.0 J/kmol. It follows from Eq. (18) that the reference state for enthalpy can be any state for which the molar enthalpy of water is less than

the molar enthalpy of liquid water at the triple point by 11.0 J/kmol. This difference could be achieved by lowering the temperature of liquid water by 0.0026K while keeping pressure constant at 611.2 N/m², for example. Liquid water at this condition (metastable, by the way) has an enthalpy which is less than the enthalpy of liquid water at the triple point by 11.0 J/kmol. However, other states could also serve as the reference state.

One does not have to make an actual choice of reference state for enthalpy once the reference state for internal energy is decided upon. This is so because when these reference states satisfy Eq. (16) for every compound or element, then the relation between *relative* enthalpy and internal energy is the same as the relation between *absolute* enthalpy and internal energy. Thus, if the reference states involve the pure elements, we have for the system

$$U_t = U_t' + \sum_j \sum_k N_j \epsilon_{jk} u_{krU}^E$$

and

$$H_t = H_t' + \sum_j \sum_k N_j \epsilon_{jk} h_{krH}^E$$

so

$$H_t - U_t = (H_t' - U_t') + \sum_j \sum_k N_j \epsilon_{jk} (h_{krH}^E - u_{krU}^E) = H_t' - U_t' \quad (19)$$

if Eq. (16) is satisfied. Similarly, one can show that $h_q - u_q = h_q' - u_q'$ if Eq. (16) is satisfied. For equilibrium systems a system pressure can be defined and $H_t - U_t = H_t' - U_t' = pV$ so the relative value of enthalpy is fixed once the relative value of internal energy is stated, provided that Eq. (16) is satisfied by the choice of reference states.

AN APPLICATION

Problem 5.11 in the book of Modell and Reid [4] provides an interesting application of the foregoing ideas. In this problem the total internal energy of a gas (helium) in a tank is to be held constant as gas flows out of the tank, and this is to be done by addition of heat to the gas in the tank at the proper rate; one is to calculate how the pressure and temperature of the gas vary with the amount of gas remaining in the tank. Since no chemical reactions occur, reference state 1 may be used. Indeed, reference states 1 and 2 are identical in this problem, but they would not be if the gas involved was a chemical compound composed of two or more elements.

The system to which mole and energy balances are to be applied is the gas in the tank, and the simplifying assumption that the gas has a spatially

uniform state at any time is made. Eqs. (5a) and (16) then provide, for an interval of time t to $t + dt$,

$$dU_t = dU_t' + u_{rU} dN = dU_t' + h_{rH} dN \quad (20)$$

and in addition we have

$$H_t - U_t = H_t' - U_t' = pV \quad (21)$$

when $u_{rU} = h_{rH}$. Finally, the energy balance yields

$$dU_t' = dQ_t + h'dN \quad (22)$$

when mechanical energy terms in the equation are assumed to cancel one another. No expansion work term appears in this equation since the system volume is constant and no useful work term appears because we assume energy is added or removed by heat transfer rather than by performance of useful work.

If we interpret the statement of the problem in the Modell and Reid book to mean that *absolute* internal energy (total) is constant, then $dU_t = 0$ and from Eqs. (20-22) we obtain after some manipulation

$$-hdN = Ndh' - Vdp (= dQ_t) \quad (23)$$

where the volume, V , of the system is constant. Since N , h , and h' are functions of T , p , and V this is an ordinary differential equation in the two state variables T and p . Certainly, we can write equations for the functional dependence of N and h' on these quantities for any given gas, once a choice of reference state has been made, but we cannot do the same for the absolute molar enthalpy, h . Hence, this interpretation of the problem statement leads to a problem that cannot be solved: we cannot know how to adjust the heat transfer rate to the gas so that its absolute total internal energy remains constant as its mass changes.

On the other hand, if we interpret the statement of the problem to mean that the relative internal energy (total) is constant, then $dU_t' = 0$ and from Eqs. (20-22) we get

$$-h'dN = Ndh' - Vdp (= dQ_t) \quad (24)$$

Every term in this equation may be evaluated. If, for example, we assume that helium is a perfect gas with molar heat capacity c_p independent of temperature, then

$$h' = c_p(T - T_{rH}) \quad (25)$$

$$N = \frac{pV}{R_g T} \quad (26)$$

and Eq. (16) requires that the temperatures in the

reference states for internal energy and enthalpy satisfy

$$\gamma T_{rH} = T_{rU} \quad (27)$$

where $\gamma \equiv c_p/c_v$. One notes in passing that reference state temperatures for internal energy and enthalpy are substantially different in the case of a gas; as we noted, these temperatures were practically the same for a condensed phase because the pressure-volume product is usually very small for such.

Substitution of Eqs. (25-27) into Eq. (24) yields the differential equation

$$\frac{dp}{p} = \frac{dT}{T} + \frac{dT}{T_{rU} - T} \quad (28)$$

and this may be integrated subject to an appropriate initial condition to yield the relation between T and p that must be satisfied if U_t' is to be constant when N varies. The result contains the reference temperature T_{rU} , and this is to be expected, since if we change T_{rU} , we change the relative internal energy of the system when it is in a given state. \square

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NOTATION

c_p, c_v	Heat capacities at constant pressure and volume, respectively, per mole
H_t	Enthalpy, total
h	Enthalpy, per mole
K_t	Kinetic energy, total
k	Kinetic energy, per mole
N	Number of moles in system
n	Unit outer normal vector to boundary ∂B of system B
p	Pressure
Q	Rate of heat transfer into system
Q_t	Amount of heat transferred, total
q	Heat flux vector

REQUEST FOR FALL ISSUE PAPERS

Each year CHEMICAL ENGINEERING EDUCATION publishes a special fall issue devoted to graduate education. This issue consists of articles on graduate courses and research written by professors at various universities, and of announcements placed by ChE departments describing their graduate programs. Anyone interested in contributing to the editorial content of the fall 1983 issue should write to the editor, indicating the subject of the paper and the tentative date it can be submitted. Deadline is June 15th.

R	Rate of reaction
R_g	Gas constant
S	Rate of entropy transfer into system
S_G	Rate of entropy generation in system
S_t	Entropy, total
s	Entropy, per mole
T	Absolute temperature
t	Time
U_t	Internal energy, total
u	Internal energy, per mole
V	Volume
v	Volume, per mole
W_t	Work, total
$-W_{exp}$	Rate at which system does expansion work on surroundings
$-W_u$	Rate at which system does useful (shaft, electrical, etc.) work on surroundings
w	Molar flow rate
x	Mole fraction
α_{ij}	Stoichiometric coefficient of j^{th} compound in i^{th} reaction
γ	Ratio of heat capacities
ϵ_{jk}	Number of atoms of k^{th} element in one molecule of j^{th} compound
Φ_t	Potential energy, total
ϕ	Potential energy, per mole

Superscripts

E	Denotes property of a pure element
$'$	Denotes a relative property

Subscripts

G	Generation
i	Denotes i^{th} reaction
j	Denotes j^{th} chemical compound
k	Denotes k^{th} element
q	Denotes q^{th} process stream
t	Total
rH, rS, rU	Denote reference states for enthalpy, entropy, and internal energy