Point by point response to reviewer comments

Reviewer 1:

RF: Thanks for indicating the various minor issues. They have been fixed.

1. Recent warming 2023

Review 1: „There is an emphasis in the Abstract and Introduction on the alarming and unexplained global warming of 2023-2024. In the context of an academic review paper on ocean thermodynamics I think that this might be overdone and might make the review seem a bit dated when read in say 10 years' time. I recommend playing this down somewhat by delaying its discussion so that, while this issue is still there to gain the reader's attention, it does not distract from what is essentially a scholarly work."

RF: The 2023 warming is taken as a current example for the urgency and importance of the questions raised. This "teaser" is presented as just a single quotation. To make this more obvious, the section has been split into 2 paragraphs:

"…the reported ocean's average warming rate amounts to 1.3 W m^{-2}, and is apparently even increasing.

The currently observed *ocean heat content* (OHC) represents a merely transient maximum after a decade-long systematic warming process in the past, see Fig. 18 in **Section 6**, which may proceed to even higher values in the future. In **Section 3**, thermodynamic aspects of related OHC definitions will be considered. Regarding the long-term period since 1971, "the drivers of a larger Earth energy imbalance in the 2000s than [before] are still unclear. … Future studies are needed to further explain the drivers of this change" (von Schuckmann et al. 2023: p. 1694). Laterally, the observed heat excess is unevenly distributed over the world ocean (Fig. 1), in contrast to what naively may be expected from rising atmospheric CO_2 concentrations. Rather, warming seems to be most pronounced in the austral and boreal west-wind belts. Selected thermodynamic relations between OHC and cloudiness are briefly discussed in **Section 6**."

2. OHC

Review 1: „ I identify one small part of this manuscript that I think is wrong and should be deleted, namely the part around Eq. (5)."

RF: I have described my intention behind eq. (5) in more detail now:

"The process depicted in Fig. 6 measures the total heat flux $\int \mathrm{d}h = \int T \mathrm{d}\eta$ which changes the entropy of the given sample from the current value, η, to some arbitrary reference value, η_{ref}, and this way, the process also changes the parcel's enthalpy from $h^{\text{SW}}(S, \eta, p_0)$ to $h^{\text{SW}}(S, \eta_{\text{ref}}, p_0)$. Integration over all ocean samples results in an OHC value of

$$OHC^* = \int \left[h^{\text{SW}}(S, \eta, p_0) - h^{\text{SW}}(S, \eta_{\text{ref}}, p_0) \right] \rho^{\text{SW}}(S, \eta, p) \mathrm{d}V. \tag{5}$$

While the choice of the OHC reference state is - in principle - entirely arbitrary, such as simply putting $\eta_{\text{ref}} = 0$, it is reasonable to better adapt this selection to the purpose of the OHC definition. The main purpose of estimating OHC is keeping track of the ocean's long-term energy balance, in particular of the ocean's share of global warming. Three conditions appear immediately plausible in order to achieve this goal,

(i) *The OHC definition should ensure that OHC differences represent a suitable spatial integral over the heat fluxes crossing the ocean's boundaries*. As discussed in more detail in Section 5.3, production of entropy, $\mathrm{d_i}\eta$, caused by irreversible processes between different parcels within the ocean, does not affect the ocean's total enthalpy budget. This is quite in contrast to entropy exchange, $\mathrm{d_e}\eta$, of the given sample in the form of reversible heat flux across its boundary. Such irreversible processes affect the ocean's total potential enthalpy much less than its total entropy (McDougall et al. 2021). For this reason the OHC reference state should explicitly be defined in terms of potential enthalpy, $h^{\mathrm{SW}}(S, \eta_{\mathrm{ref}}, p_0)$, and this way only implicitly in terms of entropy by specifying $\eta_{\mathrm{ref}}(S)$.

(ii) *Provided that the ocean's mass remains the same between any two ocean states (1) and (2), the difference OHC(1) – OHC(2) should depend only on the surface heat flux balance during the time in between*. For this reason, the OHC reference value should be independent of changes occurring in the density distribution, $\rho^{\mathrm{SW}}(S, \eta, p)$. This can be achieved by assigning to each ocean parcel the same reference potential enthalpy, $h^{\mathrm{SW}}(S, \eta_{\mathrm{ref}}, p_0) = \mathrm{const}$, even though such a state may hardly ever be observed in the real ocean.

(iii) *Quantitatively, OHC values estimated at different times or places should be mutually comparable without estimation bias resulting from possibly changing methods of OHC calculation*. For this reason, resulting OHC values should be independent of the inevitable arbitrary, physically irrelevant reference-state conditions imposed on energy and entropy, such as eqs. (1)-(3). This can be achieved by assigning to each ocean parcel the same standard-ocean enthalpy as its reference potential enthalpy, $h^{\mathrm{SW}}(S, \eta_{\mathrm{ref}}, p_0) = h_{\mathrm{SO}}$. In the special case of TEOS-10 enthalpy, this value is defined by eq. (2), $h_{\mathrm{SO}} = 0$. This choice is implicitly made by the definition (4) but needed to be considered explicitly as soon as alternative equations for seawater enthalpy or entropy are employed, such as those of Millero and Leung (1976) and Millero (1982, 1983)."

3. Bible quotation

Review 1: "I discourage the inclusion of religion in scientific papers. First, the bible is not a scientific book, nor is it scientifically correct since its discussion of the arrival of humans on earth (in its first chapter) contradicts the known science of evolution. Second, scientific papers should be able to be read by authors of all religions without them encountering quotes which somehow endorses the basic textbook of one religion. Hence, I think that biblical quotes, just like quotes from the textbooks of any religion, should not be allowed in Ocean Science. Please delete these lines."

RF: I agree that religious arguments should be excluded from scientific papers. However, more than 2000 years ago, there was no science apart from religion; modern science and modern religion have common roots. They diverged when religious branches turned into frozen dogmatic prescriptions to be used as instruments of political power, while science remained open for change, correction and evolution. Regardless of that, both religion and science still are – even if very distinct – mental models for the structure and the causal functioning of the perceived world.

With respect to the hydrological cycle, the Bible quotations in the paper are the oldest documented observations of nature that I could find. Similar other "holy books", such as the *Popol Vuh* of the Maya, or the *Teaching of Buddha*, are almost exclusively focussed on human life and history, rather than observations of natural phenomena (although the scientific term *hurricane* is borrowed from the Maya god *Huracan*). People of the past had noticed that all rivers discharge into the sea whose level did not rise though, and that clouds may release vast amounts of water while floating virtually weightlessly across the sky. They had no plausible causal explanations for such mysteries and credited those to divine intervention.

The history of understanding the hydrological cycle has ancient roots and is, remarkably, not finished yet. This paper addresses relevant pending problems of modelling that cycle, and in so far it seems scientifically appropriate to refer to the exceptionally few written cases of revealing the poor very beginning of this understanding.

4. SMOW

Review 1: “Surely the water which IAPWS-95 describes is not Standard Mean Ocean Seawater”

RF: IAPWS-95 describes IAEA Standard Mean Ocean Water (SMOW) which is the solvent of IAPSO Standard Seawater.

5. Absolute Salinity

Review 1: “Line 201 and in hundreds of places throughout the paper, Absolute Salinity and Conservative Temperature are used without their upper-case letters. This goes against what IOC et al. (2010) and Valladares, J., Fennel, W., and Morozov, E.G (2011) and Spall et al (2013) [see below] dictate. I think the field should stick with the upper-case letters, simply because there are many different possible definitions of absolute salinity and of conservative temperature, but there is only one definition (each) of Absolute Salinity and Conservative Temperature.”

RF: In section 2, the paragraph introducing salinity has been edited to read:

“… The variable S, at which a subscript A is omitted here for simplicity, is the specific or *Absolute Salinity*, the mass fraction of dissolved salt in seawater, which differs from *Practical Salinity*, S_{P}, measured by present-day oceanographic instruments, as well as from various other obsolete salinity scales (Millero et al. 2008). Throughout this paper, the term “salinity” is short hand exclusively for TEOS-10 Absolute Salinity. …”

Lower-case conservative temperature appears only once in the text; fixed.

6. Internal energy *E* or *U*

Review 1: “Replace E with U in this and subsequent equations. IOC et al (2010) has used U and u for internal energy (extensive and intensive), and this review paper should do the same.”

RF: The use of E rather U has now been justified below eq. (B.1):

“Note that IOC et al. (2010) uses the symbol U for the *internal energy* rather than E in eq. (B.1). This replacement is done here for denoting with u the wind speed, eq. (6), rather than specific internal energy, which is defined here by $e = E/m$, eqs. (1) and (B.3). The symbols E and e are frequently used for internal energy in the thermodynamic literature, for example by Gibbs (1873a) or Landau and Lifschitz (1966).”

Appendix B is just about thermodynamics in general without special emphasis on oceanography.

7. Minus sign of eq. (B.10)

Review 1: “equation (B.10) has a sign error. The last term should be added, not subtracted.”

RF: Consider the seawater case $n = 2$, $w_0 = 1 - S$, $w_1 = S$. We get from (B.10)

$$\mu_S = \mu_1 = g + \left(\frac{\partial g}{\partial w_1}\right)_{T,p} - \sum_{j=1}^{1} w_j \left(\frac{\partial g}{\partial w_j}\right)_{T,p} = g + (1 - S)\left(\frac{\partial g}{\partial S}\right)_{T,p}$$

in agreement with eq. (2.9.5) of the Manual. No sign error.

Despite this, for clarity, the sentence above (B.10) has been changed to

"Because the Gibbs function depends only on the independent intensive variables, $g(w_1, \dots, w_{n-1}, T, p)$, the solutes' chemical potentials, $i > 0$, are"

8. Partial derivative of (B.11)

Review 1: "The things that are held constant during the differentiation in the last term in this equation are not correct. They should be the same as the corresponding term in the next equation. Eq. (B.11)."

RF: Yes, but (B.11) is to be adjusted to (B.10). Corrected to

$$\mu_0 = \left(\frac{\partial G}{\partial m_0}\right)_{T,p,m_{j>0}} = \left(\frac{\partial (m\, g)}{\partial m_0}\right)_{T,p,m_{j>0}} = g - \sum_{j=1}^{n-1} w_j \left(\frac{\partial g}{\partial w_j}\right)_{T,p,w_{k\neq j}}. \qquad \text{(B.11)}$$

Reviewer 2:

RF: Thanks for careful reading and detailed discussing.

1. **OHC**

Review 2: „Section 3. Unlike the other sections, this section uses persuasive writing rather than scientific writing to convince the reader of the legitimate and rigorous character of the TEOS10 approach to defining ocean heat content. In essence, this amounts to providing a solution to a question that has not been properly formulated first; as result, the reader is not given the scientific elements necessary to assess the legitimacy of the author's assertions. Moreover, the topic is not properly reviewed or discussed in the context of past research on the issue. As a result, this section does not conform to accepted scientific standards, and therefore should either be significantly improved, or removed from the paper.

… the problem of how to define heat was originally defined as the problem of how to separate the total energy transport into a dynamical and thermodynamic part …

TEOS-10 or the author's section gives the impression that there is only a unique way to address the problem and that there is nothing left to be solved, when this is clearly not the case."

RF: Entropy (here, "*N*") was originally discovered and defined by Clausius describing heat exchange in the form of dN = dQ/T. Using Clausius entropy, a problem of defining heat does not exist: entropy is formally defined for the first time in terms of heat whatever "heat" may actually be. Meanwhile, there are various alternative definitions of entropies in the subsequent literature, more or less related to heat, but here empirical Clausius entropy is used in the same sense as by numerous textbooks from Gibbs to Prigogine.

Section 3 explains OHC in terms of surface entropy flux. This is no balance of the total ocean energy, nor is it a description of the real heat exchange between ocean and atmosphere. Section 3 proposes a fictitious thermodynamic process by which proper heat exchange is formally related to thermodynamic state properties.

Definitions are neither right nor wrong per se; they may be more or less useful for a certain purpose. OHC is a matter of definition. The main intention of Section 3 is placing emphasis on the physical arbitrariness of any OHC definition. It is up to the oceanographic community to adopt one option as a standard to ensure comparability of reported figures. Note that Section 3 had already substantially been modified in response to Reviewer 1.

As a measurable physical quantity, "heat" is defined only as a heat exchange between two bodies rather than any "heat substance" contained in a volume. It is clearly said that the common term "OHC" is thermodynamically sloppy and ambiguous; Section 3 suggests one option of defining a heat flux and a reference state consistent with the TEOS-10 OHC definition given by McDougall et al. (2021). This simple option does not require any details of complex energy transformation processes within the real ocean. However, a sentence hinting on more complex analyses of the OHC problem has been added to Section 3:

"OHC as a part of the total energy balance of the ocean is analysed by Tailleux (2010, 2018) and Tailleux and Dubos (2024)".

2. **Line 65.**

Review 2: "Typically, present numerical climate models suffer from an "ocean heat budget closure problem" (Josey et al. 1999) and describe the m–2 m–2 ocean-atmosphere heat flux only to within uncertainties between 10 W and 30 W (Josey et al. 2013).

I find this statement confusing because my understanding of the Josey et al papers relate to the `observational' closure problem arising from the technical difficulties of measuring the different heat fluxes component reliably enough and with the desired accuracy. The closure problem in numerical ocean models is a completely different thing. Numerical ocean models will in general exhibit drift depending on many different factors, such as model resolution, and various model errors. The author needs to review the literature more carefully to avoid confusing observational and modelling issues."

RF: I do not see the need for such a distinction in the context of my paper. Numerical models can hardly describe ocean surface heat fluxes more precisely than observations by which they were tuned. If those models have numerical problems even larger than 10 W and 30 W per m-2, they lack significance in explaining the discussed effects of 1 W per m-2.

3. **Lines 70-72.**

Review 2: "… countless climate projections have been published that reproduce ocean warming like that observed. Presumably, air-sea interactions in such simulations have been analysed. It would therefore be useful if the author could summarise the state of knowledge on the matter, including discussions of the nature of uncertainties, rather than just speculate on the matter."

RF: I myself do neither run nor assess climate models or similar products; I just report published statements of renowned experts. All analyses I am aware of do conclude that the uncertainty in estimating the global mean air-sea heat flux is hardly any better than 10 W m-2, if at all. Contributions to this uncertainty are various and complicated, and are certainly not the topic of this paper. What does matter here, however, is the plausible conclusion that a model with uncertainty larger than 10 W m-2, see e.g. Fig. 5.10 in Josey et al. (2013), cannot reliably distinguish and explain effects of the magnitude of 1 W m-2. Attempts to blindly do this may well be considered as speculative.

"Despite a certain success it must still be stated that the modellers among my colleagues are not yet aware of the severity of the problem. As a rule, they work with energy-balance equations whose coefficients had been verified by measurements, while their latent-heat fluxes are mostly determined as the remaining left-over term, which therefore received the residual as an additive. This has implications for the surface temperature that is important for most of the models, and in particular for the water-vapour flux" (Daniela Kracher et al. 2009, doi:10.1127/0941-2948/2009/0412). "The global water cycle and the exchange of freshwater between the atmosphere and ocean is poorly understood" (Penny Holliday et al., 2011). "For most products, it is not possible to close the [global ocean] heat budget to within 10 W m-2 and in some cases the bias is of the order of 30 W m-2" (Simon Josey et al. 2013: p. 128). "The drivers of a larger Earth energy imbalance in the 2000s than [before] are still unclear. … Future studies are needed to further explain the drivers" (Karina von Schuckmann 2023). "Climate models struggle to explain why planetary temperatures spiked suddenly. … No year has confounded climate scientists' predictive capabilities more than 2023" (Gavin Schmidt, Nature, 21 March 2024).

4. **Lines 78-80.**

Review 2: "it would be useful to the reader if the author could translate these numbers in terms of implied change in net evaporation or precipitation, assumes that the two balance on average."

RF: A global mean evaporation / precipitation of about 1000 mm corresponds to an oceanic latent heat flux of roughly 100 W m-2. RH uncertainty of 1 – 5 %rh corresponds to 5 – 25 W m-2 latent heat flux uncertainty, or 50 - 250 mm of annual precipitation. Related text inserted:

"Unfortunately, marine RH is observed only with uncertainties between 1 and 5 %rh (Lovell-Smith et al. 2016), or, accordingly, between 5 and 25 W m–2 of latent heat flux, which is roughly corresponding to unknown variations ranging up to 50 … 250 mm evaporation."

Review 2: "May be the author could also discuss the fact that global warming is expected to heat up land area faster than ocean area. As a result, this may decrease relative humidity, with a possible compensating effect over the ocean like the one suggested by the author."

RF: Such a compensation effect is speculative. Dominating 85% of global evaporation occur at the ocean. Global warming on land is rather different from that at sea, and does not belong to "Ocean-Atmosphere Interaction" of this paper. For details see e.g.: Blunden, J., Boyer, T., and Bartow-Gillies, E. (eds.): State of the Climate in 2022, Bull. Amer. Meteor. Soc. 104, S60–S61, https://doi.org/10.1175/2023BAMSStateoftheClimate.1, 2023

5. **Line 95.**

Review 2: "…It seems to me that while TEOS10 is clearly a success in providing such improved formulations, it is unclear how it can claim to contribute to the understanding of the functioning of the ocean heat engine… "

RF: TEOS-10 does not describe the "heat engine" dynamics of the climate system; TEOS-10 only provides the most accurate, comprehensive and mutually consistent thermodynamic tools for use in climate research. This paper explains that and just offers some simple tutorial examples for the use of TEOS-10 in the climate context.

6. **Figures 3 and 4.**

Review 2: "Shouldn't credit or copyright for the photo be indicated? Can these be re-used by others?"

RF: Ocean Science is publishing under the Creative Commons Attribution 4.0 License.

7. **Lines 129-134.**

Review 2: "The question is whether the TEOS-10 definition of heat is as rigorous as the author claims, as the definition seems an ad-hoc one to me. TEOS-10 proposes a solution to a question that they never define in the first place. See my comments in the major points section."

RF: Neither TEOS-10 nor this paper have ever attempted to define "heat". Clausius' original definition of entropy is in terms of heat exchange. "We have … two of the fundamental ideas of the science of heat – the idea of temperature … and the idea of heat as a measurable quantity, which may be transferred from hotter bodies to colder one" (James Clerk Maxwell 1888, Theory of Heat, Longmans & Green: p. 9). "The variation in entropy during an infinitesimal reversible transformation is obtained by dividing the amount of heat absorbed by the system by the temperature of the system" (Enrico Fermi 1937, Thermodynamics. Prentice-Hall: p. 52).

8. **Line 200-203**.

Review 2: "Can the author provide some explanation about why a Helmholtz potential is preferred in that case rather than a Gibbs function? The use of a Gibbs function as the basis for TEOS10 is generally understood from the fact that S, T, and p are variables that are the most easily measured/fixed in practice. We are also told that density is a variable that is very hard to measure in practice, which makes the usefulness of a Helmholtz function hard to understand. So, what are the physical arguments in favour of it?"

RF: In statistical physics, a canonical ensemble with the partition function Z determines the Helmholtz energy by $F = - kT \ln Z$. The function Z depends on the particle number N, the temperature T and the volume V, and is a functional of the microscopic particle interaction energy, entirely independently of the macroscopic phase the substance may actually take. For a given substance or mixture, this formula $F(N, T, V)$ is single-valued and universally valid, be it a gas, a liquid, or any solid phase, such as for water around its critical point and for each of the various ice phases. By contrast to F, the Gibbs energy $G(N, T, p)$ is multi-valued in the T-p vicinity of phase transitions, where each phase is represented by its own separate "leaf" of G that intersects the leaf of the other phase. TEOS-10 includes a single Helmholtz function jointly for liquid water and water vapour, but two different Gibbs functions. References to related textbooks introducing that matter have been added to this paper:

"For theoretical reasons (namely, the statistical so-called *canonical ensemble*, Landau and Lifschitz 1966: §31; Kittel 1969: Ch. 18), …"

9. **Line 259-260.**

Review 2: Conservative Temperature "Preferred by whom?"

RF: Preferred by ocean modellers who started using TEOS-10, see e.g. Almeida et al. (2018), as far as I know this. See also Young (2010), https://doi.org/10.1175/2009JPO4294.1; https://en.wikipedia.org/wiki/Conservative_temperature; or Pawlowicz, R. (2013) Key Physical Variables in the Ocean: Temperature, Salinity, and Density. Nature Education Knowledge 4(4):13

10. **Line 358, Equation 6:**

Review 2: "Can you be more specific as to the form of the transfer coefficient Df(u) by providing examples from the literature? I am confused by the author's statement that such a coefficient only depends on u, because my understanding is that such a coefficient also depends on many other things, such as a sea surface roughness, nature of the boundary layer, and so on…"

RF: In fact there is a wealth of different definitions of the transfer coefficient Dq(u) of latent heat in oceanography, meteorology and hydrology. In this paper reference is only made to the recent definitions given by Josey (2013: eq. 5.1), Stewart (2008: eq. 5.10c) or Pinker et al. (2014, doi:10.1002/2013JC009386: eq. 1) who parameterise this coefficient simply as a linear function of wind speed, independent of the various other surface properties. To my knowledge, there is no suggestion available yet from the literature for the functional form of Df(u).

11. **Lines 396-398.**

Review 2: "This sounds like an important result warranting further attention. However, can the author guarantee that Dq(u) does not depend indirectly on q in a way that would compensate the effect discussed? Change in q may modify the nature of the turbulent boundary layer and the transfer coefficient."

RF: Available from TEOS-10 for the first time, relative fugacity is the proper irreversible thermodynamic driving force for the water transport across the air-sea interface. Properties of the turbulent boundary layer may certainly depend on additional properties beyond those provided by TEOS-10.

12. **Lines 637.**

Review 2: “The author only discusses irreversibility associated with non-zero relative humidity under the assumption that the oceans and atmosphere have the same temperature. In reality, the latter may also have different temperatures. Can the author comment as to the implications that this would have for his theory?”

RF: The thermal “skin effect” of the air-sea interface has been studied by several authors such as Peter Saunders (1967) or Kristina Katsaros (1980). The sensible heat flux affected by this effect is generally small compared to the latent heat flux. In the sense of Onsager linear irreversible thermodynamics, the heat flux driven by the temperature difference, and the evaporation flux driven by the different chemical potentials (that is, relative fugacity) will also have a cross effect of evaporation driven by the temperature gradient and, symmetrically, of sensible heat flux driven by the relative fugacity. However, the magnitude of the cross effect is unclear and has so far been assumed to be negligible.

13. **Lines 723-725.**

Review 2: “My understanding is that the Zlcl is to be obtained by integrating the hydrostatic relationship, which can only lead to the author’s formula (52) if the entropy and specific humidity are perfectly uniform from the surface to the bottom of the cloud. Is that really the case in reality?”

RF: In the LCL model presented here, it is assumed that the uplift of air occurs at constant entropy and specific humidity in order to compute the LCL pressure. The same assumption is also applied for computing the LCL height. Of course, this is an idealised model of reality. Figure 20 in Feistel et al. (2010a) shows measured radiosonde profiles of those quantities with an approximately isentropic surface layer over the tropical Atlantic.

14. **Lines 930-934.**

Review 2: “I am surprised to see the quantities $-pdV$ and $Td\eta$ equated with the work and heat transfers δW and δQ, because this is only true for reversible and quasi-static transfers. As far as I am aware, the exact relations are $T\ d\eta \geq \delta Q$ and $-p\ dV \leq \delta W$. This can be verified for an adiabatic expansion of a piston in a vacuum. In that case, δQ=0 yet the entropy increase; moreover, δW=0, yet V increases so that $-p\ dV$<0. Moreover, note that p, V, T and eta relates to internal properties of the fluid, while the concepts of heat and work transfers relate to external properties describing the interactions of the fluid with its environment, so that it is dangerous and confusing to equate internal and external properties without further discussion.”

RF: It is true that TEOS-10 describes equilibrium thermodynamics of seawater, ice and humid air. In classical thermodynamics all exchange processes are idealised as reversible and quasi-static. For application of TEOS-10 to geophysical processes, TEOS-10 may be generalised under the assumption of local equilibrium, see e.g. Feistel and Hellmuth (2024a) and the discussion of entropy production in Section 5.3 of this paper.

The discussion on OHC in this paper is explicitly focussed on the fact that heat is an exchange quantity rather than a state quantity. “We have … a right to speak of heat as a *measurable quantity*, … however, … we have no right to treat heat as a *substance*” (J. C. Maxwell, 1888, Theory of Heat, p. 7).

As an aside, the gas expansion into vacuum violates the condition of local equilibrium (namely, the existence of a local Maxwell distribution of particle velocities) so that neither temperature nor entropy may properly be defined in that case.

15. **Lines 962-963.**

Review 2: “I thought that this condition was also true in the presence of gravity. Can the author explain how gravity affects these conditions, given that this is obviously relevant to the oceanic case?”

RF: Under gravity, the equilibrium condition of equal (molar) chemical potentials μ is replaced by the condition that for each species the form $(\mu + M\,\phi)$ must take equal values across a volume, where M is the molar mass and ϕ is the gravity potential (Guggenheim 1949: chapter XI).