

Time-scales to reach chemical equilibrium in ices at snowline distance around compact objects: the influence of accretion mass in the central object

G. A. Carvalho   and S. Pilling 

Instituto de Pesquisa e Desenvolvimento (IP&D), Universidade do Vale do Paraíba (UNIVAP), Av. Shishima Hifumi 2911, São José dos Campos, SP CEP 12244-000, Brazil

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ABSTRACT

In this work, we analyse soft X-ray emission due to mass accretion on to compact stars and its effects on the time-scale to reach chemical equilibrium of eventual surrounding astrophysical ices exposed to that radiation. Reaction time-scales due to soft X-ray in water-rich and pure ices of methanol, acetone, acetonitrile, formic acid, and acetic acid were determined. For accretion rates in the range $\dot{m} = 10^{-12}$ – $10^{-8} M_{\odot} \text{ yr}^{-1}$ and distances in the range 1–3 LY from the central compact objects, the time-scales lie in the range 10 – 10^8 yr, with shorter time-scales corresponding to higher accretion rates. Obtained time-scales for ices at snow-line distances can be small when compared to the lifetime (or age) of the compact stars, showing that chemical equilibrium could have been achieved. Time-scales for ices to reach chemical equilibrium depend on X-ray flux and, hence, on accretion rate, which indicates that systems with low accretion rates may not have reached chemical equilibrium.

Key words: astrochemistry – stars: black holes – stars: neutron – (stars:) white dwarfs – ISM: molecules – X-rays: stars.

1 INTRODUCTION

In recent years some works have drawn the attention of researchers to the important fact that X-rays induce a chemical equilibrium in astrophysical ices after a certain interval of time, i.e. ices exposed to radiation no longer change their chemical composition after a typical reaction time-scale (de Souza Bonfim et al. 2017; Rachid, Faquine & Pilling 2017; Vasconcelos et al. 2017; Pilling et al. 2019; Freitas & Pilling 2020b). To know those time-scales it is important to monitor chemical evolution and to infer chemical abundances as well as different chemical properties of the ice molecules in space.

The chemical equilibrium phase, also dubbed equilibrium branching ratio (EBR), is defined as the moment the ice no longer changes its composition even with continuing irradiation, which means variations in its molecular abundances are negligible (generally less than 1 per cent), since destruction and formation rates of the molecules are very similar.

In this work, we focus on the calculation of time-scales of astrophysical ices to reach chemical equilibrium in the vicinity of compact objects, one of the strongest X-ray sources in space. X-rays are a very important ionizing agent and their emission is expected from a broad range of stellar sources (Pavlov 1984; van der Woerd 1988; Barret 2001; Lewin & van der Klis 2006; Mereghetti 2013; Potekhin, Chugunov & Chabrier 2019; Zorotovic & Schreiber 2019; Balman 2020; Mondal 2020). Despite being the product of intense explosions, white dwarf, neutron stars, and black holes can have low temperature material (molecules in ice phase) in their surroundings

(Bailes, Lyne & Shemar 1991; Wolszczan & Frail 1992; Wolszczan 1994; Zuckerman et al. 2010; Yan et al. 2013; Koester, Gänsicke & Farihi 2014; Stephan, Naoz & Zuckerman 2017; Debes et al. 2019; Manser et al. 2019; Wada, Tsukamoto & Kokubo 2019; Vanderbosch et al. 2020). Icy molecules can be formed or acquired after formation of the compact object and could rely on planetary debris, dust rings, planetesimals, and so on (Wada et al. 2019). The X-ray radiation produced by the central object induces chemical reactions at the surrounding astrophysical ices, which is vital for the molecular evolution of those ices. Compact objects are responsible for releasing large quantities of X-ray radiation widely contributing to the integrated X-ray emission from the Galaxy Mukai (2017).

The time-scale to reach chemical equilibrium due to X-ray irradiation can also provide insights on molecular abundances and composition of ices at the vicinity of compact stars. The distances where molecules are found in ice phase, viz., snow line distance, were previously estimated as 1 LY for white dwarfs, approximately 2 LY for neutron stars, and 3 LY for massive black holes (Carvalho & Pilling 2020a, b). Some X-ray pulsars are linked with the possibility of being accreting white dwarfs with high mass and magnetic field instead of being a neutron star with particularly low rotation (Borges et al. 2020). Accretion luminosity depends on mass and radius, and therefore power emitted will be different for a white dwarf and for a neutron star. So, the nature of the compact source and accretion rate are fundamental to determine X-ray spectrum and powered energy. Monitoring the reaction time-scales for the ices may provide an estimation of the accretion rates, which in turn could give additional clues to help identify the nature of the compact object.

The X-ray emission due to accretion generally has a ‘soft’ component as exemplified by Fig. 1 (Pavlov 1984; Barret 2001; Borges et al. 2020). Broad-band X-rays from 6 eV to 2 keV were

* E-mail: geanderson.araujo.carvalho@gmail.com (GAC); sergiopilling@yahoo.com.br (SP)

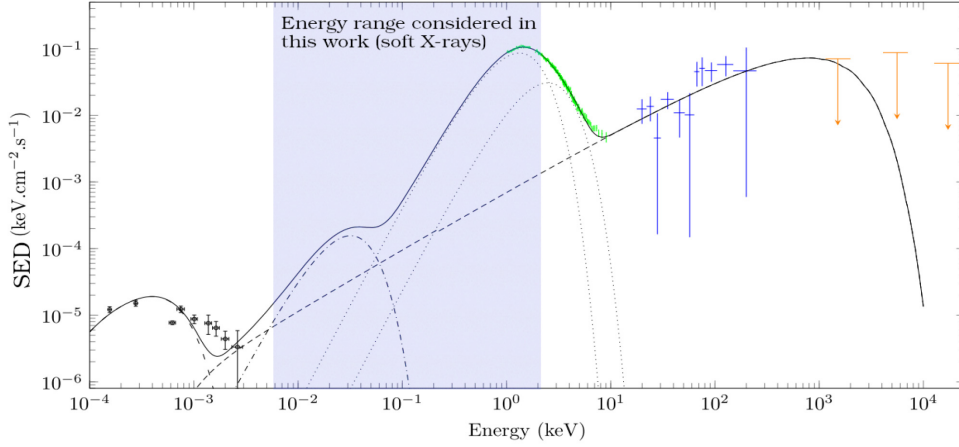


Figure 1. Spectral energy distribution (SED) of the anomalous X-ray pulsar 4U 10142+61 (adapted from Borges et al. 2020). The green crosses are data for the soft X-ray emission, blue ones are the hard X-ray, and black the optical and infrared observed emission. The solid black curve is a complete fit, while other curves are fit components (such as hotspot and white dwarf photosphere components in the range of 6–2000 eV).

used in previous experimental studies to obtain the fluence where astrophysical ices (composed of a specific mixture of molecules) reach the chemical equilibrium (see e.g. Pilling et al. 2019; Freitas & Pilling 2020b). This photon energy interval is analogous to that generated from thermal heating due to accretion in compact systems.

The next sections of this work are organized as follows: Section 2 reviews the basic mathematical approach for X-ray accretion luminosity, and Section 3 discusses how we obtain the reaction time-scales. Section 4 highlights our results and Section 5 gives our conclusions.

2 EMISSION DUE TO ACCRETION MECHANISMS

As a first approximation, we consider that most part of the accretion luminosity is emitted in the soft X-ray spectrum (10 eV–10 keV), thus, soft X-ray luminosity is simply estimated by using the mass accretion parameter, \dot{m}

$$L_{AC} = \frac{GM\dot{m}}{R}, \quad (1)$$

where M and R are the mass and radius of the object, respectively, which can be either a white dwarf, neutron star, or black hole. Mass-radius relation is employed to estimate radius in case of white dwarfs and neutron stars (see e.g. Barstow 1991, 1993; Lopes & Menezes 2012; Berti 2013; Carvalho, Marinho & Malheiro 2018; de Santi & Santarelli 2019; Carvalho et al. 2020), and Schwarzschild radius is taken for black holes. We reinforce that the model above is only a way to estimate the X-ray flux produced by compact objects due to accretion. The accretion rate, \dot{m} , is the parameter which defines the luminosity for a given system. However, in this work, we will not study any particular object, instead we will take fiducial values for mass and radius of the compact object along with standard values for snow line distances to estimate the time-scales ices need to reach chemical equilibrium. So, the model does not define if the compact object is isolated or in a binary system. We assume that accretion rate, \dot{m} , is constant on time, which means that the systems we are studying are well behaved, not presenting any sudden infall of matter, bursts, substantial outflows, or strong winds. The main aim, as stated, is to obtain an estimate of the time-scales for ices to reach chemical equilibrium. The assumption of constant accretion rate is feasible in most cases because the time-scale for ices close to compact systems to

reach chemical equilibrium is smaller than the time-scale for changes on mass, as one can notice from power-law parametrizations (Chen et al. 2019), where we see that \dot{m} scales with Myr or Gyr, while the time-scales for chemical equilibrium are at most 0.1 Myr for distances smaller than 100 LY, as we are going to show.

3 TIME-SCALE FOR ICES TO REACH CHEMICAL EQUILIBRIUM

Time-scales for the ices to reach chemical equilibrium in astrophysical environments were derived by comparing laboratory results employing X-rays on ices and monitoring it with infrared spectroscopy (e.g. Pilling & Bergantini 2015; Pilling et al. 2019). The time-scale to reach chemical equilibrium is an important quantity since it gives insight on molecular evolution and abundances. A methodology to estimate the time-scales was previously given. It is obtained from the fluence of equilibrium

$$TS_E = 3 \times 10^{-8} \times \frac{F_E}{\phi} [\text{yr}], \quad (2)$$

where F_E is the fluence in which ices reach chemical equilibrium (determined experimentally) at constant temperature in units of photons per cm^2 and ϕ is the photon flux given in units of photons $\text{cm}^{-2} \text{s}^{-1}$. To calculate the reaction time-scales for chemical equilibrium, we used F_E values of Table 1.

To estimate the soft X-ray flux of compact objects, we take a representative photon energy value of 1 keV and employ the following equation

$$\phi = \frac{1}{4\pi d^2} \frac{L_X}{E} [\text{photons cm}^{-2} \text{s}^{-1}], \quad (3)$$

where L_X is the X-ray luminosity in units of erg s^{-1} , d is the distance from the central compact object, and energy $E \sim 1 \text{ keV} \approx 1.6 \times 10^{-9} \text{ erg}$. Finally, time-scale for the ices to reach chemical equilibrium becomes

$$TS_E = \frac{4.8 \times 10^{-17} F_E 4\pi d^2}{L_X} [\text{yr}]. \quad (4)$$

Fluence of chemical equilibrium are of magnitude $10^{18} \text{ photons cm}^{-2}$, and particularly, values for ice mixtures (water-rich ices) are very similar, which lie in the range $2\text{--}3 \times 10^{18} \text{ photons cm}^{-2}$, so the

Table 1. Fluence, F_E , where ice molecules reach chemical equilibrium. Values were determined by X-ray irradiation experiments of astrophysical ice analogues. Values in this table are used to estimate time-scales to reach chemical equilibrium of astrophysical ices at the surroundings of compact objects.

Molecule (mixture)	F_E (10^{18} photons cm^{-2})	References
CH ₃ CN 13K	1.5	Carvalho & Pilling (2020a)
CH ₃ COCH ₃ 12K	2	Carvalho & Pilling (2020b)
CH ₃ OH 12K	4.5	Freitas & Pilling (2020b)
SO ₂ 12K	1.6	de Souza Bonfim et al. (2017)
CH ₃ COOH 12K	1.6	Rachid et al. (2017)
HCO ₂ CH ₃ 12K	1.8	Rachid et al. (2017)
CH ₃ CH ₂ OH	3	Freitas & Pilling (2020a)
HCOOH 12K	1	da Silva & Pilling (2020)
N ₂ -CH ₄ (19:1) 12K	6	Vasconcelos et al. (2017)
H ₂ -CO ₂ -NH ₃ -SO ₂ (10:1:1:1) 50K	2	Pilling & Bergantini (2015)
H ₂ -CO ₂ -NH ₃ -CH ₄ (10:1.4:1:0.9) 20K	2	Pilling et al. (2019)
H ₂ -CO ₂ -NH ₃ -CH ₄ (10:2.9:0.3:3.2) 80K	3	Pilling et al. (2019)

time-scale for chemical equilibrium depends mostly on distance and X-ray luminosity.

4 RESULTS

The X-ray luminosity depends on accretion rate, which we considered in the range 10^{-12} – 10^{-5} M_{\odot} yr^{-1} for white dwarfs, and 10^{-12} – 10^{-8} M_{\odot} yr^{-1} for neutron stars and 10^{-12} – 10^{-7} M_{\odot} yr^{-1} for black holes, see Figs 2–4. The upper limit for accretion rate, \dot{m} , is relative to the moment accretion luminosity reaches the Eddington limit, so, radiation would start to induce mass-loss by driving a particle wind (Neilsen 2013). White dwarf, neutron star, and black hole emission due to accretion is mainly thermal and mostly within the soft and hard X-ray wavelengths (van der Woerd 1988; Barret 2001; Zorotovic & Schreiber 2019; Balman 2020). The experiments where the values of photon fluence for chemical equilibrium were obtained have considered the X-ray range of 6 eV to 2 keV (VUV and soft X rays). We take the values for fluence of equilibrium from Table 1 to calculate the time-scales, and also use the accretion luminosity to estimate photon fluxes. Accretion also depends on mass and radius parameters. The mass distribution for white dwarfs peaks at 0.6 M_{\odot} (Amuel et al. 1988), and the typical neutron star mass is 1.4 M_{\odot} (Bhattacharyya 2010). LIGO/VIRGO detection on binary black hole mergers shows that a common mass of stellar black holes is 20 M_{\odot} (Abbott et al. 2019), which will be assumed as a fiducial value for the black hole mass. These fiducial values for masses and their correspondent radii are listed in Table 2.

Snow region of compact objects were estimated in previous studies (see Carvalho & Pilling 2020a, b). A typical planetary nebula has a 1 LY size (Balick & Frank 2002), so we take the standard distance of 1 LY to study snow region of white dwarfs. The 1 LY distance is taken as standard once we are not interested in studying a particular system, but for specific cases the snow line distance can be smaller, for example, the M1-92 protoplanetary nebula presents an ice-band spectra that revealed the presence of H₂O ice grains within the dust torus and it has a 0.31 LY size. On the other hand, neutron star and black holes will have far snow line distances, ≈ 2 LY for neutron stars and 3 LY for black holes. Those values are also taken as fiducial. The 2 LY distance is taken as a reference from Crab nebula, which has a ~ 5 LY size. For black holes, the 3 LY distance is inspired by the theoretical work of Wada et al. (2019), who estimated the snow region of supermassive black holes to be located at distances 0.3–30 LY.

Using values of Table 2, we calculate the time-scales for ices at constant temperature ($T < 50$ K) to reach chemical equilibrium under the presence of soft X-rays as a function of distance and accretion rate on to the white dwarfs in Fig. 2. We first fixed the accretion rate at $\dot{m} = 7.4 \times 10^{-5}$ M_{\odot} yr^{-1} to calculate time-scales as a function of distance only, and more importantly we fixed distance at 1 LY (snow region) to study the effects of X-ray flux produced by accretion on the ices. For accretion rates from 10^{-12} M_{\odot} yr^{-1} to a maximum of 7.4×10^{-5} M_{\odot} yr^{-1} time-scales span eight orders of magnitude smaller than the characteristic lifetime of white dwarfs (\sim Gyr). For time-scales of order Gyr, accretion rate would be 10^{-14} M_{\odot} yr^{-1} , or equivalently $\sim 10^{10}$ g s^{-1} .

For neutron stars, we fixed distance at 2 LY to analyse the time-scales as a function of accretion rate in the interval 10^{-12} – 10^{-8} M_{\odot} yr^{-1} . We also fixed accretion rate at 1.2×10^{-8} M_{\odot} yr^{-1} and varied distance to obtain time-scales for neutron stars with maximum accretion. Time-scales vary from 10^5 to less than 1 yr in case of fixed accretion rate. So, chemical changes could be monitored within a reasonable time-scale. Lifetime of accreting neutron stars is comparable to time-scales for ices to reach chemical equilibrium – e.g. age of Sco X-1 is about $\sim 10^5$ yr – which indicates that astrophysical ices subjected to energetic X-rays from close accreting neutron stars may no longer change their chemical composition in a relevant way.

In Fig. 4, we show the results for time-scales for ices to reach chemical equilibrium at the vicinity of stellar black holes. The distance was fixed to be 3 LY (panel a) and accretion rate was fixed at $\approx 10^{-7}$ M_{\odot} yr^{-1} (panel b). For the considered range of accretion rate, ices at the snow region of stellar black holes have time-scales of 1 – 10^6 yr, smaller time-scales corresponding to higher accretion rates. The upper limit is similar to that for neutron stars, but the lower limit on time-scales has order of months (0.1 yr). These time-scales are clearly below the age of most detected X-ray accreting black holes candidates, such as Cygnus X-1, which has an age of 5 Myr (Mirabel & Rodrigues 2003).

Fig. 5 provides an overview on time-scales of astrophysical ices, exposed to soft X-ray radiation from accreting compact stars, to reach chemical equilibrium. In Fig. 5, an average value for fluence of equilibrium was employed ($\bar{F}_E = 2.45 \times 10^{18}$ photons cm^{-2}). Snow line distances and maximum values for accretion rate were also used. The inset image is a simple representative picture of the process. The shaded orange region in panel b of Fig. 5 is related to Eddington critical limit. From Fig. 5, one can observe that the larger the distance (or the smaller the accretion rate) the greater is the time-scale for

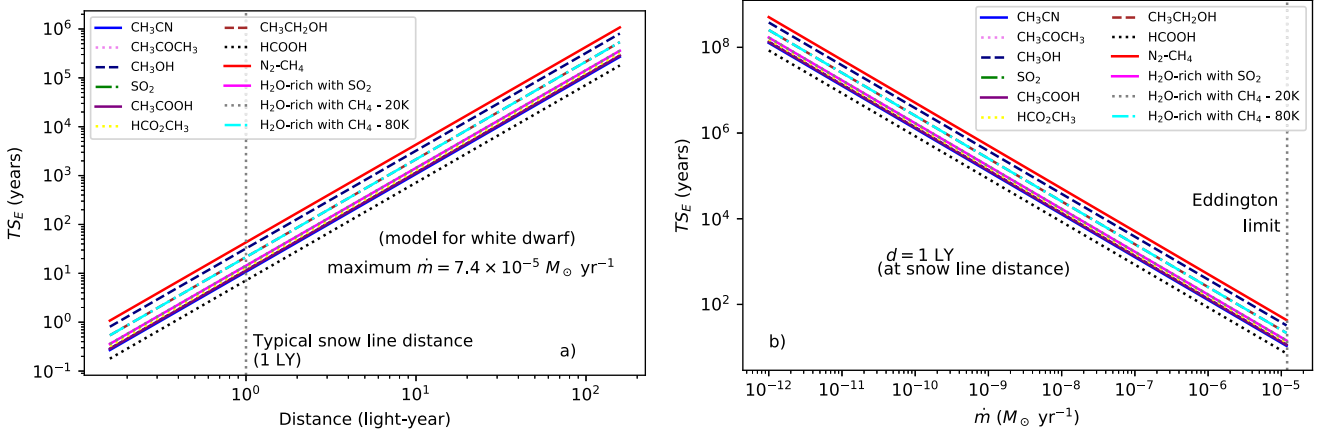


Figure 2. (a) Time-scales for astrophysical ices to reach chemical equilibrium versus distance from the central white dwarf; accretion rate was fixed at a maximum of $7.4 \times 10^{-5} M_{\odot} \text{ yr}^{-1}$ ($L_X = 7.4 \times 10^{37} \text{ erg s}^{-1}$) (van der Woerd 1988). (b) Time-scales for ices to reach chemical equilibrium at the snow line distance from the central white dwarf ($d \sim 1 \text{ LY}$) as a function of the accretion rate, see details in the text.

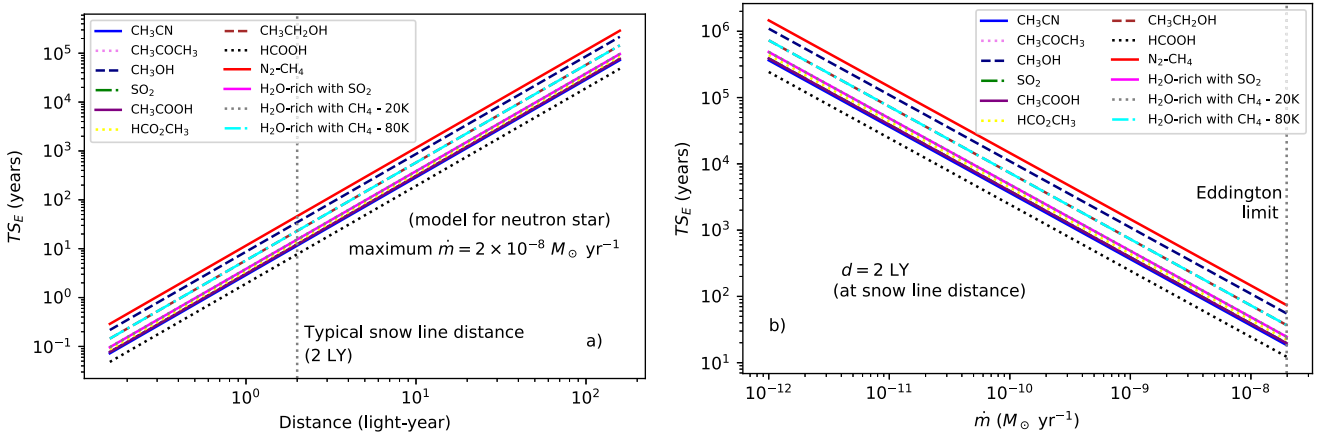


Figure 3. (a) Time-scales for astrophysical ices to reach chemical equilibrium versus distance from the central neutron star; accretion rate was fixed at $\sim 10^{-8} M_{\odot} \text{ yr}^{-1}$ ($L_X = 1.7 \times 10^{38} \text{ erg s}^{-1}$) (Barret 2001). (b) Time-scales for ices to reach chemical equilibrium at the snow line distance from the central neutron star ($d \sim 2 \text{ LY}$) as a function of the accretion rate, see details in the text.

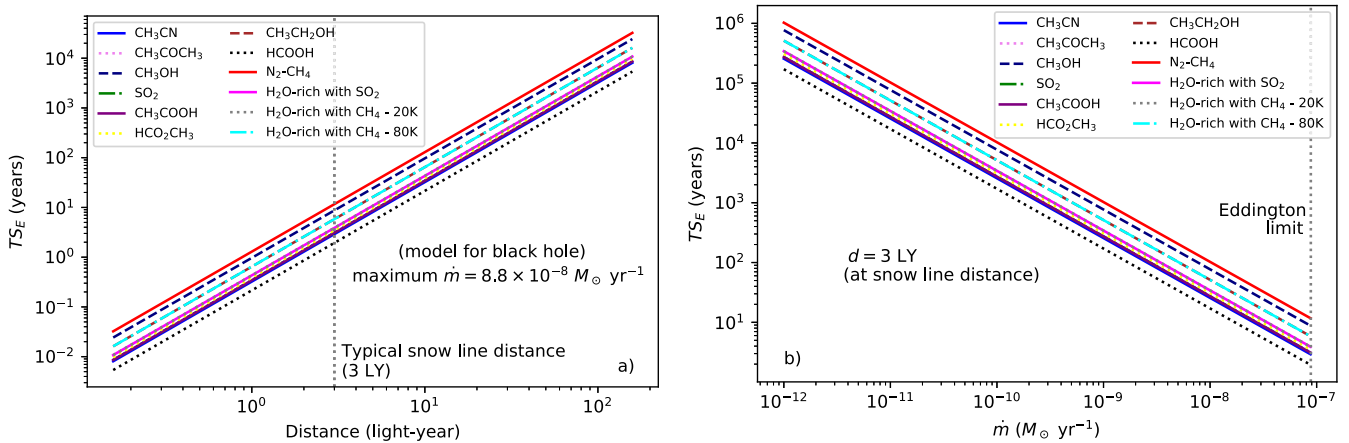


Figure 4. (a) Time-scales for astrophysical ices to reach chemical equilibrium versus distance from the accreting black hole; accretion rate was fixed at $\sim 10^{-7} M_{\odot} \text{ yr}^{-1}$ ($L_X = 2.5 \times 10^{39} \text{ erg s}^{-1}$) (Barret 2001). (b) Time-scales for ices to reach chemical equilibrium at the snow line distance from the accreting black hole ($d \sim 3 \text{ LY}$) as a function of the accretion rate, see details in the text.

Table 2. Model parameters and emission due to soft X-rays. Values of mass, radius, and snow-line distance listed in this table are taken as fiducial to obtain X-ray luminosity and time-scales for chemical equilibrium.

Type of object	Mass (M_{\odot})	Radius (km)	maximum \dot{m} ($M_{\odot} \text{ yr}^{-1}$)	Snow-line distance estimate (LY)	Typical L_X (erg s^{-1})	Maximum luminosity (Eddington limit) (erg s^{-1})
White dwarf	0.6	7752	1.2×10^{-5}	1	$\sim 10^{32}$	7.4×10^{37}
Neutron star	1.4	13	2×10^{-8}	2	$\sim 10^{36}$	1.7×10^{38}
Black hole	20	58	8.8×10^{-8}	3	$\sim 10^{32}$	2.5×10^{39}

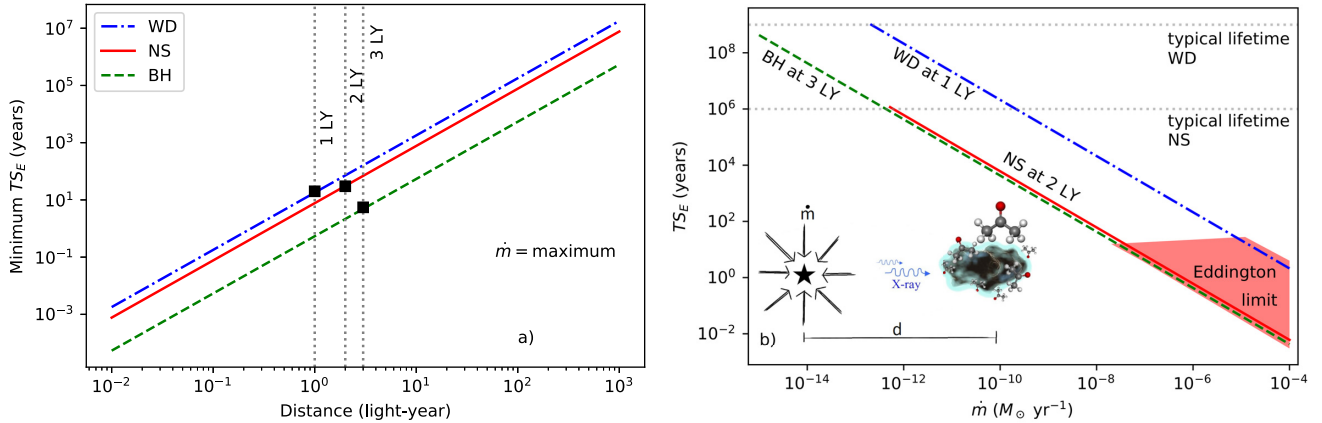


Figure 5. (a) Minimum time-scale for astrophysical ices to reach chemical equilibrium versus distance from the accreting compact star; accretion rate was fixed to maximum in each case (Barret 2001), see also Table 2. (b) Time-scales for ices to reach chemical equilibrium at the snow line distance from the accreting compact object ($d \sim 1\text{--}3$ LY) as a function of the accretion rate, and the orange region corresponds to the Eddington critical limit (e.g. $1.26 \times 10^{38} \text{ erg s}^{-1}$ for one solar mass object), see details in the text. In both plots, an average value for fluence of equilibrium was employed ($\bar{F}_E = 2.5 \times 10^{18} \text{ photons cm}^{-2}$). WD represents white dwarf, NS the neutron star, and BH represents black hole, see Table 2 for parameter details.

ices to reach chemical equilibrium. So, a particular combination of distance and accretion rate for the systems can provide a certain X-ray flux to a region in space, which in turn could imply chemical equilibrium phase to that region. For instance, given the X-ray flux of Sagittarius A* as $2 \times 10^{14} \text{ photons cm}^{-2} \text{ s}^{-1}$ at 1 au and considering a flux attenuated only by the geometric factor as given in equation (3), at Earth (8 kpc) the time-scales for ices to reach chemical equilibrium would be as high as 10 Tyr. However, for the maximum accretion rate considered here the time-scales for chemical equilibrium would be less than 1 Gyr at the distance of Earth. This indicates that galaxies with moderate active galactic nuclei ($L_X \sim 10^{42} \text{ erg s}^{-1}$) may reach chemical equilibrium throughout the system on \sim Myr time-scales. At Earth, the brightest X-ray source is Sco X-1, which is about $2 \times 10^{38} \text{ erg s}^{-1}$ in X-rays at a distance of 2800 pc. That would give an equilibrium time of about 600 Myr, assuming there is always a source at least that bright. That would also be roughly the time-scale if Sgr A* were at $2.5 \times 10^{39} \text{ erg s}^{-1}$ in X-rays. From Fig. 5 panel a, we determine the minimum time-scales which ices at snowline would be subjected to in case of high X-ray photon fluxes; those minimum time-scales lie in the range 10^{-4} – 10^7 yr.

5 CONCLUSION

In this work, we address the question whether ice molecules close to compact objects would be affected by X-ray radiation produced due to accretion and its implications for reaction time-scales for the ices to reach chemical equilibrium. We have seen that accretion generates high X-ray luminosities being capable to induce chemical reactions with low time-scales compared to the lifetime of the accreting compact systems. Generally, accreting compact systems have ages

of order 10^5 – 10^9 yr depending on the progenitor of the compact object and its kind itself, while obtained time-scales for ices to reach chemical equilibrium scales to 1– 10^8 yr considering accretion rates between 10^{-14} and $10^{-8} M_{\odot} \text{ yr}^{-1}$. For white dwarfs, ages are about a Gyr and the accretion rate which induces a comparable time-scale is about $10^{-14} M_{\odot} \text{ yr}^{-1}$. Similarly, in order for the time-scales to be equivalent to the age of the accreting neutron star or black hole, the accretion rate must be of order 10^{-11} – $10^{-13} M_{\odot} \text{ yr}^{-1}$. We also observe that time-scales for ices to reach chemical equilibrium in the vicinity of compact sources are small ($TS_E < 10^7$ yr) for the given maximum accretion rate allowed; this implies that high accretion rate systems may have reached chemical equilibrium even at large distances $d > 100$ – 1000 LY as it can be seen from Fig. 5. The minimum time-scales derived from using maximum accretion rates can also be as small as 0.01 yr.

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DATA AVAILABILITY

The data underlying this article will be shared on reasonable request to the corresponding author.

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